Supplementary Material

The behaviour of β-triketimine cobalt complexes in the polymerization of isoprene.

Mohammed N. Alnajrani and Francis S. Mair

Organic Materials Innovation Centre (OMIC), School of Chemistry, The University of Manchester, Brunswick Street, Manchester M13 9PL.

Contents

1. Kinetic Analysis 2
2. Numbers of Chains and Numbers of Active centers 2
3. Chain transfer to monomer: 6
4. Chain transfer to Aluminium 9
5. Comparisons of Rates 11
6. Determination of the microstructure of the Co-catalysed polyisoprene samples. ...22
7. References 25
8. Appendices: 28
   8.1 Appendix A: Crystal data for **3** 28
   8.2 Appendix B: Crystal data for **5** 38
   8.3 Appendix C: Crystal data for **6** 48
   8.4 Appendix D: Crystal data for **7** 62
   8.5 Appendix E: 75
      Differential Scanning Calorimetry Data (DSC) 75
      Dynamic Mechanical Thermal Analysis Data (DMTA) 76

1. Kinetic Analysis

A series of polymerizations with different termination times were performed using catalyst **6**. Firstly, the conventional First order kinetic plot of ln[Monomer]$_0$/[Monomer]$_t$ vs time (h) gave a straight line passing through the origin ($R^2 = 0.96$).

Consequently, from Figure 1 we can conclude:

1. The reaction is first order in monomer.
2. The number of active centres is constant over the time recorded (6h).
3. The gradient of the line is 7.3×10^{-5} s^{-1}, giving the rate constant of propagation at 35 ˚C. This compares with values of 3.9×10^{-6} for Nickeloctoate/$BF_3.OEt_2$/Et_3Al at 60 ˚C,[1] and 13.2×10^{-4} for $TiCl_4$/Al^iBu_3 at 20 ˚C.[2]

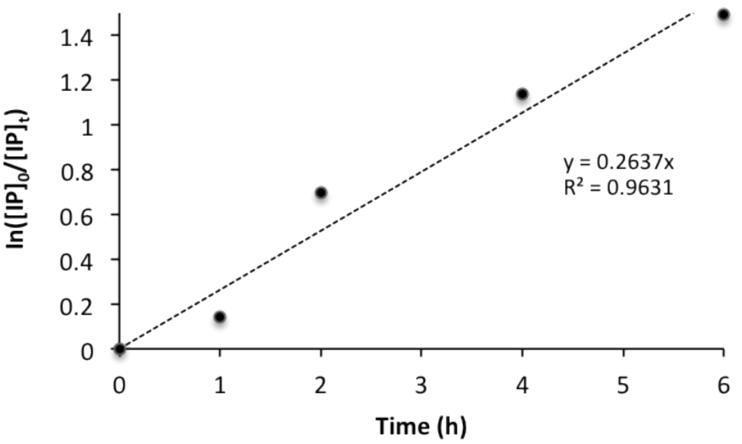


Figure 1: First-order kinetic plot for polymerization of isoprene (IP) by 6 at 35 ˚C.

2. Numbers of Chains and Numbers of Active centers

It was further noted that M_n values increased with time, though the trend was more of an exponential increase than a linear one (Figure 2):

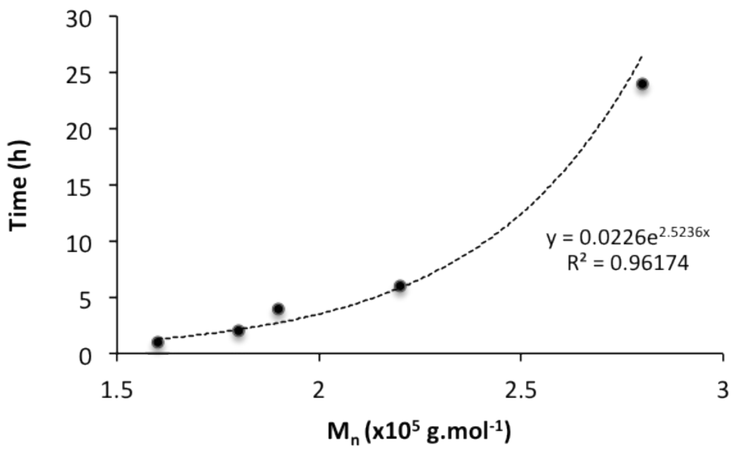


Figure 2: M_n as a function of polymerization time.

This is probably because chain transfer to polymer events at later time-points became more common and introduced high-molecular weight tail to the distribution. In fact, while the distribution of molecular weights at early time points was monomodal, at the end of polymerization, there were bimodal features present; see Figure 3.

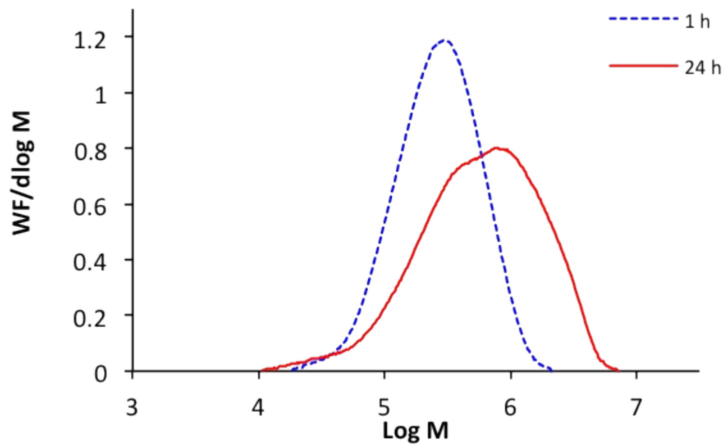


Figure 3: GPC curves of Polyisoprene by **6** for an hour and a day.

The plot of M_n against conversion is displayed in Figure 4.

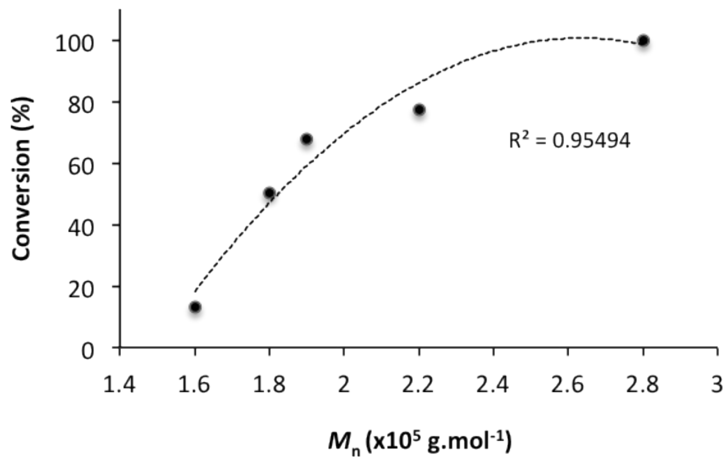


Figure 4: M_n as a function of conversion.

However, the first 3 datapoints seem to fit better to a straight line, with the later two deviating, in such a way that it appears that this system is tending towards a steady state with constant M_n, as would be expected where significant chain transfer was in operation. However, the time taken to reach this steady state of M_n was several hours, rather than minutes as found for typical metallocene-catalysed ethylene polymerizations,[3, 4] for example, so it is clear that chain transfer processes were rather slow.

Below is the same graph of M_n x 10^5 *vs.* conversion plotted with just the first 3 datapoints (Figure 5), when monomer was still plentiful.

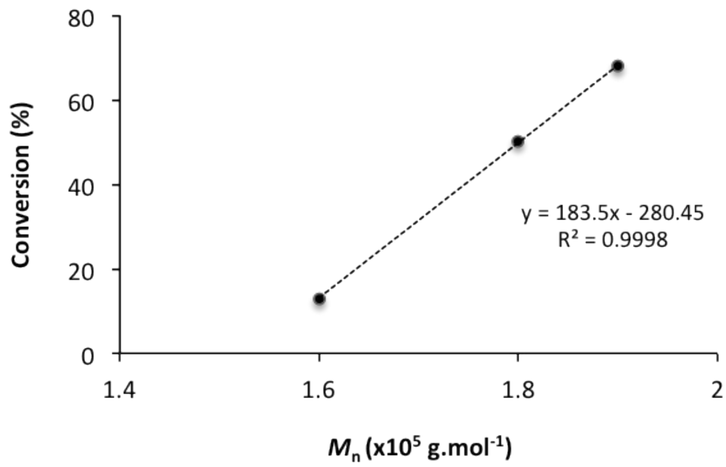


Figure 5: M_n x 10^5 *vs.* conversion (%), linear portion (data up to 70% conversion).

Given that polymer yields were available for all datapoints, an informative alternative way to view the data, especially when wishing to investigate chain transfer, is to plot the number of chains.

Values for the number of chains were obtained by use of the following equation

$$no.\,of\ chains\ at\ time\ t\ (N_C) = \frac{yield\ at\ time\ t\ (g)}{M_n\ (g\ mol^{-1})} * Avogadro\ number(mol^{-1})$$

A value for the number of chains at zero conversion was sought, i.e. before there was any opportunity for chain transfer. This value would then represent the number of active centres, C*, at the outset of polymerization, assuming that active centre formation was fast relative to propagation. This method is essentially that as described by Boucher *et al.*[5]

This assumes that initiation, i.e. generation of active centres, was fast relative to propagation and transfer. The safety of this assumption was evidenced by the rapid colour change observed immediately upon addition of DEAC (Diethylaluminium chloride). The rate of chain transfer was obtained as the intercept at zero conversion of the linear portion of the plot of N_c *vs*. conversion (Figure 6): 35.81 x 10^{16}.

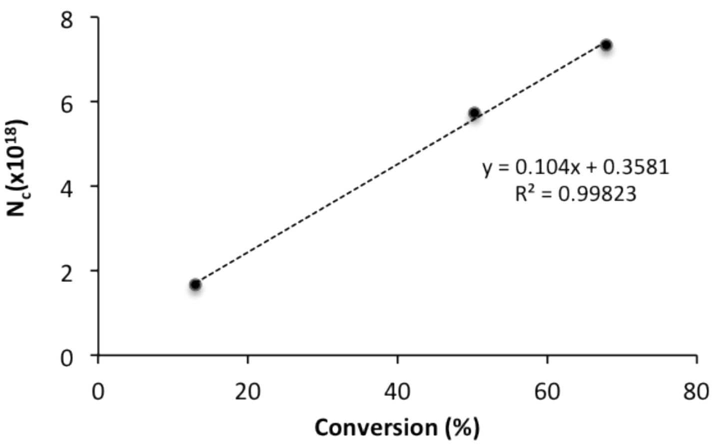


Figure 6: the plot of number of chains (N_c) *vs*. conversion (Linear portion).

Beyond 70%, the increase in the number of chains slowed, most probably a reflection of the fact that monomer was less available, hence reducing the rate of chain transfer to monomer, and the alternative chain transfer to polymer did not generate new chains, but in fact decreased number of chains.

Given that the initial [monomer] was known at 1.67 M, and that C* was determined by the intercept in Figure 6 as 35.81 x 10^{16} in a volume of 35 mL. Therefore, the concentration of the active centres [C*] is 1.7 x 10^{-5} M. The concentration of cobalt catalyst added was 5 μmol in 35 mL, which means [Co] is 1.428 10^{-4} M. This shows that only 11.9% of cobalt present was active.

3. Chain transfer to monomer:

$$R_{ctm} = k_{ctm}[IP]\,[C^*]$$

Where R_{ctm} = rate of chain transfer to monomer, k_{ctm}= rate constant for chain transfer to monomer and [IP] is the concentration of isoprene.

If we assume that at early conversion, chain transfers are to monomer only, then it is possible to extract a rate for this. We now have [C*]

R_{ct} = rate of chain transfer, N_c per unit time, which can be measured from the gradient of a plot of number of chains *vs*. time.

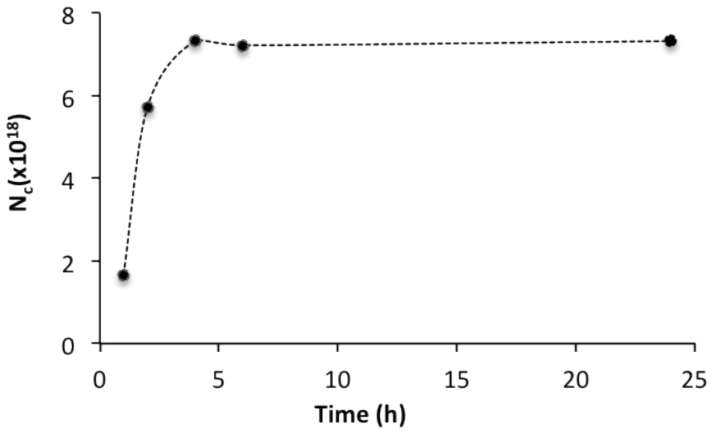


Figure 7: Number of chains N_c as a function of polymerization time.

There are three types of chain transfer likely to be significant: chain transfer by direct transfer of a *β*–hydrogen from polymer to co-ordinated monomer, or the alternative hydride transfer to metal then re-addition to monomer (chain transfer to monomer),[4] attack of a polymeryl chain end on an already enchained alkene, rather than a fresh diene monomer (chain transfer to polymer), and chain transfer to aluminium. The key intermediates in these three processes are shown below (Chart 1):

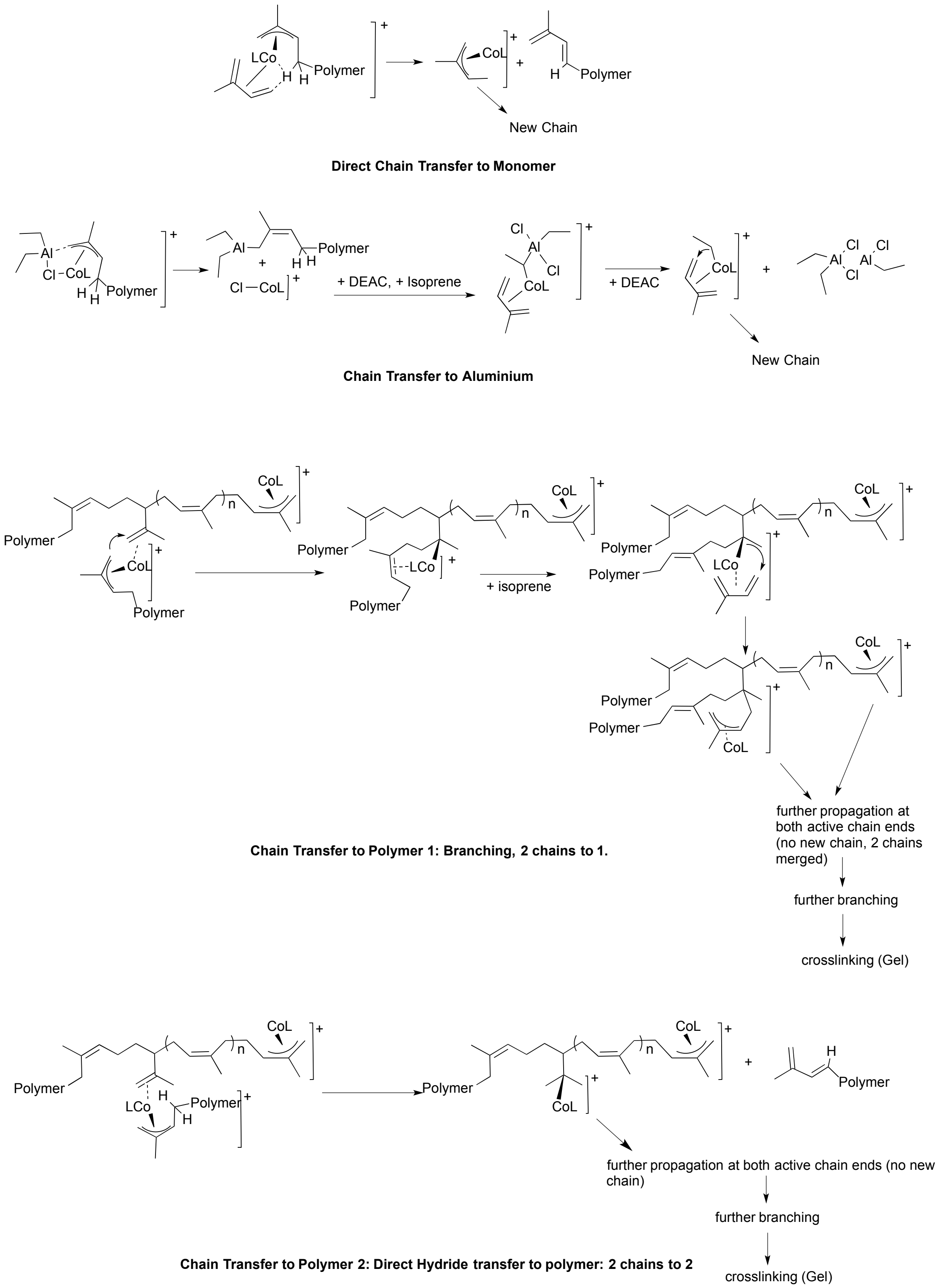


Chart 1: Chain transfer processes.

At low conversion, there is minimal polymer, and much monomer, so chain transfer to monomer dominates, resulting in a rapid increase in number of chains with time (early part of Figure 7). Focusing on this early portion, by the third datapoint the conversion had already reached 68%, so monomer was outnumbered by polymer, but was more mobile, and hence still preferred, though transfer has slowed somewhat. More datapoints at early conversion would have given a more reliable estimate of chain transfer to monomer rate. But with the available data, and ignoring chain transfer to Al, an estimate of R_{ctm} can be arrived at by the gradient of a best-fit straight line to the first three datapoints:

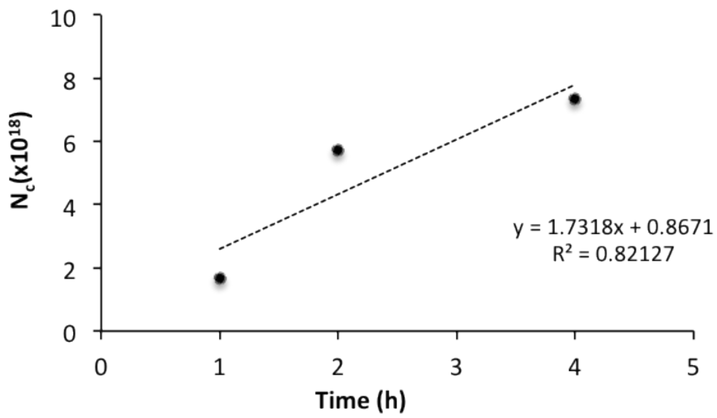


Figure 8: Number of chains N_c as a function of polymerization time (first three hours).

From Figure 8, the gradient gives $R_{ctm} = 1.732 \times 10^{18}$ chains h^{-1} (4.811×10^{15} s^{-1}).

If we take our earlier value of C* obtained by extrapolating number of chains to zero conversion, (35.81×10^{16} active centres), the rate of transfer is 1.34×10^{-2} transfers per second per active centre. Chain transfers are slow relative to propagation, which is a requirement for high molecular weights, which we observe.

The above data analysis assumes that all of the observed chain transfer at early datapoints was chain transfer to monomer. Though at early datapoints, chain transfer to polymer may be neglected, what of chain transfer to aluminium?

For chain transfer to aluminium to be important, given that the aluminium concentration was essentially constant throughout, and the active centre concentration [C*] appeared constant throughout, one would expect a contribution to chain transfer to be constant throughout the polymerization. However, the number of chains stopped increasing at high conversions, so either chain transfer to aluminium is not occurring at a significant rate, or it is occurring at a rate balanced by the reduction in chains resulting from chain transfer to polymer, route 1 as defined in Chart 1 This question was addressed with a study of the effect of aluminium concentration.

4. Chain transfer to Aluminium

Two compounds, **2** and **7**, were selected for a study of the effect of aluminium ratio. The plot of number of chains at the end of polymerization against Al/Co for **2** is shown below:

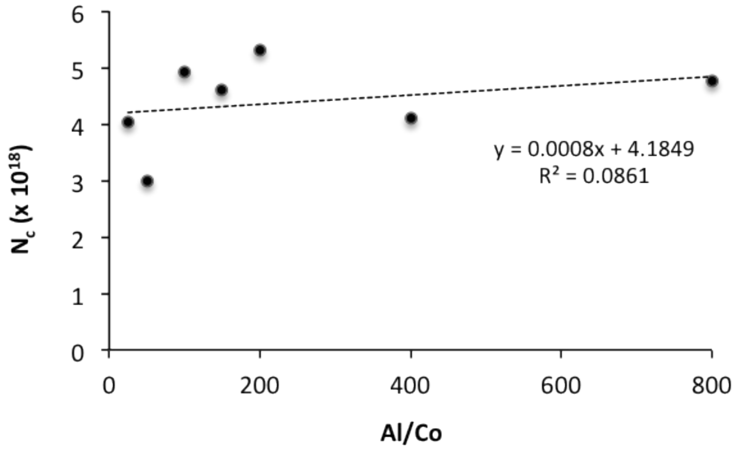


Figure 9: The number of chains N_c as a function of Al/Co ratio for compound 2.

It is clear from Figure 9 that there is a poor correlation to the expected linear dependence, with no clear relationship discernible for **2**, suggesting the conclusion that the rate of chain transfer is zero order in [Al]. This was further tested by a similar plot for **7** (Figure 10):

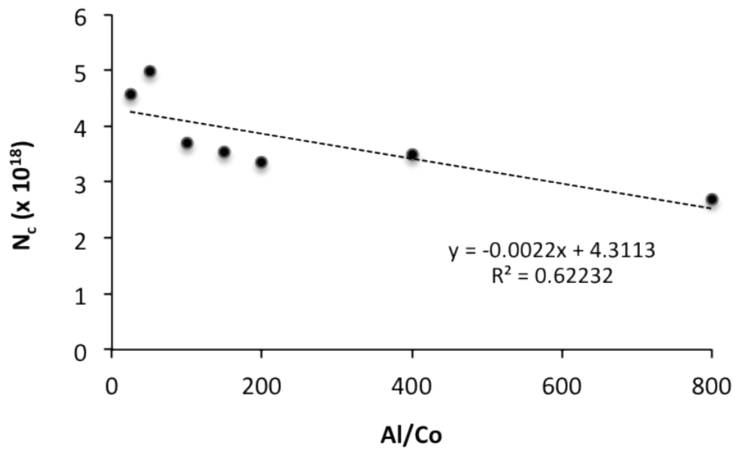
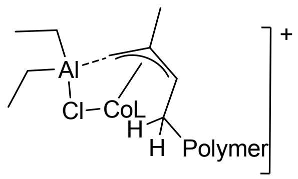


Figure 10: The number of chains N_c as a function of Al/Co ratio for compound 7.

A similarly flat plot, with a similarly poor correlation with linear dependence, seems to confirm the view that chain transfer is zero order in [Al]. This could mean either that chain transfer to aluminium is not occurring to a significant extent, or that it is occurring, but its rate is not sensitive to [Al] if there is a saturated pre-equilibrium involving a resting state comprised of a Cobalt-aluminium mixed species with a chloride bridge, which, given the clear advantage of chloride in this case (EASC outperforms DEAC, which outperforms MAO and all R_3Al tested), seems highly likely:

Putative dormant state, formed even at relatively low Aluminium concentrations, hence masking order in [Al].



So, overall $R_{ct} = k_{ctm}[IP][C^*] + k_{ctAl}[C^*] + k_{ctp}[\text{polymerized monomer}][C^*]$

There was insufficient data to justify a more rigorous modelling of the evolution of the molecular weight distribution as has recently been performed for metallocenes in ethylene polymerization,[6] and the additional factor of chain transfer to polymer, much more important here than for ethylene, adds to the challenge of extracting several constants from a model of variation of a single parameter. Consequently, it is not possible for us at this time to comment authoritatively on whether chain transfer to aluminium is occurring but balanced with chain transfer to polymer, thought this seems far from likely, or whether it is suppressed.

To conclude on propagation,

$R_p = k_p[\text{monomer}][C^*]$

Therefore, R_p varies throughout the polymerization as [monomer] dwindles, i.e. the instantaneous rate is dependent on progress of the reaction.

The value of k_p is fixed at a given temperature, and is the gradient of the kinetics plot, $7.3 \times 10^{-5}\ s^{-1}$.

This value compares with one obtained using similar methodology for a so-called Ziegler-Natta catalyst system $Ni(octoate)_2/BF_3/Et_3Al$, which produced a similar *cis*-1,4 polybutadiene, of $3.9 \times 10^{-6}\ s^{-1}$.[1] In that paper, they found similar first-order behaviour in monomer, fractional active sites (5.4% of all Ni), and levelling of M_n over time after initial rapid increase.

5. Comparisons of Rates

R_{pmean}, mean rate of polymerization, averaged over the whole polymerization is 5.78 x 10^{-7} mol IP s^{-1}. This is the only value obtainable for all catalyst **1-7**, since the detailed kinetic analysis was only performed for **6**.

This could for comparative purposes be expressed per mol of Co per hour i.e. total cobalt, or, perhaps more accurately, as per mole of Co*, active cobalt, per hour, which would be a factor of approximately 10 greater.

No. of moles of catalyst: 5 x 10^{-6}.

No. of active Co*: 35.8x10^{16}

No. of moles of active Co*: 5.95 x 10^{-7} (i.e. approx. 12% of all cobalt)

R_{pmean} = 5.78 x 10^{-7} mol IP s^{-1} x 3600 s h^{-1}/5.95 x 10^{-7} mol Co* = 3499.2 mol IP mol^{-1} Co* h^{-1}

Or, 416 mol IP mol^{-1} Co h^{-1}

Or, 28.3 kg IP mol^{-1} Co h^{-1}

Though a comparison of true relative rates of different catalysts is marred by a range of concentrations, catalyst loadings, conversion rates, reaction times and temperatures used, given the rarity in the field of determination of rate constants, overall mean activity comparison is all that is available for a wide range of catalysts. This is presented in Table 1, below, with data converted into the units of mol IP mol^{-1} metal h^{-1}, so as to facilitate comparisons.

Table 1: A comparison of activities and selectivities of a range of catalysts of isoprene polymerization

Catalyst	**Rate mol IP mol^{-1} Metal h^{-1}**	**Main selectivity**	**Other isomers**	**Notes**	**ref**
1/DEAC	243	*cis*-1,4 (74 %)	3,4 (26%) *trans*-1,4 (1 %)	24 h, 35 ˚C (58 % conv.) M_n = 280,000. PDI = 2.57	This work
2/DEAC	262	*cis*-1,4 (74%)	3,4 (24.5%) *trans*-1,4 (0.5%)	24 h, 35 ˚C (63 % conv.) M_n = 280,000. PDI = 2.64	This work
3/DEAC	278	*cis*-1,4 (75%)	3,4 (24.5%) *trans*-1,4	24 h, 35 ˚C (67 % conv.) M_n = 250,000.	This work

			(0.5%)	PDI = 3.32	
4/DEAC	313	*cis*-1,4 (77 %)	3,4 (23%)	24 h, 35 ˚C (75 % conv.) M_n= 240,000. PDI = 3.33	This work
5/DEAC	410	*cis*-1,4 (80%)	3,4 (20%)	24 h, 35 ˚C (98 % conv.) M_n= 200,000. PDI = 3.35	This work
6/DEAC	416	*cis*-1,4 (76%)	3,4 (24%)	24 h, 35 ˚C (100% conv.) M_n= 280,000. PDI = 3.25	This work
6/DEAC	676	*cis*-1,4 (78%)	3,4 (21.6%) *trans*-1,4 (0.4%)	4 h, 35 ˚C (68% conv.) M_n= 190,000. PDI = 2.53	This work
6/EASC	1,000	*cis*-1,4 (80%)	3,4 (18%) *trans*-1,4 (2%)	4 h, 35 ˚C, (100% conv., crosslinked) M_n= 80,000. PDI = 5.5	This work
7/DEAC	367	*cis*-1,4 (74%)	3,4 (25%) *trans*-1,4 (1%)	24 h 35 ˚C (88.2% conv.) M_n= 280,000. PDI = 3.21	This work
Co$\{O_2CCHEt(CH_2)_3CH_3\}_2$/DEAC	1,442	3,4 (46%)	*cis*-1,4 (43%) *trans*-1,4 (9%)	2 h, 20 ˚C (100% conversion) Hexane. In-situ catalyst prep. No M_n data.	7
As above, but pre-formed catalyst, not in-situ	29, 400	*cis*-1,4 (44%)	3,4 (43 %) *trans*-1,4 (10%)	15 min, 20 ˚C (98% conversion)	
Co$\{O_2CCHEt(CH_2)_3CH_3\}_2$/EASC	43,650	*cis*-1,4 (45%)	3,4 (38%) *trans*-1,4 (15%)	10 min, 20 ˚C (97% conversion)	
$[(Ph_2{}^iPrP)_2$**Co**$Cl_2]$/MAO	200	3,4 (57%)	*cis*-1,4 (43%)	20 ˚C. Over 5 h. (100% conv.) M_n = 37,000 PDI = 1.9	8
$[(Ph_2{}^iPrP)_2$**Co**$Cl_2]$/MAO	108	*alt*-3,4/1,4 *cis*	n.d.	20 ˚C. Over 5.5 h. (89% conv.) higher catalyst loading than above entry, i.e. lower IP conc.	9

				M_n = 68,00 PDI = 1.5	
[$(Ph_2MeP)_2$**Co**Cl_2]/MAO	593	*alt*-3,4/1,4 *cis*		20 ˚C. Over 1 h. (89% conv.) M_n = 171,00 PDI = 2.2 (other phosphines were reported, but this was most active)	9
(Dimethylglyoxime)$_3$**Co**/Et_3Al	0.015	*cis*-1,4 (75%)	3,4 (24 %)	35 ˚C, 168 h, M_w 'very high' (not measured)	10
2-(N-Et-benzimidazolyl)-6-(1-2,6-dimethylphenyl)ethyl)pyridine**Co**Cl_2/EASC	51,380	*cis*-1,4 (94%)	3,4 (6%)	30 ˚C, over 0.5 h, (51% conv.) M_n = 16,342. PDI = 2.57	11
Benzimidazolyl-aryliminoethylpyridine**Co**Cl_2/EASC (i.e. as above; the two papers have a great deal of overlap)	47,270	*cis*-1,4 (95%). This value was obtained by NMR and IR, but presented spectral data look less selective than this.	3,4 (5%)	30 ˚C, over 0.5 h, (50% conv.) Comparison, it took 2 h to get to 50% conversion for **6**. No Mw data presented. EASC better than DEAC	12
CoF_2/PhMgBr/$PhCH_3$/H_2O	12	*cis*-1,4(50%)	No data, but reported as 'binary'	50˚C, 24 h E_a = 96 kJ mol^{-1}.	13
CoI_2/$PhCH_2MgBr$/$PhCH_3$/MeOH	5.5	3,5 (55%)	*cis*-1,4 (45%)	55 ˚C. 7 h (89% conv.)	14
CoCl_2/SiO_2/DEAC	190,320	*cis*-1,4 (66%)	3,4 (32%) *trans*-1,4 (2%)	65 ˚C. 0.5 h Sealed autoclave, heptane (no M_n data)	15
Ni(Octoate)$_2$.BF_3.OEt_2/$AlEt_3$	5.4	No data	Na data	60 ˚C over 10 h. A detailed kinetic analysis is present. M_n about 400,00, PDI about 2, as judged from reading off graph	1
TiCl_4/$^iBu_3Al$/heptane 'Ziegler-Natta'	668	'essentially *cis*-1,4' (qualitative, IR only).		10 ˚C Solid Ti(III) catalysts produced in situ. (Conv. ca. 40%)	2
Py-2-CH=N($CMe_2CH_2Bu^t$)**Fe**Cl_2/$AlBu^i_3$/[Ph_3C	500	*trans*-1,4	3,4 (8%)	23 ˚C. 2 h (100% conv.)	16

][$B(C_6F_5)_4$]		(92%)		M_n = 62,500. PDI = 2.0	
As above, but increased monomer supply.	1,000	As above		23 ˚C. 5 h (100% conv.) M_n = 166,667. PDI = 3.9	
Py-2-CH=N(2,4,6-$Ph_3C_6H_2$))**Fe**Cl_2/$AlBu^i_3$/[Ph_3C][$B(C_6F_5)_4$]	1,000	*cis*-1,4 (66%)	3,4 (33%)	23 ˚C. 1 h (100% conv.) M_n = 78,950 PDI = 1.9	
As above, but lower T, longer time.	250	*cis*-1,4 (86%)	3,4 (14%)	-78 ˚C. 4 h (100% conv.) M_n = 82,350 PDI = 1.7	
As above, but increased monomer supply, decreased temperature	1,250	*cis*-1,4 (83%)	3,4 (17%)	-78 ˚C, 4 h (100% conv.) M_n = 228,570 PDI = 3.5	
$(Bipy)_2$**Fe**Et_2/MAO	824,000	3,4 (85%) (estimate)	Not defined.	25 ˚C. Over 3 min atactic. Lower activity but higher crystallinity at lower T . M_n = 147,781 PDI = 2.36	17
$(Bipy)_2$**Fe**Cl_2/MAO	800,000	3,4 (67%)	*cis*-1,4 (33%)	20 ˚C. Over 30 s. atactic. (100% conv.) M_n = 1,400,000 PDI = 1.3 (assumes given data is M_n, not M_w)	18
2-(methyl-2-benzimidazolyl)-6-(1-(2,6-Et_2-4-MeC_6H_2)imino)ethylpyridine**Fe**Cl_3/$AlBu^i_3$	19.8	*cis*-1,4 (83%)	1,2 (10%) 3,4 (7%)	40 ˚C. 24 h (5% conv.) M_n = 2,000 + oligomer	19
Diisopropylanilidophenanthrenequinone**Cr**Cl_2.thf_2/MAO	818	*cis*-1,4 (79%)	3,4 (21%)	20 ˚C, 0.5 h (82% conv.) M_n = 23,800 PDI =1.54	20
2,6-bis (2,6 diethylphenylaldimino)phenyl**Cr**Cl_2.thf/Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$] 'pincer' complex	4,000	*trans*-1,4 (86%)	3,4 (14%)	20 ˚C, 15 min (100% conv.) M_n = 1,049,000 PDI = 1.81	21
$Me_4C_5SiMe_2P$(*cyclo*-	300	3,4 (99%)	-100% claimed at	25 ˚C, 2 h (100% conv.)	22

$C_6H_{11})$**Y**$(CH_2SiMe_3)_2/[Ph_3C][B(C_6F_5)_4]$			lower T, but activity poor. Tm 162 at best.	M_n = 120,000 PDI =1.3	
Nd$Cl_3.(thf)_n/3LiNR_2$/R'COOH/TMA [gives $Ln(AlMe_4)_3$ in situ which can then react with carboxylates or silanols to generate similarly active, similarly selective catalysts.	416.6 (all polymerizations were run for 24h on 1000 equiv. of Isoprene per metal)	*cis*-1,4(99%+)		40 ˚C, 24h (100% conv.) M_n = 250,000 PDI = 2.82 M_n raises to 700,000 on immobilization on MCM48 zeolite, or 500,00 on reaction with $HOSi(O^tBu)_3$ (PDI 1.51)	23-25
$[N(o\text{-}C_6H_4PPh_2)_2$**Y**$(CH_2SiMe_3)_2.thf]/[PhMe_2NH][B(C_6F_5)_4]$	3,384	*cis*-1,4 (98.7%)	3,4 (1.3%)	50˚C, 20 min. M_n = 140,000 PDI = 1.05 Living.	26
7-{(N-2,6-Me_2)iminomethyl}indolyl**Sc**$(CH_2SiMe_3)_2$.thf/$Al^iBu_3/[Ph_3C]$ $[B(C_6F_5)_4]$	12,000	*cis*-1,4 (72%)	3,4 (18 %) *trans*-1,4 (10%)	20 ˚C, 5 min (100% conv.) M_n = 159,000 PDI =1.77	27
7-{(N-2,6-$^iPr_2$)iminomethyl}indolyl**Sc**$(CH_2SiMe_3)_2$.thf/$Al^iBu_3/[Ph_3C]$ $[B(C_6F_5)_4]$	5,700	*cis*-1,4 (88%)	3,4 (9 %) *trans*-1,4 (3%)	20 ˚C, 5 min (95% conv.) M_n = 180,000 PDI = 1.77	27
$[PhC(N\{2,6\text{-}^iPr\}_2C_6H_3)_2$**Y**$(CH_2\{2\text{-}Me_2NC_6H_4\})_2]/[Ph_3C]$ $[B(C_6F_5)_4]$	22,504	3,4 (91%) isotactic	*cis*-1,4 (9%)	25 ˚C, 2 min (100% conv.) M_n = 137,000 PDI = 1.3	28
[**La**$(AlMe_4)_2C_5Me_5]/(C_6F_5)_3B$	42	*trans*-1,4 (99.5%)		40 ˚C, 24 h (100% conv.) M_n = 240,000 PDI =1.2	29, 30
[**Y**$C_5Me_4(2\text{-}Me_2NC_6H_4)(C_3H_5)_2]/Al^iBu_3/[PhMe_2NH][B(C_6F_5)_4]$	3000	*cis*-1,4 (95%)		20 ˚C, 20 min. (100% conv.) M_n = 128,000 PDI =1.36	31
$[\{(2\text{-}NPPh_2)pyridyl\}_2$**Sc**$CH_2SiMe_3/[Ph_3C]$ $[B(C_6F_5)_4]$	11,760	*cis*-1,4 (95%)	3,4 (3.5 %) *trans*-1,4 (1.5 %)	20 ˚C, 5 min. (98 % conv.) M_n = 230,000 PDI = 3.07	32
Nd$Cl_3.3^iPrOH$/MMAO	928	*cis*-1,4 (96%)	3,4 (4%)	50 ˚C, 4 h (99 % conv.) M_n = 1,200,000	33

				PDI = 2.08	
[34)$_2$**Y**(1,3($Me_3Si)_2C_3H_3$)]/Mg^nBu_2	92.4	*trans*-1,4(53%)	3,4 (47%)	60 °C, 27 h (100% conv.) M_n = 7,100 PDI 1.5	34
(8-diisopropylanilidoquinolyl)**Y**($CH_2SiMe_3)_2$.thf/$AlMe_3$/[Ph_3C] [$B(C_6F_5)_4$]	333	*trans*-1,4 (87%)	3,4 (8%) *cis*-1,4 (5%)	40°C, 15 h (100% conv.) M_n = 689,000 PDI =1.71	35
{*N,N*-(2,6-dimethylphenyl)2-*C*-cyclohexylamidinate}**Y**{$N(SiMe_3)_2$}$_2$ $AlMe_3$/[Ph_3C] [$B(C_6F_5)_4$]	14,974	*cis*-1,4 (92%)	Not stated	25°C, 2 min. (100% conv.) M_n 94,300 PDI =1.9	36
2,6-(^{i}Pr)$_2C_6H_3$NCHMe(2-pyridyl)**Sc** ($CH_2SiMe_3)_2$.thf/Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$]	30,000	3,4 (63%)	1,4 (*cis*/*trans* ratio not stated) (37%)	20°C, 2 min (100% conv.) M_n = 89,000 PDI =1.1	37
2,5-bis[38]pyrrolyl**Y**($CH_2SiMe_3)_2$/[Ph_3C] [$B(C_6F_5)_4$]	400	*cis*-1,4 (94%)	*trans*-1,4 (1%) (3,4 not stated, but implied 5%)	20°C, 2.5 h (100% conv.) M_n = 103,000 PDI =1.22	38
Nd(O-2,6-$^tBu_2C_6H_3)_3$/MMAO/	45,360	*cis*-1,4 (69%)	*trans*-1,4 (28%) 3,4 (3%)	20 °C, 1 min (100% conv.) M_n = 104,000 PDI = 2.1	39
N($Ph_2PO)_2$**Y**($CH_2SiMe_3)_2$.thf/Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$]	2000	*cis*-1,4 (71%)	3,4 (20%) *trans*-1,4 (9%)	25°C, 30 min (100% conv.) M_n = 56,400 PDI = 1.59	40
Nd($O^iPr)_3$/MAO/Bu^tCl	1,600 Approx (not stated explicitly)	*cis*-1,4 (90%)	3,4 (10%)	30 °C, 1 h (ca. 80% conversion, not specifically stated) M_n = 577,000 PDI = 1.32	41
N,N,Bis(2,6-dimethylphenyl)diketiminate**Y**(CH_2SiMe_3)$_2$.thf/Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$]	6,000	*cis*-1,4 (94%)	3,4 (4%) *trans*-1,4 (2%)	30 °C, 1 h (100% conv.) M_n = 64,000 PDI =1.4	42
2,6(2,6-$Me_2C_6H_3NCH)_2C_6H_3$-*C*-**Gd**Cl_2.thf$_2$/ Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$]	491	*cis*-1,4 (97.7%)	*trans*-1,4 (1.7%) 3,4 (0.6 %)	40 °C, 1 h (98% conv.) M_n = 101,300 PDI = 2.46	43
N,N-bis{(2-isopropyloxazolinyl)phenyl}amido **Lu**($CH_2SiMe_3)_2$/Al^iBu_3/[Ph_3C] [$B(C_6F_5)_4$]	10,000	*trans*-1,4 (99%)	-	90 °C, 12 min (100% conv.) M_n = 21,000	44

				PDI = 2.26	
[{**Nd**(O_2CCHPh_2)$_3$.thf$_2$}$_2$]/HAl^{i}Bu$_2$	3,167	*cis*-1,4 (97%)	*trans*-1,4 (3%)	50 ˚C, 3 h (95 % conv.) M_n = 147,000 PDI = 4.37	45
Nd(O^{i}Pr)$_3$/MAO	750	*cis*-1,4 (91%)	3,4 (8%)	50˚C, 4 h (90% conv.) M_n = 398,000 PDI =1.51	46
2,6-bis(isopropyloxazolinyl)Phenyl**Y**Cl_2 .thf$_2$/ Al^{i}Bu$_3$/[PhNHMe$_2$] [B(C_6F_5)$_4$]	6,000	*cis*-1,4 (97.4%)	*trans*-1,4 (1.4%) 3,4 (1.2%)	50˚C, 5 min (100% conv.) M_n = 107,000 PDI = 1.65	47
[**Nd**{N(SiMe$_3$)$_2$}$_3$]/B(C_6F_5)$_3$/ ^{i}Bu$_3$Al	60,188	*cis*-1,4 (96%)	3,4 (4%)	25˚C, 2 min (67% conv.) M_n = 134,000 PDI = 1.53	48
pyridylmethylenefluorenyl**Y**(CH_2SiMe_3)$_2$. thf/Al^{i}Bu$_3$/[Ph$_3$C] [B(C_6F_5)$_4$]	5,200	3,4 (83%)	*cis*-1,4 (17%)	15˚C, 6 min (52% conv.) M_n = 13,000 PDI = 2.1	49
2-(5-methylthiazole)-6-CMe$_2$N(2,6-^{i}Pr$_2C_6H_3$)-pyridyl**Er**(CH_2SiMe_3)$_2$/[Ph$_3$C] [B(C_6F_5)$_4$]	1980	*trans*-1,4 (65%)	3,4 (28%) *cis*-1,4 (7%)	50 ˚C, 30 min (99 % conv.) M_n = 147,000 PDI = 1.41	50
MesitylN-Heterocyclic carbene/Amidinate N,N,C-**Lu**(CH_2SiMe_3)$_2$/[Ph$_3$C] [B(C_6F_5)$_4$]	3,000	3,4 (97%)	-	80 ˚C, 10 min (100% conv.) M_n = 37,000 PDI = 1.06 'living 3,4, atactic, syndio bias.	51
PhS{N(2,6-^{i}Pr$_2C_6H_3$)}$_2$**Lu**(CH_2SiMe_3)$_2$.thf/ ^{i}AlBu$_3$ /[PhMe$_2$NH] [B(C_6F_5)$_4$]	6,000	3,4 (98%)	-	10 ˚C, 10 min (100% conv.) M_n = 147,000 PDI = 2.3 Isotactic (92% mm), rising to >99% mm at -30 ˚C T_m 170 (highest yet) if done at -30 ˚C	52
HC{N(2,6-^{i}Pr$_2C_6H_3$)}$_2$**Nd**(CH_2SiMe_3).thf/Al ^{i} Bu$_3$ /[PhMe$_2$NH] [B(C_6F_5)$_4$]	1,293	*trans*-1,4 (55%)	*cis*-1,4 (36%) 3,4 (9%)	20 ˚C, 45 min (97% conv.) M_n = 130,000 PDI = 1.8	53
Dinuclear [{**Dy**(aminoIndolyl)CH_2SiMe_3.thf}$_2$]//Al^i Bu$_3$/[Ph$_3$C][B(C_6F_5)$_4$]	1,000	*cis*-1,4 (98.5%)	3,4 (1.3%) *trans*-1,4 (0.2%)	20 ˚C, 2h (100% conv.) M_n = 291,000 PDI = 1.8 (Y slower, Yb	54

				inactive)	
$C_5H_4CH_2CH_2NMe_2$**Y**$C_3H_5)_2$/PhNHMe$_2$][$B(C_6F_5)_4$]/$AlMe_3$	2,000	*trans*-1,4(71%)	3,4 (29%)	40 C, 30 min (100% conv.) M_n = 54,000 PDI = 1.24 Selectivity effects with Aluminium.	55
*sec*Bu**Li** in benzene (Anionic)	48.3	*cis*-1,4 (80%)	*trans*-1,4 (16%) 3,4 (4%)	20 ˚C, 18 h (conversion not stated, nor is yield in g; assumed 100% for purposes of activity calculation. Note: lower Temps can do better than this (industrial product)	56
ZnBr_2/Cl_3CO_2H/CH_2Cl_2 (cationic)	48	1,4-*trans* (65%)	1,4-*cis* (26%) 3,4 (5%), 1,2 (4%)	20 ˚C, over 4h low Mw. cationic	57
Ph_3**B**/2-cyclohexylideneethanol/CH_2Cl_2 (cationic)	0.94	1,4-*trans*	Head-head, tail-tail and saturated groups. Not quantified.	20 ˚C. activity expressed in terms of Ph_3B.	58

When attempting to draw comparisons, it must be noted that there are at least three distinct figures of merit to compare: 1. Activity; 2: selectivity and 3: molecular weight.

These activity comparisons do suffer from the fact that the values can be manipulated by increasing initial monomer concentrations, and there is no doubt that some of the observed variations are ascribable to this effect. Notable, too, is the strong effect of different co-catalysts and solvents on the same pre-catalyst. Hence, a given precatalysts cannot be fully investigated before a range of solvents and precatalysts is screened. With these caveats in mind, a few points can be made.

Taking activity first: It becomes clear that catalysts **1**-**7** are moderately active; much more active than cationic or anionic polymerizations, more active that nickel salts, more active than some lanthanum and lanthanide catalyst, but less active than many. Within the area of Co catalysts, it is clear that there is a strong preference for the presence of chloride, as has been previously discussed. This is underlined by the near-doubling of yield achieved from catalyst **6** upon replacement of DEAC with EASC.

The activities are broadly in line with most other Co complexes, which is to say, in the range of hundreds to a few thousands of mol IP mol^{-1} catalyst h^{-1}.[8-15] A few cases stand out from this range: Cobalt octoate with EASC reached a value of 43, 650 mol IP mol^{-1} Co h^{-1}, but at the expense of selectivity (only 45% *cis* 1,4), and molecular weight (M_n only 37,000).[7] In fact, it is clear that within the field of cobalt, it is possible to obtain a wide range of selectivities, from alternating 3,4/1,4-*cis*,[9] to mixtures of all three main types of enchainment (e.g. 3,4/*cis*-1,4/*trans*-1,4 of 46/43/9%)[7] to those more strongly biased to 3,4 (e.g. 55%,[14] 57%[8]). Most commonly with Co, *cis*-1,4 is favoured, from the aforementioned very modest levels of 45%,[7] through 50%,[13] a respectable 66% attained with silica-supported $CoCl_2$ (with very high activity, though no M_n data are reported),[14] to 75% attained with very low activity from Cobalt(dimethylglyoxime),[10] to our own values ranging from 74 to 80%, up to the highest yet-reported selectivities for cobalt in isoprene polymerization, ranging from 70% even up to 96% claimed, with catalysts similar to ours, from He, Sun and co-workers.[10,11] However, their meridional N_3 ligands, dosed as neutral dichloride complexes rather than as bromide BArF salts, while giving good selectivities and activities, had much lower M_n than achieved by our facial N_3-ligated catalysts. Hence, the rate of chain transfer was lower in our case. This allows a combination of reasonable *cis*-1,4 selectivity (up to 80%) with high Molecular weight and good activity. Though higher activities and selectivities have been reported for Co, no other case of which we are aware provides this optimum combination.

Broadening the comparison to other metals, Nickel offers only low activities[1] and undefined selectivity; while chromium can match the selectivity and activity attained by **1-7** (diisopropylanilidophenanthrenequinone$CrCl_2$ with methylaluminoxane activation gives polyisoprene with 75% *cis*-1,4 enchainment at a rate of 818 mol IP mol^{-1} Cr h^{-1}) again it is limited in applicability by the low M_n (23,800) attained.[20] With a diiminopyridine ligand on Cr, selectivity changes to *trans*-1,4 (86%), and both activity and M_n improve (to 4,000 mol IP mol^{-1} Cr h^{-1} and 1 x 10^6, respectively).[21] However, the market for *trans*-isoprene is limited in comparison to that of the *cis* isomer. That market, where not served by natural rubber, has historically been served by traditional Zeigler-Natta catalysts based on Ti; these give *cis*-1,4 values in excess of 90%, and respectable activities and M_n values, though the academic open literature on them is surprisingly sparse;[2] for high-value applications where colour, odour or protein content of natural rubber may be an issue, such as in surgical gloves, anionically polymerized isoprene has been used, though low temperatures are required to keep cis-1,4 selectivity high with the organolithium initiators used.[59]

The most recent work in the area has been dominated by investigation of Rare Earths (Sc, Y, La, Lanthanides, collectively termed Ln): these give mostly high-*cis*, but can give other selectivities depending upon the metal, ligand, co-catalyst and conditions. They can give very high *cis* (99%+),[23-25] and reasonably good activity (416.6 mol IP mol^{-1} Ln h^{-1} with good molecular weight (M_n = 250,000), these values achieved with Ln($AlMe_4$)-derived species,[23-25] or higher activity with slightly reduced *cis*-1,4 selectivity (3384 mol IP mol^{-1} Ln h^{-1}, 98.7%,),[26] (3000 mol IP mol^{-1} Ln h^{-1} , 95%),[31] (11,760 mol IP mol^{-1} Ln h^{-1} , 95%),[32] with a range of substituted cyclopentadienyl or amidophosphine ligands. Even simple $NdCl_3$ with ^{i}PrOH and modified methylaluminoxane gave 928 mol IP mol^{-1} Ln h^{-1} at 96% *cis*-selectivity and high M_n, though with unmodified methylaluminoxane the selectivity dropped to 90%.[33, 46]

It is not appropriate to give an exhaustive list here; there are very many Ln organometallic and metal-organic catalysts known, and the area has been reviewed.[60] Among the most recent results reporting *cis*-1,4-selective catalysts, those of Wang and co-workers, on a dinuclear dysprosium indole complex, stand out, with activity of 1000 mol IP mol^{-1} Ln h^{-1} and *cis*-selectivity of 98.5%, and an M_n of 291,000.[54] It is oft-stated that Ln complexes are strongly *cis*-1,4-selective, and are becoming increasingly widely used industrially where the reliable processing characteristics of the highly linear, high *cis* polymers and the low rolling resistance of the resultant tyres offer advantage over natural rubber. The industrially used compounds are long-chain carboxylates, which are modelled by the results of Anwander[23-25] and also by the fully characterised [Nd(O_2CCHPh_2)$_3$.thf$_2$}$_2$]activated with HAl^{i}Bu$_2$, which gave 97% *cis*-1,4 polyisoprene, with an activity of 3,167 mol IP mol^{-1} Ln h^{-1} to M_n = 147,000.[45] However, 3,4 polymer is also available from lanthanides: In some cases, this has been highly isotactic, generating crystalline polymers, as yet to find an application: T_m of 162 ˚C was recorded for the 99% 3,4 polyisoprene obtained from a cyclopentadienyl phosphide-yttrium complex, if the polymerization was at a sufficiently low temperature.[22] More recently, T_m of 170 ˚C was recorded for an even more highly isotactic 3,4 polyisoprene crystalline polymer obtained using α-diimidosulfonate ligands on Lu.[52] Finally, *trans*-1,4 polymer, analogous to that obtainable naturally from gutta percha, is also obtainable from lanthanides in 99%+

purity, from $\{LaC_5Me_5\}^{2+}$ complexes with rather low activity (42 mol IP mol^{-1} Ln h^{-1} but high M_n (240,000),[29, 30] or from amidooxazoline Lu complexes with excellent activity (10,000 mol IP mol^{-1} Ln h^{-1}) but low M_n (21,000);[44] it seems likely that further research will furnish an optimum of both parameters. However, there is a long-term problem with use of lanthanides for this purpose. As discussed in our previous paper on butadiene,[61] there are strongly competing uses for the unique magnetic properties of the lanthanides, and it is strongly preferable to use base metals where possible. In fact, the most abundant transition metal, iron, would be ideal, and has some precedent. Some time ago Fe was shown to provide very high activity of 824,00 mol IP mol^{-1} Fe h^{-1} but a moderate M_n (1.5 x 10^4) atactic 3,4-polymer in 85% selectivity with $[(bipy)_2FeEt_2]$,[17] or a lower selectivity (67%) but higher M_n (1.4 x 10^6)[18] with $[(bipy)FeCl_2]$, in both cases activated by methylaluminoxane. It seems highly probable that one of the bipy ligands was stripped off by the excess aluminium reagent as part of the activation. More recently, replacement of one pyridyl group with a bulky imine has presented intriguing results: Firstly, tetrahedral precatalysts with single bidentate ligands $LFeCl_2$ were isolable, so that no stripping of ligand was necessary. Secondly, if the imine was aliphatic, a *trans*-1,4 polyisoprene (92% selective) was obtained with good activity (1000 mol IP mol^{-1} Fe h^{-1}) and good M_n (166,667) if sufficient monomer was used, while if an aromatic imine was used, then *cis*-1,4 polymer was obtained, in selectivities which ranged from 66 to 86%, with the balance in all cased being predominantly 3,4 polymer. However, in order to attain a good activity (1,250 mol IP mol^{-1} Fe h^{-1}) and a good *cis*-1,4 selectivity (83%), and sufficient M_n (228, 570) it was necessary to use cryogenic temperatures (-78˚C).[16] Most recently, a *mer*-tridentate benzimidazolyl-imino-pyridine ligand has been placed on $FeCl_3$ to generate a pseudo-octahedral precatalysts which when activated with Al^iBu_3 gave poor activity (19.8 mol IP mol^{-1} Fe h^{-1}) of a moderately *cis*-1,4 polymer (83%) with, surprisingly, a balance of 1,2 and 3,4 units, at very low molecular weight (M_n = 2000, + lower oligomer).[19]

Consequently, the search remains for a catalyst to make polymers to replace natural rubber, so as to protect against the economic and commercial effects of a catastrophic attack on the South-East Asia-Pacific rubber plantations by South American leaf blight,[62] and protect scarce supplies of lanthanides by substituting more readily and widely available metals, as well as give the advantages of processing and reproducibility attendant to synthetic rubbers.[63] While iron remains the best catalytic candidate for long-term supply, it has not yet reached the levels of activity and molecular weight at industrially relevant ambient or above-ambient temperatures, to yield 75-80% *cis*-1,4 rubbers, that we have attained with our cobalt catalysts **1**-**7**. Supply of cobalt, as a byproduct of copper and nickel production, is less under immediate threat than that of lanthandides.[64] Hence, we consider that our results contained herein, reporting good activity, moderately good 1,4 selectivity and high molecular weight for cobalt complexes of triketimines, may be of interest for applications where a modest degree of 3,4 enchained polymer, facilitative of efficient vulcanization, could offer advantage. Indeed, patents underline the improved wet-skid resistance of tyres with 3,4-content, while low rolling resistance of 1,4-cis polymer remains a primary concern to reduce vehicular fuel emissions.[65, 66]

6. Determination of the microstructure of the Co-catalysed polyisoprene samples.

The obtained polyisoprene was characterized by $^{13}C\{^1H\}$NMR in order to investigate its microstructure according with the literature.[41, 46, 67] Methyl group (CH_3) resonances were observed at 23.47, 16.06 and 18.34 ppm for the *cis*-1,4-, *trans*-1,4-, and 3,4 units, respectively. The relative integrals of these well-resolved peaks were used to assess microstructure content. Though data were collected with extended delay times and additional relaxant [Cr(acac)$_3$], nuclear Overhauser effects on the intensity of ^{13}C peaks meant that the data was not truly quantitative between peaks with different numbers of hydrogens. However, when comparing peaks with the same number of attached hydrogens, quantitative data was accessible. The spectra of two different samples with different microstructure are displayed in Figure 11-14. Polyisoprene obtained using catalyst **5** at 35 ˚C resulted in approximately 80% *cis*-1,4 enchainment, but there are also significant amounts of 3,4-vinyl and a very small amount of *trans*-1,4-enchained monomers, as shown by figures 11 and 12. Furthermore, there appears to be some evidence of regioerrors, in the form 4,1-1,4 linkages, especially after 3,4-enchainments. It seems that the chain end resulting from a 3,4 addition is rather poorly selective. This conclusion is drawn from the fact that there are two environments of almost equal abundance in the area of chemical shift expected for C3 of a 3,4-monomer. In order to assign all of the many environments possible from these events, it is helpful to consider all possible triads. Even excluding cases of consecutive 3,4 additions, and neglecting trans additions (since they were at a low level in this sample), it is possible to envisage up to 8 distinct monomer triad environments. Of course, different chemical shifts for all 5 carbons are unlikely to be resolved for all 8 of this restricted menu of possibilities (which would result in 40 peaks), but a substantial portion of them are indeed resolvable. The most abundant triads would be **A** and **C**. Peaks are labelled according to this key.

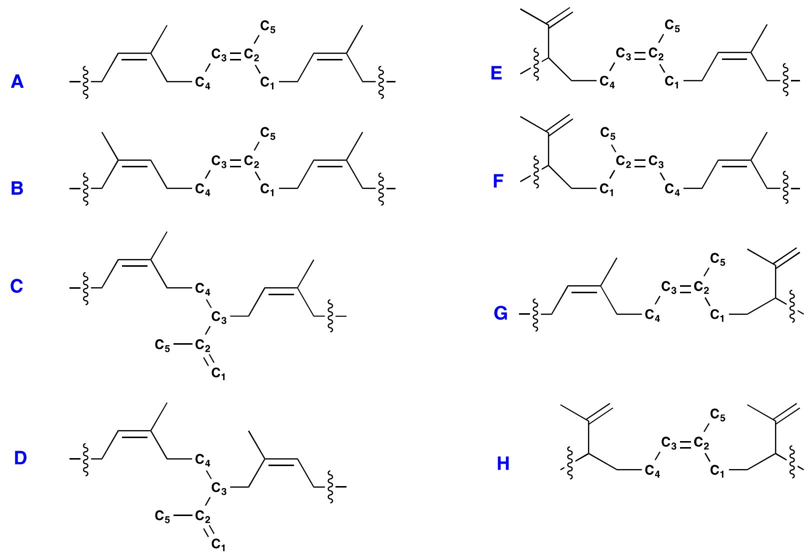


Chart 2. NMR Assignments for high-*cis*-1,4 polyisoprene (*trans* triads and consecutive 3,4 diads neglected).

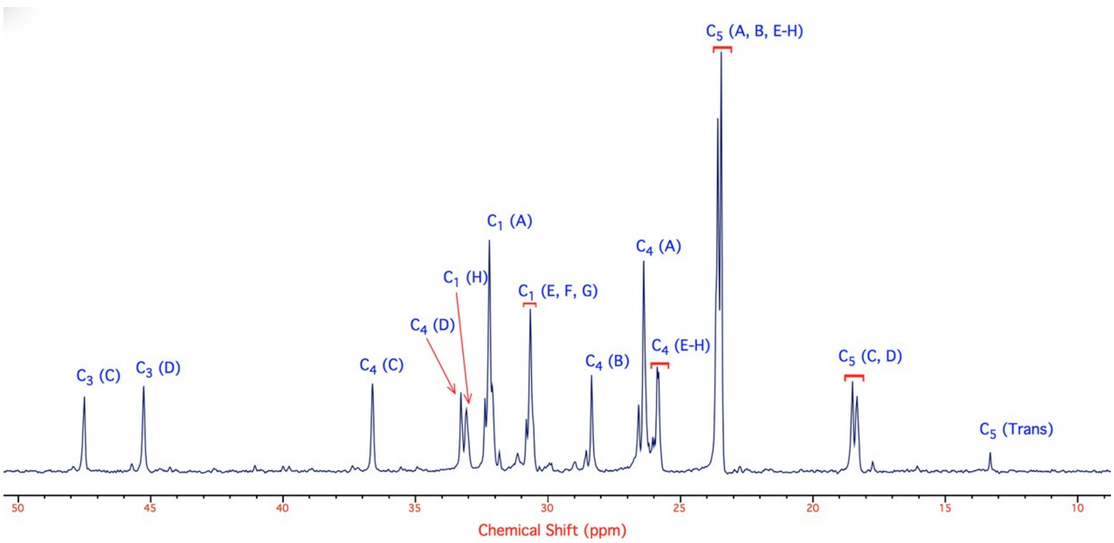


Figure 11: ^{13}C NMR spectrum (sp^3 region) of PI Sample (80% *cis*-1,4-, 0.5 % *trans*-1,4-, and 19.5% 3,4-microstructures).

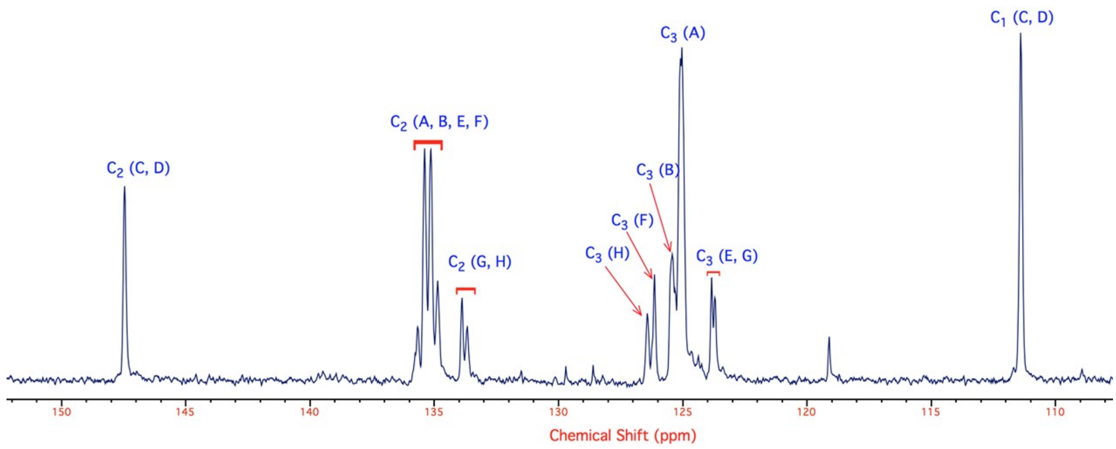


Figure 12: ^{13}C NMR spectrum (sp^2 region) of PI sample (80% *cis*-1,4-, 0.5 % *trans*-1,4-, and 19.5% 3,4-microstructures).

Use of lower temperatures substantially increase trans content, though the yields were also much-reduced. The data shown in Figures 13 and 14 are heavily contaminated with BHT (Butylhydroxytoluene), which was added to all polymers on isolation to discourage oxidation or radical-initiated crosslinking. However, it is clear that the spectra have fewer peaks, indicating a more stereo-selective polymerization, as expected of a lower reaction temperature. The reason for the switch to *trans*-selectivity is addressed in the main discussion. Assignment of the peaks in this high-*trans* polymer requires the definition of further triads incorporating *trans* units. Some of these are shown in Chart 2. Since rather few are well-resolved, and exhaustive list of the possible triads is not given.

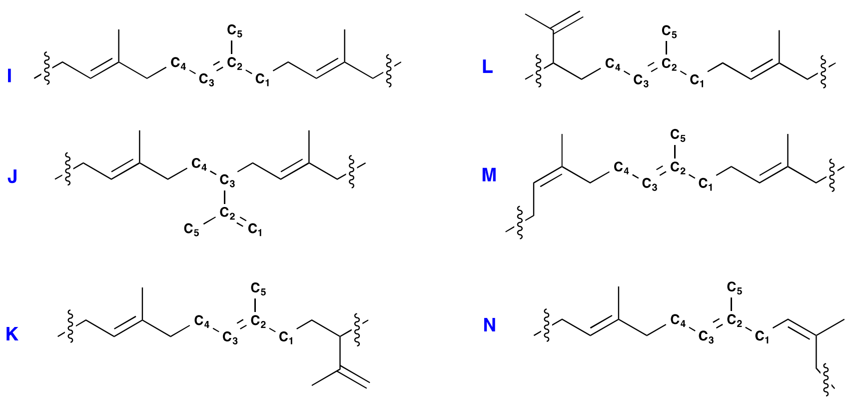


Chart 3: Polymer triads expected in a high-*trans*-1,4 polyisoprene.

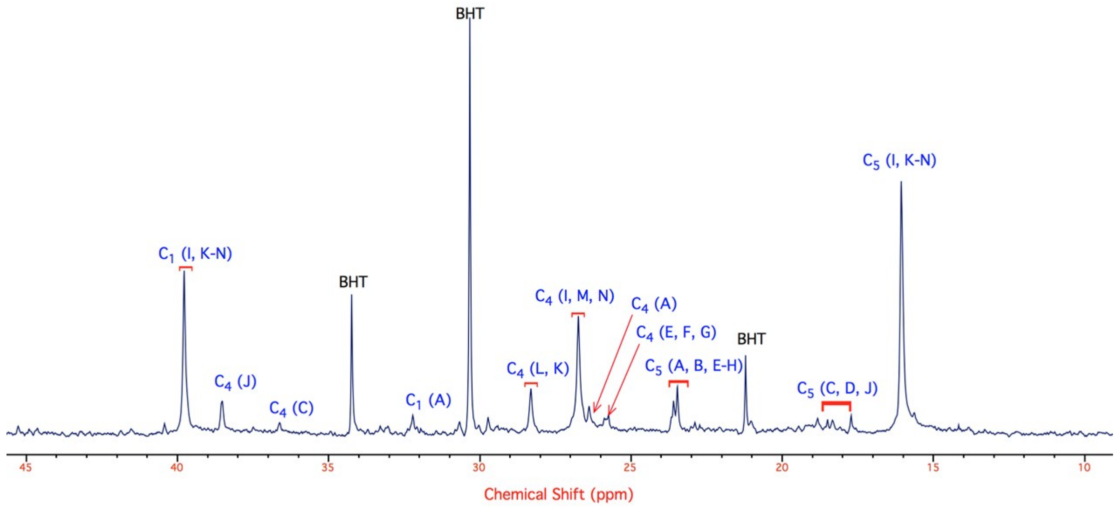


Figure 13: [13]C NMR spectrum (sp^3 region) of PI sample (16.4% *cis*-1,4-, 75.5% *trans*-1,4-, and 7.1% 3,4-microstructures).

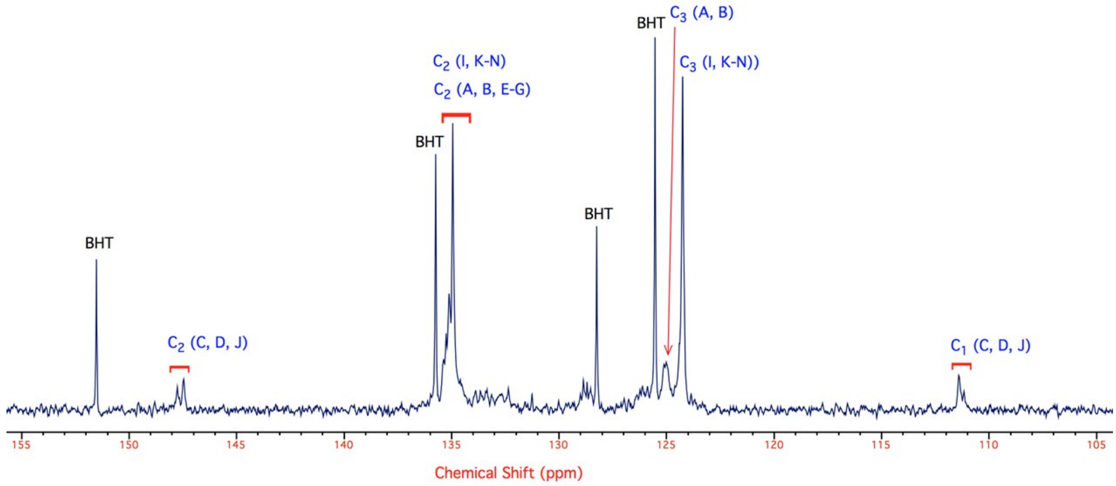


Figure 14: [13]C NMR spectrum (sp^2 region) of PI sample (16.4% *cis*-1,4-, 75.5% *trans*-1,4-, and 7.1% 3,4-microstructures)

7. References

1. U. Gebauer, S. Engelmann and K. Gehrke, *Acta Polym.*, 1989, **40**, 341
2. W. M. Saltman, W. E. Gibbs and J. Lal, *J. Am. Chem. Soc.*, 1958, **80**, 5615.
3. G. Talarico and P. H. M. Budzelaar, *Organometallics*, 2008, **27**, 4098.
4. A. F. Dunlop-Briere, M. C. Baird and P. H. M. Budzelaar, *J. Am. Chem. Soc.*, 2013, **135**, 17514.
5. D. G. Boucher, I. W. Parsons and R. N. Haward, *Makromol. Chem.*, 1974, **175**, 3461.
6. F. Ghiotto, C. Pateraki, J. R. Severn, N. Friederichs and M. Bochmann, *Dalton Trans.*, 2013, **42**, 9040.
7. V. A. Yakovlev, I. F. Gavrilenko, N. N. Glebova and G. N. Bondarenko, *Polym. Sci., Ser. B*, 2014, **56**, 31.
8. G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti and F. Bertini, *Macromolecules*, 2005, **38**, 1064.
9. G. Ricci, G. Leone, A. Boglia, A. C. Boccia and L. Zetta, *Macromolecules*, 2009, **42**, 9263.

10. H. Noguchi and S. Kambara, *J. Polymer. Sci. Part B: Polym Lett*, 1964, **2**, 593.
11. A. He, G. Wang, W. Zhao, X. Jiang, W. Yao and W.-H. Sun, *Polym. Int.*, 2013, **62**, 1758.
12. G. Wang, X. Jiang, W. Zhao, W.-H. Sun, W. Yao and A. He, *J. Appl. Polym. Sci.*, 2014, **131**, 39703.
13. G. Delheye and F. Dawans, *Makromol. Chem.*, 1966, **98**, 164.
14. F. Dawans and P. Teyssie, *Makromol. Chem.*, 1967, **109**, 68.
15. K. Soga, K. Yamamoto and S.-I. Chen, *Polym. Bull.*, 1981, **5**, 1.
16. J. Raynaud, J. Y. Wu and T. Ritter, *Angew. Chem., Int. Ed.*, 2012, **51**, 11805.
17. C. Bazzini, A. Giarrusso, L. Porri, B. Pirozzi and R. Napolitano, *Polymer*, 2004, **45**, 2871.
18. G. Ricci, D. Morganti, A. Sommazzi, R. Santi and F. Masi, *J. Mol. Catal. A: Chem*, 2003, **204–205**, 287.
19. X. Jiang, X. Wen, W.-H. Sun and A. He, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 2395.
20. B. Gao, X. Luo, W. Gao, L. Huang, S.-m. Gao, X. Liu, Q. Wu and Y. Mu, *Dalton Trans.*, 2012, **41**, 2755.
21. Z. Liu, W. Gao, X. Liu, X. Luo, D. Cui and Y. Mu, *Organometallics*, 2011, **30**, 752.
22. L. Zhang, Y. Luo and Z. Hou, *J. Am. Chem. Soc.*, 2005, **127**, 14562.
23. A. Fischbach, F. Perdih, E. Herdtweck and R. Anwander, *Organometallics*, 2006, **25**, 1626.
24. A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer and R. Anwander, *Angew. Chem., Int. Ed.*, 2004, **43**, 2234.
25. M. Zimmermann, N. A. Froeystein, A. Fischbach, P. Sirsch, H. M. Dietrich, K. W. Toernroos, E. Herdtweck and R. Anwander, *Chem. - Eur. J.*, 2007, **13**, 8784.
26. L. Zhang, T. Suzuki, Y. Luo, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.*, 2007, **46**, 1909.
27. Y. Yang, Q. Wang and D. Cui, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 5251.
28. L. Zhang, M. Nishiura, M. Yuki, Y. Luo and Z. Hou, *Angew. Chem., Int. Ed.*, 2008, **47**, 2642.
29. M. Zimmermann, K. W. Tornroos, H. Sitzmann and R. Anwander, *Chem. - Eur. J.*, 2008, **14**, 7266.
30. M. Zimmermann, K. W. Toernroos and R. Anwander, *Angew. Chem., Int. Ed.*, 2008, **47**, 775.
31. Z. Jian, D. Cui, Z. Hou and X. Li, *Chem. Commun.*, 2010, **46**, 3022.
32. Y. Yang, K. Lv, L. Wang, Y. Wang and D. Cui, *Chem. Commun.*, 2010, **46**, 6150.
33. G.-l. Li, C.-y. Ren, W.-m. Dong, L.-s. Jiang, X.-q. Zhang and F.-s. Wang, *Chin. J. Polym. Sci.*, 2010, **28**, 157.
34. L. Annunziata, M. Duc and J.-F. Carpentier, *Macromolecules*, 2011, **44**, 7158.
35. D.-T. Liu and D.-M. Cui, *Dalton Trans.*, 2011, **40**, 7755.
36. Y. Luo, S. Fan, J. Yang, J. Fang and P. Xu, *Dalton Trans.*, 2011, **40**, 3053.
37. Z. Jian and D. Cui, *Dalton Trans.*, 2012, **41**, 2367.
38. L. Wang, D. Liu and D. Cui, *Organometallics*, 2012, **31**, 6014.
39. M. J. Vitorino, P. Zinck and M. Visseaux, *Eur. Polym. J.*, 2012, **48**, 1289.
40. W. Rong, D. Liu, H. Zuo, Y. Pan, Z. Jian, S. Li and D. Cui, *Organometallics*, 2013, **32**, 1166.
41. Y. Hu, W. Dong and T. Masuda, *Macromol. Chem. Phys.*, 2013, **214**, 2172.
42. L. Li, C. Wu, D. Liu, S. Li and D. Cui, *Organometallics*, 2013, **32**, 3203.
43. J. Zhang, Z. Hao, W. Gao, L. Xin, L. Zhang and Y. Mu, *Chem. - Asian J.*, 2013, **8**, 2079.
44. H. Liu, J. He, Z. Liu, Z. Lin, G. Du, S. Zhang and X. Li, *Macromolecules*, 2013, **46**, 3257.
45. D. M. Roitershtein, A. A. Vinogradov, A. A. Vinogradov, K. A. Lyssenko, Y. V. Nelyubina, I. V. Anan'ev, I. E. Nifant'ev, V. A. Yakovlev and N. N. Kostitsyna, *Organometallics*, 2013, **32**, 1272.

46. Y. Hu, C. Zhang, X. Liu, K. Gao, Y. Cao, C. Zhang and X. Zhang, *J. Appl. Polym. Sci.*, 2014, **131**, 40153.
47. Y. Pan, T. Xu, G.-W. Yang, K. Jin and X.-B. Lu, *Inorg. Chem.*, 2013, **52**, 2802.
48. N. Martins, F. Bonnet and M. Visseaux, *Polymer*, 2014, **55**, 5013.
49. B. Liu, X. Wang, Y. Pan, F. Lin, C. Wu, J. Qu, Y. Luo and D. Cui, *Macromolecules*, 2014, **47**, 8524.
50. L. Luconi, D. M. Lyubov, A. Rossin, T. A. Glukhova, A. V. Cherkasov, G. Tuci, G. K. Fukin, A. A. Trifonov and G. Giambastiani, *Organometallics*, 2014, **33**, 7125.
51. C. Yao, D. Liu, P. Li, C. Wu, S. Li, B. Liu and D. Cui, *Organometallics*, 2014, **33**, 684.
52. B. Liu, L. Li, G. Sun, J. Liu, M. Wang, S. Li and D. Cui, *Macromolecules*, 2014, **47**, 4971.
53. L. Guo, X. Zhu, S. Zhou, X. Mu, Y. Wei, S. Wang, Z. Feng, G. Zhang and B. Deng, *Dalton Trans.*, 2014, **43**, 6842.
54. G. Zhang, Y. Wei, L. Guo, X. Zhu, S. Wang, S. Zhou and X. Mu, *Chem. - Eur. J.*, 2014, **21**, 2519.
55. L. N. Jende, C. O. Hollfelder, C. Maichle-Mössmer and R. Anwander, *Organometallics*, 2014, **34**, 32.
56. K. Ratkanthwar, N. Hadjichristidis, S. Lee, T. Chang, Z. Pudukulathan and D. Vlassopoulos, *Polym. Chem.*, 2013, **4**, 5645.
57. V. A. Rozentsvet, V. G. Kozlov, E. F. Ziganshina, N. P. Boreiko and S. V. Kostjuk, *Polym. Int.*, 2013, **62**, 817.
58. S. Ouardad, T. Lebarbe, A. Deffieux and F. Peruch, *Polym. Chem.*, 2013, **4**, 407.
59. B. Krutzer, M. Ros, J. Smit and W. de Jong, *Rubber World*, 2012, **247**, 18, 31.
60. Z. Zhang, D. Cui, B. Wang, B. Liu and Y. Yang, *Struct. Bonding*, 2010, **137**, 49.
61. M. N. Alnajrani and F. S. Mair, *Dalton Trans.*, 2014, **43**, 15727.
62. *Protection against South American leaf blight of rubber in Asia and the Pacific region*, FAO Regional Office for Asia and the Pacific, 2011.
63. N. Nakajima, *Science and Practice of Rubber Mixing*, RAPRA Technology Ltd, Shawbury, Shropshire, UK, 2000.
64. G. B. Brook and E. A. Brandes, *Smithells Light Metals Handbook*, Elsevier Science, Burlington, 1998.
65. J. Wolpers, H. B. Fuchs, C. Herrmann and W. Hellermann, EP456902A1, 1991.
66. J. D. Massie II, W. L. Hsu, A. F. Halasa and P. H. Sandstrom, US5356997A, 1994.
67. V. A. Rozentsvet, A. S. Khachaturov and V. P. Ivanova, *Polym. Sci. Ser. A*, 2009, **51**, 870.

8. Appendices:

8.1 Appendix A:

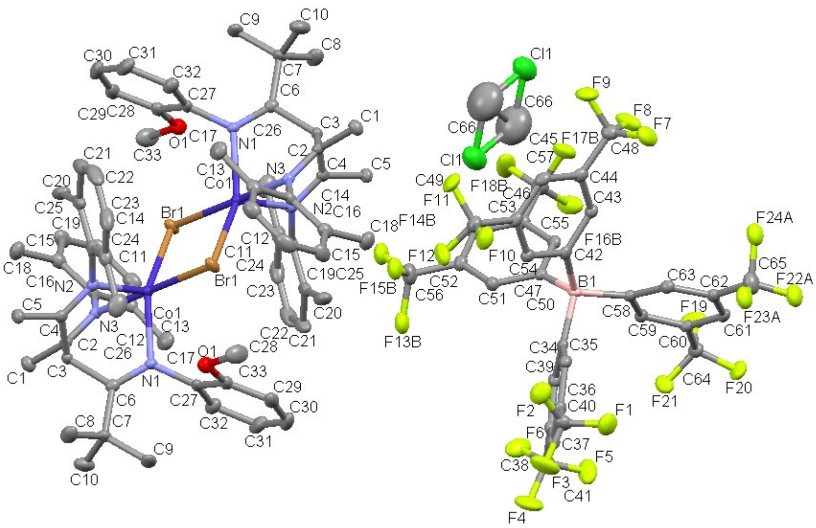


Figure A1: Thermal Ellipsoid plot (50% probability) of **3**, showing BArF anion and dichloromethane of solvation. Hydrogen atoms and minor components of rotational disorder in CF_3 groups are removed.

Table 1: Crystal data and structure refinement for 3.

Identification code	**3**
Empirical formula	$C_{132}H_{110}B_2Br_2Cl_2Co_2F_{48}N_6O_2$
Formula weight	3094.45
Temperature/K	99.90(14)
Crystal system	triclinic
Space group	P-1
a/Å	12.6292(4)
b/Å	16.5399(5)
c/Å	16.5440(6)
α/°	77.217(3)
β/°	76.631(3)
γ/°	85.363(3)
Volume/Å^3	3277.2(2)

Z	1
$\rho_{calc}g/cm^3$	1.568
μ/mm^{-1}	1.026
F(000)	1560.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.958 to 54.758
Index ranges	$-16 \le h \le 9$, $-19 \le k \le 19$, $-20 \le l \le 21$
Reflections collected	19773
Independent reflections	12632 [R_{int} = 0.0268, R_{sigma} = 0.0509]
Data/restraints/parameters	12632/72/905
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1533
Final R indexes [all data]	R_1 = 0.0670, wR_2 = 0.1671
Largest diff. peak/hole / e Å^{-3}	1.62/-0.97

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	4806.8(3)	4496.5(2)	4264.8(2)	20.39(12)
Co1	4241.1(4)	4206.1(3)	5835.5(3)	13.29(13)
F11	4429.5(19)	421.2(15)	7145.1(16)	31.7(5)
F10	5148(2)	-267.3(15)	6186.0(15)	31.9(6)
F21	12250.5(18)	-2475.1(15)	8807.3(16)	30.4(5)
F12	6062(2)	658.0(14)	6426.8(17)	35.0(6)
F9	3707.6(18)	-1824.0(17)	9621.5(16)	36.1(6)
F1	9616(2)	-2258.2(15)	4909.0(16)	35.9(6)
F6	12483(2)	-38.9(17)	6636.6(19)	43.4(7)
F19	11447(2)	-2902.7(18)	10114.9(16)	37.4(6)
F20	12135.7(18)	-3781.1(14)	9340.4(16)	30.5(5)
F2	8647(2)	-1136.3(16)	4783.2(16)	35.0(6)
F15B	7888(5)	1903(4)	7569(4)	31.3(5)
F7	4538(2)	-2905.1(16)	9247.4(17)	40.0(6)
F4	13012(2)	-359(2)	5421.9(17)	45.7(7)
O1	3785(2)	5500.0(16)	7551.6(17)	25.2(6)
F8	5065(2)	-2373.9(18)	10151.2(15)	37.4(6)
F5	12989(2)	-1287.5(17)	6554(2)	49.7(8)
F3	10316(2)	-1133(2)	4114.4(15)	47.2(7)
F17B	7336(6)	-784(7)	11204(5)	35.5(19)
F18B	7988(14)	371(4)	11203(5)	48(3)
N3	3357(2)	3149.4(17)	5809.4(18)	13.0(6)
F16B	9032(7)	-723(9)	11133(8)	40(2)
F22A	9108(4)	-5199(3)	8981(3)	33.8(5)
N2	5117(2)	3397.8(18)	6611.3(18)	15.4(6)
F13B	9589(4)	1941(3)	7498(3)	31.3(5)
C55	8534(3)	-723(2)	9449(2)	17.5(7)
C39	10517(3)	-874(2)	7000(2)	18.4(7)
C43	6576(3)	-1737(2)	8678(2)	16.5(7)

C3	3350(3)	2834(2)	7307(2)	14.7(7)
C2	3033(3)	2660(2)	6522(2)	14.4(7)
N1	3012(2)	4302.5(17)	6938.4(18)	14.6(6)
C36	9969(3)	-1237(2)	5600(2)	18.8(7)
C47	6903(3)	-697(2)	7416(2)	17.0(7)
C63	8649(3)	-2957(2)	8472(2)	17.8(7)
F24A	7583(4)	-4576(3)	9349(3)	33.8(5)
C50	8687(3)	-575(2)	8565(2)	16.3(7)
C44	5456(3)	-1643(2)	8720(2)	18.7(7)
C53	8422(3)	744(2)	9457(2)	19.3(8)
C65	8575(4)	-4490(3)	8750(3)	33.8(5)
C35	9206(3)	-1305(2)	6371(2)	17.2(7)
C6	2799(3)	3652(2)	7526(2)	15.6(7)
C12	2461(3)	3521(2)	4608(2)	20.6(8)
C60	10523(3)	-3042(2)	9064(2)	16.9(7)
C41	12439(3)	-625(2)	6212(3)	24.2(8)
C54	8409(3)	-80(2)	9891(2)	18.9(7)
C51	8714(3)	260(2)	8146(2)	17.5(7)
F23A	8319(4)	-4490(3)	8025(3)	33.8(5)
C42	7335(3)	-1270(2)	8020(2)	15.8(7)
C59	10028(3)	-2280(2)	8801(2)	16.7(7)
C11	3175(3)	2983(2)	5030(2)	16.7(7)
C61	10067(3)	-3779(2)	9063(2)	18.3(7)
C5	5092(3)	2171(2)	7774(2)	19.5(8)
C57	8218(3)	-286(2)	10838(2)	25.5(8)
C27	2454(3)	5106(2)	6958(2)	18.4(7)
C16	3766(3)	2340(2)	4676(2)	20.2(8)
C37	11027(3)	-1004(2)	5528(2)	21.2(8)
C24	6609(3)	3863(2)	7104(3)	25.3(8)
F14B	8434(5)	2355(2)	8520(3)	31.3(5)
C14	2999(4)	2820(3)	3437(2)	28.6(9)
C46	5783(3)	-593(2)	7460(2)	18.1(7)
C48	4698(3)	-2181(3)	9430(3)	24.7(8)
B1	8634(3)	-1300(2)	8042(2)	14.9(8)
C52	8577(3)	901(2)	8581(2)	20.6(8)
C32	1501(3)	5263(2)	6663(2)	24.8(8)
C21	8114(3)	3383(3)	5760(3)	35.2(11)
C8	2697(4)	3059(3)	9076(2)	30.9(10)
C34	9454(3)	-1121(2)	7096(2)	16.5(7)
C33	4372(4)	6157(3)	7687(3)	38.9(11)
C10	1064(4)	3071(3)	8436(3)	34.2(10)
C28	2901(3)	5731(2)	7213(2)	21.5(8)
C62	9114(3)	-3726(2)	8764(2)	18.1(7)
C19	6277(3)	3490(2)	6523(2)	19.7(8)
C49	5365(3)	43(2)	6806(3)	21.9(8)
C40	9640(3)	-1435(2)	4856(2)	25.3(8)
C30	1423(4)	6662(3)	6863(3)	34.2(11)
C64	11583(3)	-3056(2)	9334(2)	21.6(8)
C7	2058(3)	3551(2)	8423(2)	20.7(8)
C56	8560(3)	1776(2)	8074(3)	31.3(5)
C45	5052(3)	-1072(2)	8108(2)	19.8(8)

C1	2368(3)	1913(2)	6672(2)	20.0(8)
C13	2382(3)	3432(3)	3811(3)	26.9(9)
C58	9074(3)	-2209(2)	8486(2)	14.9(7)
C26	5819(4)	4111(3)	7849(3)	35.1(10)
C29	2381(4)	6512(2)	7152(3)	29.5(9)
C20	7015(3)	3234(2)	5852(3)	24.3(8)
C4	4595(3)	2838(2)	7191(2)	14.8(7)
C31	969(4)	6044(3)	6622(3)	33.8(10)
C38	11292(3)	-828(2)	6238(2)	19.1(8)
C15	3664(3)	2279(2)	3869(2)	26.1(9)
C25	6662(3)	2782(3)	5270(3)	30.1(9)
C23	7718(4)	3990(3)	6980(3)	34.9(11)
C9	1659(4)	4372(2)	8712(2)	28.0(9)
C18	4465(4)	1703(2)	5129(3)	27.5(9)
C17	1791(3)	4167(3)	5022(3)	28.4(9)
Cl1	5730.8(13)	432.7(9)	9219.4(9)	57.0(4)
C22	8458(3)	3756(3)	6317(3)	40.2(12)
C66	5548(8)	-178(7)	10190(7)	117(3)
F24B	7518(5)	-4444(4)	8954(5)	33.8(5)
F23B	8874(7)	-4651(4)	7933(4)	33.8(5)
F22B	8945(7)	-5165(5)	9239(5)	33.8(5)
F17A	7213(10)	-450(20)	11203(12)	52(4)
F18A	8520(20)	336(9)	11140(11)	41(4)
F16A	8834(19)	-940(10)	11116(17)	36(4)
F14A	7867(6)	2287(3)	8556(4)	31.3(5)
F13A	9495(5)	2116(4)	7803(4)	31.3(5)
F15A	8068(7)	1831(5)	7398(5)	31.3(5)

Table 3: Anisotropic Displacement Parameters (Å^2×10^3) for 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	28.7(2)	17.91(19)	13.47(19)	-3.25(13)	0.35(15)	-9.24(15)
Co1	14.3(2)	12.1(2)	12.1(2)	-2.14(17)	-0.34(18)	-0.87(18)
F11	26.4(12)	31.2(13)	38.4(14)	-11.0(11)	-10.7(11)	14.8(10)
F10	44.2(15)	30.1(13)	27.6(13)	-9.1(10)	-21.1(11)	8.9(11)
F21	18.1(11)	32.5(13)	39.6(14)	-1.0(11)	-9.1(10)	-4.5(10)
F12	30.7(13)	25.5(12)	45.7(15)	7.6(11)	-15.9(12)	-2.7(10)
F9	16.9(11)	49.3(15)	36.3(14)	-6.9(12)	4.3(10)	-2.2(11)
F1	47.0(15)	28.2(13)	38.8(15)	-20.1(11)	-10.1(12)	-0.3(11)
F6	23.3(12)	50.3(16)	64.9(19)	-33.9(14)	-1.9(13)	-11.8(12)
F19	26.7(13)	64.7(18)	28.4(13)	-22.1(12)	-12.0(11)	6.2(12)
F20	22.3(12)	27.6(12)	41.9(14)	-5.8(10)	-12.5(11)	9.8(10)
F2	38.3(14)	42.7(15)	31.8(14)	-15.0(11)	-18.7(11)	5.2(12)
F15B	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
F7	45.8(15)	30.3(13)	41.7(15)	-10.6(11)	3.0(13)	-17.3(12)

F4	23.5(13)	73(2)	35.3(15)	-6.8(14)	5.6(11)	-19.2(13)
O1	27.1(14)	22.1(14)	27.8(15)	-11.0(11)	-1.4(12)	-5.8(11)
F8	27.7(13)	61.9(17)	19.5(12)	4.0(11)	-6.3(10)	-14.5(12)
F5	24.2(13)	35.6(15)	86(2)	3.4(14)	-20.9(14)	0.0(11)
F3	51.5(17)	73(2)	16.3(12)	-9.4(12)	3.9(12)	-28.5(15)
F17B	32(3)	49(4)	20(2)	-2(3)	2.1(19)	-10(2)
F18B	86(7)	33(2)	22(2)	-13.5(18)	-1(4)	7(3)
N3	12.8(13)	13.9(14)	13.6(14)	-5.3(11)	-3.4(11)	-0.5(11)
F16B	29(3)	65(5)	24(3)	-2(4)	-11(2)	4(3)
F22A	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
N2	15.6(14)	15.4(14)	15.8(15)	-5.6(12)	-2.6(12)	0.9(12)
F13B	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
C55	15.1(17)	16.3(17)	20.8(18)	-2.9(14)	-4.9(14)	2.2(14)
C39	17.3(17)	16.2(17)	22.0(19)	-4.7(14)	-4.5(15)	-0.2(14)
C43	16.0(17)	17.1(17)	17.9(18)	-5.6(14)	-5.6(14)	2.1(14)
C3	17.0(17)	11.9(16)	13.2(17)	-1.5(13)	-0.3(14)	0.2(13)
C2	13.8(16)	15.4(16)	14.2(17)	-5.5(13)	-2.2(14)	1.8(13)
N1	12.8(14)	15.1(14)	15.0(15)	-5.2(11)	0.3(11)	-0.1(11)
C36	24.6(19)	14.7(17)	18.0(18)	-6.7(14)	-3.6(15)	0.8(15)
C47	16.4(17)	16.6(17)	18.9(18)	-6.9(14)	-2.3(14)	-0.2(14)
C63	16.6(17)	21.0(18)	16.2(18)	-5.6(14)	-3.3(14)	1.2(15)
F24A	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
C50	12.4(16)	17.9(17)	18.2(18)	-3.5(14)	-3.2(14)	1.0(14)
C44	17.9(17)	21.8(18)	19.8(18)	-11.7(15)	-4.2(15)	-0.8(15)
C53	18.9(18)	18.3(18)	22.4(19)	-8.5(15)	-4.7(15)	2.8(15)
C65	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
C35	14.4(17)	16.2(17)	20.3(18)	-4.0(14)	-2.5(14)	-0.3(14)
C6	14.5(16)	18.7(17)	15.6(17)	-7.1(14)	-3.8(14)	-0.5(14)
C12	18.6(18)	22.4(19)	21.5(19)	-2.2(15)	-6.5(15)	-6.1(15)
C60	14.8(17)	20.0(18)	15.7(17)	-5.9(14)	-1.8(14)	2.2(14)
C41	17.9(18)	23.9(19)	29(2)	-6.3(16)	-0.7(16)	-1.5(16)
C54	15.5(17)	22.5(18)	19.3(18)	-6.8(15)	-3.0(15)	0.6(15)
C51	19.0(17)	16.9(17)	16.6(18)	-3.9(14)	-2.9(14)	-1.3(14)
F23A	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
C42	18.5(17)	12.8(16)	18.2(18)	-8.0(13)	-3.8(14)	1.0(14)
C59	18.3(17)	16.3(17)	16.0(17)	-5.1(14)	-3.2(14)	0.1(14)
C11	21.7(18)	15.2(16)	12.9(17)	-2.3(13)	-1.4(14)	-6.8(14)
C61	20.1(18)	15.3(17)	17.0(18)	-4.1(14)	-0.4(15)	5.3(14)
C5	19.8(18)	16.1(17)	20.5(19)	-0.3(14)	-4.3(15)	1.0(15)
C57	29.3(19)	28.7(19)	18.7(18)	-7.2(15)	-4.2(15)	1.9(15)
C27	24.5(19)	11.6(16)	14.0(17)	-1.8(13)	4.6(15)	1.0(14)
C16	24.1(19)	19.5(18)	18.0(18)	-5.6(14)	-3.3(15)	-5.2(15)
C37	21.8(19)	18.0(18)	21.1(19)	-3.2(15)	-0.9(16)	1.2(15)
C24	26(2)	18.5(18)	33(2)	-0.8(16)	-13.4(18)	-1.9(16)
F14B	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
C14	37(2)	36(2)	15.4(19)	-4.5(17)	-7.4(17)	-13.8(19)
C46	18.4(17)	17.4(17)	22.4(19)	-9.2(14)	-8.7(15)	3.4(14)
C48	18.7(18)	30(2)	27(2)	-9.1(17)	-4.4(16)	-2.6(16)
B1	10.5(17)	19.5(19)	13.6(19)	-3.4(15)	-0.3(15)	-1.1(15)
C52	19.9(18)	18.6(18)	24(2)	-5.3(15)	-7.3(15)	1.7(15)
C32	27(2)	25(2)	20(2)	-6.8(16)	-3.4(16)	6.3(17)

C21	17.7(19)	32(2)	42(3)	11(2)	0.9(19)	3.0(18)
C8	43(3)	30(2)	15.8(19)	-5.6(16)	-2.5(18)	8.9(19)
C34	18.1(17)	12.4(16)	18.6(18)	-3.5(13)	-4.6(14)	3.1(14)
C33	36(2)	39(3)	48(3)	-28(2)	1(2)	-12(2)
C10	30(2)	37(2)	31(2)	-12.7(19)	10.7(19)	-8.9(19)
C28	28(2)	18.3(18)	15.6(18)	-4.2(14)	2.4(15)	-2.6(16)
C62	20.9(18)	16.4(17)	15.0(17)	-3.3(14)	0.1(15)	0.1(15)
C19	16.4(17)	13.4(17)	27(2)	2.5(14)	-6.9(15)	1.9(14)
C49	19.9(18)	20.0(18)	27(2)	-7.2(16)	-7.7(16)	2.8(15)
C40	28(2)	28(2)	19.5(19)	-7.6(16)	0.3(16)	-3.7(17)
C30	48(3)	22(2)	24(2)	-2.5(16)	2(2)	14.3(19)
C64	20.6(18)	22.6(19)	20.9(19)	-4.5(15)	-4.8(15)	3.4(16)
C7	23.3(19)	18.7(18)	15.2(18)	-2.8(14)	5.6(15)	-2.2(15)
C56	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
C45	14.2(17)	24.8(19)	23.9(19)	-11.4(15)	-6.1(15)	2.5(15)
C1	23.0(19)	19.2(18)	18.0(18)	-2.4(14)	-5.0(15)	-5.3(15)
C13	28(2)	32(2)	21(2)	-0.4(17)	-9.8(17)	-6.4(18)
C58	15.0(16)	16.4(17)	12.3(16)	-3.8(13)	-0.6(13)	0.4(14)
C26	40(3)	34(2)	42(3)	-18(2)	-21(2)	0(2)
C29	41(2)	17.8(19)	23(2)	-6.8(15)	8.4(18)	-0.6(18)
C20	20.8(19)	19.7(18)	25(2)	6.1(15)	-1.0(16)	2.0(15)
C4	17.2(17)	14.4(16)	13.8(17)	-6.8(13)	-1.6(14)	-0.6(14)
C31	35(2)	35(2)	26(2)	-6.4(18)	-4.1(19)	18(2)
C38	17.9(18)	12.2(16)	26(2)	-4.3(14)	-1.5(15)	-1.9(14)
C15	38(2)	21.1(19)	21(2)	-10.0(16)	-2.0(17)	-9.7(17)
C25	28(2)	33(2)	22(2)	-4.1(17)	5.7(17)	6.3(18)
C23	31(2)	21(2)	57(3)	1.4(19)	-25(2)	-3.3(18)
C9	37(2)	23(2)	16.2(19)	-5.4(15)	8.9(17)	2.0(18)
C18	35(2)	21.2(19)	27(2)	-9.4(16)	-6.2(18)	5.4(17)
C17	27(2)	30(2)	29(2)	-4.7(17)	-10.9(18)	6.7(18)
Cl1	69.5(9)	46.9(7)	51.1(8)	-14.4(6)	2.4(7)	-16.3(7)
C22	17(2)	34(2)	61(3)	15(2)	-12(2)	-7.3(18)
C66	113(8)	121(8)	130(9)	-32(7)	-55(7)	16(6)
F24B	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
F23B	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
F22B	40.2(11)	23.4(8)	40.3(13)	-4.7(9)	-13.7(11)	-6.1(8)
F17A	33(4)	78(11)	36(6)	-11(8)	7(4)	-2(5)
F18A	67(9)	39(5)	23(5)	-16(4)	-12(7)	-7(5)
F16A	51(7)	32(5)	28(5)	-5(5)	-19(6)	3(5)
F14A	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
F13A	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)
F15A	42.1(12)	19.2(8)	34.8(12)	-5.3(7)	-13(1)	-1.6(8)

Table 4: Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Br1	Co1	2.4777(6)	C65	F23A	1.313(6)
Br1	Co1[1]	2.4991(6)	C65	C62	1.490(6)
Co1	Br1[1]	2.4992(6)	C65	F24B	1.299(7)
Co1	N3	2.162(3)	C65	F23B	1.394(8)
Co1	N2	2.077(3)	C65	F22B	1.345(8)
Co1	N1	2.132(3)	C35	C34	1.406(5)
F11	C49	1.353(4)	C6	C7	1.543(5)
F10	C49	1.333(4)	C12	C11	1.407(5)
F21	C64	1.347(4)	C12	C13	1.386(5)
F12	C49	1.345(5)	C12	C17	1.496(5)
F9	C48	1.339(5)	C60	C59	1.387(5)
F1	C40	1.346(5)	C60	C61	1.390(5)
F6	C41	1.329(5)	C60	C64	1.504(5)
F19	C64	1.340(4)	C41	C38	1.502(5)
F20	C64	1.338(4)	C54	C57	1.495(5)
F2	C40	1.332(5)	C51	C52	1.387(5)
F15B	C56	1.297(7)	C42	B1	1.646(5)
F7	C48	1.339(5)	C59	C58	1.406(5)
F4	C41	1.336(5)	C11	C16	1.405(5)
O1	C33	1.447(5)	C61	C62	1.393(5)
O1	C28	1.353(5)	C5	C4	1.495(5)
F8	C48	1.343(5)	C57	F17A	1.294(12)
F5	C41	1.337(5)	C57	F18A	1.351(11)
F3	C40	1.341(5)	C57	F16A	1.339(13)
F17B	C57	1.378(7)	C27	C32	1.385(6)
F18B	C57	1.336(6)	C27	C28	1.402(5)
N3	C2	1.273(4)	C16	C15	1.396(5)
N3	C11	1.448(4)	C16	C18	1.502(5)
F16B	C57	1.330(8)	C37	C38	1.387(5)
F22A	C65	1.329(6)	C24	C19	1.403(6)
N2	C19	1.456(5)	C24	C26	1.508(6)
N2	C4	1.274(5)	C24	C23	1.394(6)
F13B	C56	1.428(6)	F14B	C56	1.313(6)
C55	C50	1.399(5)	C14	C13	1.394(6)
C55	C54	1.397(5)	C14	C15	1.375(6)
C39	C34	1.399(5)	C46	C49	1.493(5)
C39	C38	1.397(5)	C46	C45	1.383(5)
C43	C44	1.397(5)	B1	C34	1.644(5)
C43	C42	1.402(5)	B1	C58	1.635(5)
C3	C2	1.535(5)	C52	C56	1.505(5)
C3	C6	1.546(5)	C32	C31	1.401(6)
C3	C4	1.540(5)	C21	C20	1.397(6)
C2	C1	1.494(5)	C21	C22	1.378(7)
N1	C6	1.280(5)	C8	C7	1.546(6)
N1	C27	1.456(4)	C10	C7	1.532(6)
C36	C35	1.398(5)	C28	C29	1.394(5)
C36	C37	1.391(5)	C19	C20	1.394(6)
C36	C40	1.495(5)	C30	C29	1.386(7)
C47	C42	1.394(5)	C30	C31	1.383(7)
C47	C46	1.398(5)	C7	C9	1.546(5)
C63	C62	1.391(5)	C56	F14A	1.405(7)

C63	C58	1.394(5)	C56	F13A	1.290(7)
F24A	C65	1.402(6)	C56	F15A	1.383(9)
C50	C51	1.401(5)	C20	C25	1.503(6)
C50	B1	1.640(5)	C23	C22	1.372(7)
C44	C48	1.498(5)	Cl1	C66	1.673(10)
C44	C45	1.384(5)	Cl1	C66[2]	1.715(11)
C53	C54	1.392(5)	C66	Cl1[2]	1.715(11)
C53	C52	1.384(5)			

Table 5: Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Co1	Br1	Co1[1]	94.544(18)	C15	C16	C11	117.7(4)
Br1	Co1	Br1[1]	85.455(19)	C15	C16	C18	118.5(3)
N3	Co1	Br1	90.06(8)	C38	C37	C36	118.1(3)
N3	Co1	Br1[1]	174.15(8)	C19	C24	C26	122.5(4)
N2	Co1	Br1	122.55(8)	C23	C24	C19	117.5(4)
N2	Co1	Br1[1]	97.95(8)	C23	C24	C26	120.0(4)
N2	Co1	N3	87.63(11)	C15	C14	C13	120.2(4)
N2	Co1	N1	88.64(11)	C47	C46	C49	119.9(3)
N1	Co1	Br1	148.20(8)	C45	C46	C47	120.7(3)
N1	Co1	Br1[1]	97.05(8)	C45	C46	C49	119.4(3)
N1	Co1	N3	84.79(11)	F9	C48	F7	105.9(3)
C28	O1	C33	116.8(3)	F9	C48	F8	106.6(3)
C2	N3	Co1	115.9(2)	F9	C48	C44	112.5(3)
C2	N3	C11	121.4(3)	F7	C48	F8	106.0(3)
C11	N3	Co1	122.6(2)	F7	C48	C44	112.6(3)
C19	N2	Co1	121.3(2)	F8	C48	C44	112.7(3)
C4	N2	Co1	117.7(2)	C50	B1	C42	102.1(3)
C4	N2	C19	120.9(3)	C50	B1	C34	111.9(3)
C54	C55	C50	122.3(3)	C34	B1	C42	113.9(3)
C38	C39	C34	122.2(3)	C58	B1	C50	113.1(3)
C44	C43	C42	122.2(3)	C58	B1	C42	113.5(3)
C2	C3	C6	110.9(3)	C58	B1	C34	102.7(3)
C2	C3	C4	111.4(3)	C53	C52	C51	121.3(3)
C4	C3	C6	111.6(3)	C53	C52	C56	120.8(3)
N3	C2	C3	118.4(3)	C51	C52	C56	117.8(3)
N3	C2	C1	125.8(3)	C27	C32	C31	120.6(4)
C1	C2	C3	115.8(3)	C22	C21	C20	121.3(4)
C6	N1	Co1	118.2(2)	C39	C34	C35	115.8(3)
C6	N1	C27	124.7(3)	C39	C34	B1	120.0(3)
C27	N1	Co1	117.2(2)	C35	C34	B1	123.7(3)
C35	C36	C40	119.0(3)	O1	C28	C27	115.7(3)
C37	C36	C35	120.7(3)	O1	C28	C29	125.2(4)
C37	C36	C40	120.3(3)	C29	C28	C27	118.9(4)
C42	C47	C46	122.3(3)	C63	C62	C65	118.8(3)

C62	C63	C58	122.9(3)	C63	C62	C61	120.5(3)
C55	C50	C51	115.8(3)	C61	C62	C65	120.7(3)
C55	C50	B1	123.5(3)	C24	C19	N2	118.4(3)
C51	C50	B1	119.9(3)	C20	C19	N2	119.2(3)
C43	C44	C48	119.0(3)	C20	C19	C24	122.4(4)
C45	C44	C43	120.6(3)	F11	C49	C46	111.9(3)
C45	C44	C48	120.4(3)	F10	C49	F11	106.1(3)
C52	C53	C54	117.9(3)	F10	C49	F12	106.5(3)
F22A	C65	F24A	102.8(4)	F10	C49	C46	113.4(3)
F22A	C65	C62	115.3(4)	F12	C49	F11	105.5(3)
F24A	C65	C62	110.1(4)	F12	C49	C46	112.9(3)
F23A	C65	F22A	108.4(4)	F1	C40	C36	112.3(3)
F23A	C65	F24A	104.8(4)	F2	C40	F1	105.8(3)
F23A	C65	C62	114.3(4)	F2	C40	F3	106.5(3)
F24B	C65	C62	114.2(4)	F2	C40	C36	112.6(3)
F24B	C65	F23B	107.5(5)	F3	C40	F1	106.2(3)
F24B	C65	F22B	109.9(5)	F3	C40	C36	112.9(3)
F23B	C65	C62	109.0(4)	C31	C30	C29	120.7(4)
F22B	C65	C62	111.6(5)	F21	C64	C60	111.3(3)
F22B	C65	F23B	104.0(5)	F19	C64	F21	106.5(3)
C36	C35	C34	122.2(3)	F19	C64	C60	112.5(3)
N1	C6	C3	115.7(3)	F20	C64	F21	106.3(3)
N1	C6	C7	129.9(3)	F20	C64	F19	106.7(3)
C7	C6	C3	114.4(3)	F20	C64	C60	113.2(3)
C11	C12	C17	120.3(3)	C6	C7	C8	108.8(3)
C13	C12	C11	118.7(4)	C6	C7	C9	115.0(3)
C13	C12	C17	121.0(4)	C10	C7	C6	107.7(3)
C59	C60	C61	121.2(3)	C10	C7	C8	110.2(3)
C59	C60	C64	118.5(3)	C10	C7	C9	108.7(3)
C61	C60	C64	120.3(3)	C9	C7	C8	106.3(3)
F6	C41	F4	106.5(3)	F15B	C56	F13B	102.7(4)
F6	C41	F5	106.5(3)	F15B	C56	F14B	110.8(4)
F6	C41	C38	112.6(3)	F15B	C56	C52	113.8(4)
F4	C41	F5	106.4(3)	F13B	C56	C52	109.4(3)
F4	C41	C38	112.8(3)	F14B	C56	F13B	103.9(4)
F5	C41	C38	111.6(3)	F14B	C56	C52	115.0(4)
C55	C54	C57	119.2(3)	F14A	C56	C52	110.3(4)
C53	C54	C55	120.5(3)	F13A	C56	C52	115.2(4)
C53	C54	C57	120.3(3)	F13A	C56	F14A	107.6(4)
C52	C51	C50	122.2(3)	F13A	C56	F15A	109.4(5)
C43	C42	B1	121.6(3)	F15A	C56	C52	111.5(5)
C47	C42	C43	115.8(3)	F15A	C56	F14A	101.9(5)
C47	C42	B1	122.0(3)	C46	C45	C44	118.4(3)
C60	C59	C58	122.2(3)	C12	C13	C14	120.4(4)
C12	C11	N3	118.2(3)	C63	C58	C59	115.5(3)
C16	C11	N3	120.3(3)	C63	C58	B1	123.7(3)
C16	C11	C12	121.4(3)	C59	C58	B1	120.2(3)
C60	C61	C62	117.7(3)	C30	C29	C28	120.6(4)
F17B	C57	C54	112.1(4)	C21	C20	C25	120.6(4)
F18B	C57	F17B	104.0(5)	C19	C20	C21	117.3(4)
F18B	C57	C54	114.3(5)	C19	C20	C25	122.0(3)

F16B	C57	F17B	103.4(6)	N2	C4	C3	118.1(3)
F16B	C57	F18B	108.0(6)	N2	C4	C5	125.5(3)
F16B	C57	C54	113.9(6)	C5	C4	C3	116.4(3)
F17A	C57	C54	112.9(10)	C30	C31	C32	119.0(4)
F17A	C57	F18A	108.3(9)	C39	C38	C41	118.7(3)
F17A	C57	F16A	107.7(11)	C37	C38	C39	121.0(3)
F18A	C57	C54	111.4(8)	C37	C38	C41	120.3(3)
F16A	C57	C54	111.9(12)	C14	C15	C16	121.5(4)
F16A	C57	F18A	104.2(9)	C22	C23	C24	121.2(4)
C32	C27	N1	118.6(3)	C66	Cl1	C66[2]	58.8(5)
C32	C27	C28	120.1(3)	C23	C22	C21	120.2(4)
C28	C27	N1	121.2(3)	Cl1	C66	Cl1[2]	121.2(5)
C11	C16	C18	123.7(3)				

Table 6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3.

Atom	*x*	*y*	*z*	U(eq)
H55	8516	-1268	9754	21
H39	10715	-735	7459	22
H43	6825	-2122	9100	20
H3	3078	2383	7788	18
H47	7376	-373	6968	20
H63	8027	-2941	8258	21
H53	8329	1176	9747	23
H35	8510	-1476	6406	21
H51	8827	389	7557	21
H59	10337	-1800	8835	20
H61	10388	-4290	9255	22
H5A	5870	2176	7590	29
H5B	4840	1642	7764	29
H5C	4883	2267	8341	29
H37	11540	-968	5019	25
H14	2961	2777	2893	34
H32	1210	4847	6491	30
H21	8624	3227	5313	42
H8A	2873	2510	8972	46
H8B	2260	3025	9640	46
H8C	3357	3337	9022	46
H33A	4540	6570	7172	58
H33B	5036	5931	7849	58
H33C	3931	6403	8130	58
H10A	697	3367	8006	51
H10B	575	3015	8983	51
H10C	1296	2531	8327	51
H30	1082	7184	6831	41

H45	4307	-1011	8132	24
H1A	2177	1876	6153	30
H1B	1717	1959	7097	30
H1C	2782	1424	6864	30
H13	1913	3783	3523	32
H26A	5163	4341	7678	53
H26B	6140	4517	8045	53
H26C	5651	3631	8300	53
H29	2680	6935	7306	35
H31	321	6145	6435	41
H15	4055	1863	3619	31
H25A	7254	2746	4795	45
H25B	6054	3077	5069	45
H25C	6451	2233	5573	45
H23	7961	4238	7354	42
H9A	2275	4696	8669	42
H9B	1256	4252	9290	42
H9C	1199	4678	8355	42
H18A	4626	1900	5590	41
H18B	5131	1609	4738	41
H18C	4084	1194	5347	41
H17A	1386	3910	5573	43
H17B	1295	4438	4678	43
H17C	2260	4569	5081	43
H22	9194	3850	6242	48
H66A	5897	84	10526	140
H66B	5951	-694	10131	140

Table 7: Atomic Occupancy for 3.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F15B	0.578(5)	F17B	0.67(3)	F18B	0.67(3)
F16B	0.67(3)	F22A	0.613(5)	F13B	0.578(5)
F24A	0.613(5)	F23A	0.613(5)	F14B	0.578(5)
F24B	0.387(5)	F23B	0.387(5)	F22B	0.387(5)
F17A	0.33(3)	F18A	0.33(3)	F16A	0.33(3)
F14A	0.422(5)	F13A	0.422(5)	F15A	0.422(5)

8.2 Appendix B:

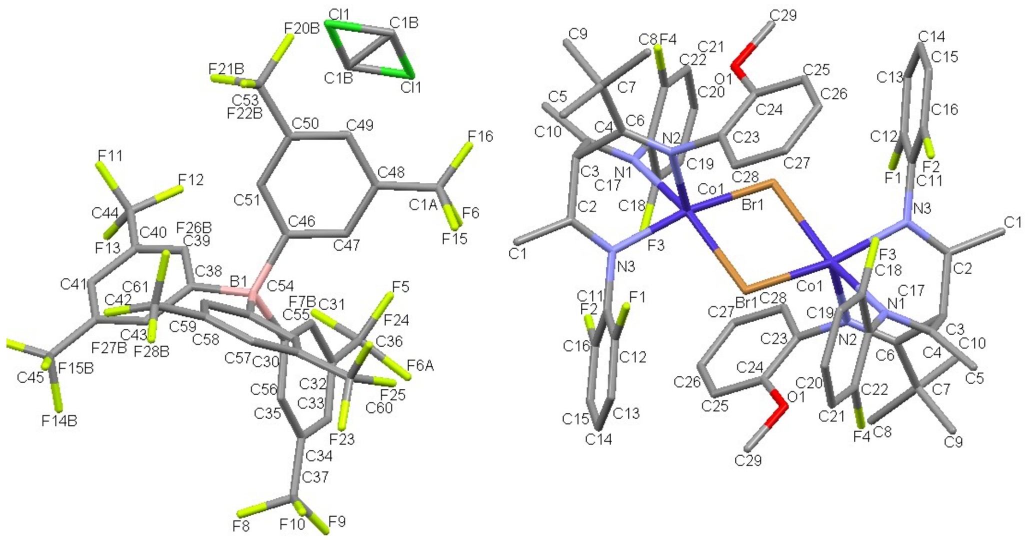


Figure A2: Thermal Ellipsoid plot (50% probability) of **5**, showing BArF anion and dichloromethane of solvation. Hydrogen atoms and minor components of rotational disorder in CF_3 groups are removed.

Table 1: Crystal data and structure refinement for 5.

Identification code	**5**
Empirical formula	$C_{122}H_{82}B_2Br_2Cl_2Co_2F_{56}N_6O_2$
Formula weight	3098.13
Temperature/K	150.01(11)
Crystal system	triclinic
Space group	P-1
a/Å	12.3778(6)
b/Å	16.0019(7)
c/Å	17.1622(8)
α/°	77.298(4)
β/°	83.896(4)
γ/°	78.943(4)
Volume/Å^3	3247.2(3)
Z	1
ρ_{calc}g/cm^3	1.584
μ/mm^{-1}	1.044
F(000)	1544.0
Crystal size/mm^3	0.05 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.652 to 52.744
Index ranges	$-9 \leq h \leq 15$, $-19 \leq k \leq 20$, $-20 \leq l \leq 21$
Reflections collected	24548
Independent reflections	13245 [R_{int} = 0.0621, R_{sigma} = 0.1364]
Data/restraints/parameters	13245/0/910
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0896, wR_2 = 0.2221
Final R indexes [all data]	R_1 = 0.1702, wR_2 = 0.2747
Largest diff. peak/hole / e Å^{-3}	1.70/-1.23

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	9036.0(7)	4439.7(5)	9829.6(5)	44.3(3)
Co1	9599.4(8)	5846.6(5)	9122.5(5)	29.7(3)
F1	6877(4)	5187(3)	8473(3)	59.6(13)
F11	6240(4)	10465(3)	1521(3)	58.9(13)
F25	1496(4)	6156(3)	5899(3)	65.9(15)
F2	10446(4)	4869(3)	7274(3)	63.6(14)
N3	8830(5)	5834(3)	8084(3)	30.8(13)
F4	11046(5)	8130(3)	8893(4)	80.6(18)
F10	3902(5)	4649(3)	3848(4)	75.8(17)
F23	187(5)	6001(3)	5291(4)	78.4(17)
N2	8366(5)	6894(3)	9275(3)	28.3(13)
F13	7249(5)	9325(4)	1260(4)	88(2)
N1	10424(5)	6790(4)	8356(3)	32.8(13)

F8	4900(5)	4892(3)	2798(3)	78.6(18)
F12	7005(4)	9558(4)	2456(3)	73.8(16)
F24	-51(5)	6998(4)	5946(4)	91(2)
F9	5589(5)	4061(3)	3832(4)	96(2)
F3	12108(5)	5545(4)	8001(4)	91(2)
C30	4639(5)	7076(4)	3950(4)	26.1(14)
C54	2477(5)	7878(4)	3893(4)	26.5(15)
C11	8672(6)	5042(4)	7872(4)	28.7(15)
C46	3830(5)	8618(4)	4406(4)	24.3(14)
C35	4412(6)	6319(4)	3767(4)	26.9(15)
C55	2120(6)	7285(4)	4542(4)	29.0(15)
C51	3511(5)	9510(4)	4228(4)	25.6(14)
C31	5682(6)	7028(4)	4179(4)	32.1(16)
C38	4177(6)	8444(4)	2855(4)	27.6(15)
C59	1634(6)	8411(4)	3431(4)	34.3(17)
C50	3372(6)	10015(4)	4798(4)	30.6(15)
C2	8415(6)	6561(4)	7654(4)	29.3(15)
C32	6473(6)	6275(4)	4236(4)	35.6(17)
C43	3759(6)	8288(4)	2181(4)	32.6(16)
C40	5533(6)	9162(4)	1927(4)	33.1(16)
C34	5182(6)	5561(4)	3819(4)	30.0(15)
C6	8080(6)	7522(4)	8688(4)	31.3(16)
C41	5088(6)	9010(5)	1278(4)	38.1(18)
C33	6230(6)	5531(4)	4055(4)	34.5(17)
C47	4007(6)	8246(4)	5219(4)	29.4(15)
C42	4208(7)	8571(5)	1408(4)	40.5(19)
C3	8644(6)	7389(4)	7863(4)	30.7(16)
C56	1037(6)	7212(4)	4731(4)	34.0(16)
C48	3861(6)	8748(5)	5801(4)	35.7(17)
C39	5075(6)	8891(4)	2698(4)	30.5(16)
C12	7698(6)	4728(5)	8083(4)	39.0(18)
C4	9865(6)	7396(4)	7853(4)	32.5(16)
C17	11564(6)	6822(5)	8438(4)	37.5(17)
C49	3532(6)	9657(5)	5594(4)	38.2(18)
O1	9293(7)	7598(5)	10235(4)	82(2)
C7	7247(7)	8375(5)	8663(4)	43(2)
C23	7948(6)	6863(4)	10096(4)	36.1(17)
C1	7731(6)	6666(5)	6961(4)	38.5(18)
C16	9493(7)	4562(5)	7470(5)	42.8(19)
C60	684(7)	6589(6)	5456(6)	51(2)
C15	9369(7)	3807(5)	7262(5)	52(2)
C53	2974(8)	10968(5)	4571(5)	48(2)
C58	535(6)	8335(5)	3605(5)	39.5(19)
B1	3784(7)	8012(5)	3770(4)	28.4(17)
C13	7553(7)	3948(5)	7893(5)	47(2)
C44	6498(7)	9612(5)	1786(5)	43.7(19)
C22	11858(8)	7477(5)	8747(5)	50(2)
C37	4920(8)	4796(5)	3582(5)	46(2)
C14	8385(7)	3517(5)	7486(5)	52(2)
C57	214(7)	7746(5)	4254(5)	47(2)
C24	8463(8)	7183(5)	10604(5)	50(2)

C28	7031(8)	6468(5)	10370(5)	57(2)
C5	10314(7)	8095(5)	7276(4)	45(2)
C8	6823(8)	8600(5)	9478(5)	63(3)
C27	6653(9)	6412(6)	11189(6)	68(3)
C18	12394(7)	6178(6)	8298(5)	52(2)
C25	8123(10)	7121(6)	11398(5)	66(3)
C45	3716(9)	8397(7)	739(5)	57(2)
C61	-308(8)	8904(7)	3069(7)	63(3)
C21	12915(10)	7454(8)	8924(5)	71(3)
C26	7200(10)	6752(7)	11680(5)	73(3)
C19	13461(8)	6147(8)	8463(6)	78(3)
C10	6265(8)	8315(7)	8217(7)	82(4)
C20	13703(9)	6788(9)	8783(6)	75(3)
F21B	3521(17)	11271(8)	3865(10)	71.8(18)
F22B	1930(15)	11185(8)	4546(9)	71.8(18)
F20B	3274(14)	11402(7)	5087(8)	71.8(18)
F26B	-710(50)	9590(30)	3440(30)	110(4)
F28B	-1130(50)	8540(30)	3070(30)	110(4)
F16B	3969(10)	8875(9)	43(6)	93(2)
F15B	2637(11)	8398(9)	833(6)	93(2)
F14B	4108(10)	7563(8)	655(6)	93(2)
C29	9959(14)	7882(11)	10756(9)	139(6)
F16A	2933(16)	9094(13)	383(9)	93(2)
F15A	3110(19)	7752(15)	885(9)	93(2)
F14A	4393(17)	8219(15)	116(10)	93(2)
F27B	20(40)	9050(30)	2330(30)	110(4)
F27A	-43(7)	9644(5)	2693(7)	105(4)
F26A	-1258(7)	9108(8)	3440(5)	116(4)
F28A	-542(10)	8508(6)	2526(7)	110(4)
C36	7604(7)	6286(6)	4478(7)	61(3)
F5	7603(4)	6713(3)	5031(3)	68.7(15)
F6A	7994(11)	5437(8)	4987(12)	86(5)
F22A	2025(13)	11150(8)	4111(12)	74(6)
F20A	2643(17)	11385(8)	5167(10)	71.8(18)
F21A	3590(20)	11442(9)	4065(11)	71.8(18)
F7A	8328(15)	6260(19)	3987(12)	80(3)
F7B	8152(10)	6877(12)	3824(8)	80(3)
F6B	8313(18)	5635(13)	4407(19)	86(5)
Cl1	10818(4)	9293(4)	5372(3)	169(2)
C9	7804(9)	9126(5)	8188(6)	75(3)
C1B	9890(30)	10110(20)	5370(20)	60(16)
C1A	4013(7)	8314(7)	6646(5)	56(2)
F6	4860(20)	7607(19)	6686(10)	59.2(13)
F7	4545(10)	8908(7)	6967(5)	59.2(13)
F14	3081(8)	8369(7)	7070(5)	59.2(13)
F15	3139(10)	7764(8)	6921(6)	59.2(13)
F16	4084(11)	8702(8)	7177(6)	59.2(13)
F18	4695(18)	7603(16)	6818(8)	59.2(13)

Table 3: Anisotropic Displacement Parameters (Å^2×10^3) for 5. The Anisotropic

displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	58.6(6)	37.3(4)	37.7(5)	7.4(3)	-22.6(4)	-16.8(4)
Co1	38.6(6)	23.6(5)	25.4(5)	-2.6(4)	-9.1(4)	-0.8(4)
F1	43(3)	71(3)	73(3)	-38(3)	4(2)	-9(2)
F11	58(3)	47(3)	68(3)	0(2)	-5(3)	-10(2)
F25	43(3)	79(3)	61(3)	18(3)	-1(2)	-13(3)
F2	61(3)	63(3)	80(4)	-43(3)	24(3)	-25(3)
N3	44(4)	25(3)	22(3)	-2(2)	-6(3)	-1(3)
F4	105(5)	59(3)	91(4)	-36(3)	-22(4)	-14(3)
F10	86(4)	59(3)	97(4)	-27(3)	-5(3)	-37(3)
F23	74(4)	54(3)	110(5)	2(3)	-17(3)	-33(3)
N2	33(3)	23(3)	27(3)	-5(2)	-3(2)	-1(2)
F13	64(4)	83(4)	124(5)	-54(4)	52(4)	-22(3)
N1	34(4)	31(3)	36(3)	-8(3)	-6(3)	-6(3)
F8	125(5)	65(3)	61(4)	-35(3)	-25(3)	-17(3)
F12	57(3)	101(4)	57(3)	19(3)	-12(3)	-34(3)
F24	92(5)	64(3)	93(4)	-6(3)	54(4)	3(3)
F9	114(5)	30(3)	154(6)	-28(3)	-79(5)	11(3)
F3	66(4)	85(4)	136(6)	-70(4)	-34(4)	23(3)
C30	29(4)	29(3)	19(3)	-3(3)	-1(3)	-5(3)
C54	31(4)	22(3)	28(4)	-12(3)	-7(3)	4(3)
C11	35(4)	27(3)	24(4)	-6(3)	-7(3)	-3(3)
C46	24(4)	25(3)	23(3)	-4(3)	-3(3)	-2(3)
C35	31(4)	28(3)	24(3)	-6(3)	-5(3)	-5(3)
C55	31(4)	29(3)	27(4)	-11(3)	-7(3)	5(3)
C51	26(4)	28(3)	24(3)	-8(3)	2(3)	-8(3)
C31	34(4)	33(4)	34(4)	-16(3)	-4(3)	-6(3)
C38	34(4)	24(3)	21(3)	-5(3)	-4(3)	4(3)
C59	35(4)	31(4)	36(4)	-12(3)	-8(3)	8(3)
C50	26(4)	31(4)	36(4)	-11(3)	7(3)	-6(3)
C2	39(4)	30(4)	18(3)	-5(3)	-3(3)	-6(3)
C32	31(4)	36(4)	40(4)	-16(3)	-6(3)	3(3)
C43	40(4)	33(4)	26(4)	-10(3)	-3(3)	-4(3)
C40	30(4)	27(3)	37(4)	-6(3)	-2(3)	5(3)
C34	39(4)	24(3)	27(4)	-6(3)	-4(3)	-2(3)
C6	35(4)	33(4)	26(4)	-4(3)	-7(3)	-6(3)
C41	42(5)	40(4)	26(4)	-2(3)	5(3)	-1(4)
C33	35(4)	28(4)	39(4)	-8(3)	-6(3)	2(3)
C47	35(4)	26(3)	25(4)	-3(3)	-4(3)	-2(3)
C42	52(5)	48(4)	19(4)	-9(3)	-2(3)	3(4)
C3	38(4)	29(3)	22(3)	-4(3)	-5(3)	2(3)
C56	26(4)	35(4)	42(4)	-14(3)	-2(3)	-1(3)
C48	30(4)	49(4)	28(4)	-12(3)	-4(3)	-2(3)
C39	38(4)	28(3)	22(3)	-7(3)	-7(3)	7(3)
C12	34(4)	45(4)	35(4)	-12(3)	-3(3)	4(4)
C4	38(4)	27(3)	34(4)	-13(3)	-1(3)	-1(3)
C17	42(5)	43(4)	29(4)	-7(3)	-5(3)	-12(4)
C49	42(5)	42(4)	37(4)	-24(3)	-1(3)	-5(3)
O1	93(6)	98(5)	61(5)	-33(4)	-21(4)	-4(5)

C7	58(6)	34(4)	31(4)	-10(3)	-7(4)	13(4)
C23	49(5)	29(4)	23(4)	0(3)	-1(3)	4(3)
C1	49(5)	39(4)	25(4)	-6(3)	-9(3)	1(4)
C16	52(5)	40(4)	41(5)	-12(4)	-3(4)	-15(4)
C60	31(5)	50(5)	68(6)	-13(4)	8(4)	-3(4)
C15	48(6)	44(5)	70(6)	-40(4)	6(4)	0(4)
C53	48(6)	34(4)	65(6)	-24(4)	13(4)	-10(4)
C58	30(4)	44(4)	45(5)	-19(4)	-15(3)	11(3)
B1	34(5)	28(4)	23(4)	-10(3)	-1(3)	-1(3)
C13	41(5)	47(5)	60(5)	-20(4)	-12(4)	-9(4)
C44	49(5)	36(4)	38(5)	-2(3)	4(4)	2(4)
C22	69(6)	42(5)	40(5)	-9(4)	-6(4)	-11(4)
C37	60(6)	27(4)	52(5)	-11(4)	-18(4)	-1(4)
C14	56(6)	38(4)	72(6)	-32(4)	-14(5)	-3(4)
C57	36(5)	42(4)	66(6)	-21(4)	-10(4)	-1(4)
C24	64(6)	48(5)	34(5)	-5(4)	-6(4)	-4(4)
C28	67(6)	40(5)	51(5)	-1(4)	16(5)	0(4)
C5	52(5)	37(4)	36(4)	6(3)	-2(4)	-3(4)
C8	88(8)	38(4)	44(5)	-10(4)	5(5)	29(5)
C27	84(8)	55(5)	48(6)	2(5)	27(5)	2(5)
C18	40(5)	62(5)	60(6)	-25(5)	-6(4)	-6(4)
C25	108(9)	57(6)	28(5)	-5(4)	-19(5)	1(6)
C45	69(7)	75(6)	28(5)	-14(4)	-3(4)	-12(5)
C61	36(6)	80(7)	70(7)	-18(6)	-19(5)	9(5)
C21	98(9)	89(8)	41(5)	-6(5)	-23(6)	-57(7)
C26	108(9)	73(7)	28(5)	-12(5)	9(5)	0(6)
C19	47(6)	119(9)	67(7)	-30(7)	-7(5)	-1(6)
C10	59(7)	98(8)	89(8)	-53(7)	-28(6)	34(6)
C20	50(7)	120(10)	54(6)	1(6)	-14(5)	-31(7)
F21B	87(4)	31(2)	94(4)	-20(2)	20(4)	-8(3)
F22B	87(4)	31(2)	94(4)	-20(2)	20(4)	-8(3)
F20B	87(4)	31(2)	94(4)	-20(2)	20(4)	-8(3)
F26B	130(9)	97(6)	108(7)	-46(6)	-89(7)	39(6)
F28B	130(9)	97(6)	108(7)	-46(6)	-89(7)	39(6)
F16B	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
F15B	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
F14B	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
C29	171(16)	179(16)	101(11)	-54(11)	-38(11)	-68(13)
F16A	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
F15A	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
F14A	105(5)	143(7)	47(3)	-39(4)	-25(3)	-25(5)
F27B	130(9)	97(6)	108(7)	-46(6)	-89(7)	39(6)
F27A	94(6)	57(5)	152(9)	27(6)	-79(6)	5(4)
F26A	56(6)	182(11)	91(6)	-44(7)	-32(5)	59(6)
F28A	130(9)	97(6)	108(7)	-46(6)	-89(7)	39(6)
C36	31(5)	56(5)	103(8)	-51(5)	-16(5)	16(4)
F5	49(3)	80(4)	92(4)	-49(3)	-27(3)	2(3)
F6A	61(8)	53(6)	146(13)	-22(9)	-63(9)	16(5)
F22A	59(9)	36(6)	129(14)	-30(8)	-59(11)	31(6)
F20A	87(4)	31(2)	94(4)	-20(2)	20(4)	-8(3)
F21A	87(4)	31(2)	94(4)	-20(2)	20(4)	-8(3)

F7A	38(5)	123(11)	82(7)	-10(9)	0(4)	-34(8)
F7B	38(5)	123(11)	82(7)	-10(9)	0(4)	-34(8)
F6B	61(8)	53(6)	146(13)	-22(9)	-63(9)	16(5)
Cl1	134(4)	181(5)	164(4)	42(4)	-15(3)	-45(4)
C9	105(9)	32(5)	69(7)	-1(4)	11(6)	11(5)
C1B	40(20)	30(20)	90(30)	5(18)	20(20)	16(15)
C1A	47(6)	94(7)	23(4)	-17(4)	-7(4)	6(5)
F6	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)
F7	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)
F14	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)
F15	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)
F16	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)
F18	77(4)	75(3)	21(2)	0(2)	-4(2)	-12(3)

Table 4 Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Co1	2.4996(11)	C3	C4	1.512(10)
Br1	Co1[1]	2.5069(11)	C56	C60	1.497(11)
Co1	Br1[1]	2.5069(11)	C56	C57	1.404(10)
Co1	N3	2.114(5)	C48	C49	1.409(10)
Co1	N2	2.082(5)	C48	C1A	1.479(10)
Co1	N1	2.118(6)	C12	C13	1.406(10)
F1	C12	1.344(8)	C4	C5	1.475(10)
F11	C44	1.327(8)	C17	C22	1.394(11)
F25	C60	1.317(9)	C17	C18	1.351(11)
F2	C16	1.346(9)	O1	C24	1.355(11)
N3	C11	1.444(8)	O1	C29	1.470(13)
N3	C2	1.279(8)	C7	C8	1.534(10)
F4	C22	1.350(10)	C7	C10	1.533(12)
F10	C37	1.340(10)	C7	C9	1.534(13)
F23	C60	1.311(9)	C23	C24	1.366(11)
N2	C6	1.281(8)	C23	C28	1.393(12)
N2	C23	1.443(9)	C16	C15	1.372(10)
F13	C44	1.317(9)	C15	C14	1.373(12)
N1	C4	1.291(8)	C53	F21B	1.362(19)
N1	C17	1.444(9)	C53	F22B	1.275(18)
F8	C37	1.323(9)	C53	F20B	1.357(16)
F12	C44	1.345(9)	C53	F22A	1.434(16)
F24	C60	1.347(10)	C53	F20A	1.328(18)
F9	C37	1.316(8)	C53	F21A	1.30(2)
F3	C18	1.348(9)	C58	C57	1.368(11)
C30	C35	1.401(9)	C58	C61	1.494(11)
C30	C31	1.373(9)	C13	C14	1.346(11)
C30	B1	1.648(10)	C22	C21	1.367(13)
C54	C55	1.387(9)	C24	C25	1.370(12)
C54	C59	1.408(9)	C28	C27	1.422(12)
C54	B1	1.657(10)	C27	C26	1.388(14)
C11	C12	1.377(10)	C18	C19	1.369(12)

C11	C16	1.373(10)	C25	C26	1.380(15)
C46	C51	1.380(8)	C45	F16B	1.312(14)
C46	C47	1.414(9)	C45	F15B	1.327(14)
C46	B1	1.623(9)	C45	F14B	1.363(14)
C35	C34	1.384(9)	C45	F16A	1.40(2)
C55	C56	1.367(10)	C45	F15A	1.35(2)
C51	C50	1.378(9)	C45	F14A	1.33(2)
C31	C32	1.391(9)	C61	F26B	1.37(4)
C38	C43	1.403(9)	C61	F28B	1.26(6)
C38	C39	1.406(10)	C61	F27B	1.27(6)
C38	B1	1.634(10)	C61	F27A	1.302(13)
C59	C58	1.385(10)	C61	F26A	1.296(12)
C50	C49	1.379(10)	C61	F28A	1.321(14)
C50	C53	1.487(10)	C21	C20	1.345(15)
C2	C3	1.530(9)	C19	C20	1.358(15)
C2	C1	1.493(9)	C36	F5	1.284(9)
C32	C33	1.388(10)	C36	F6A	1.469(18)
C32	C36	1.507(11)	C36	F7A	1.165(19)
C43	C42	1.396(10)	C36	F7B	1.494(19)
C40	C41	1.380(10)	C36	F6B	1.25(2)
C40	C39	1.393(10)	Cl1	C1B[2]	1.64(3)
C40	C44	1.483(11)	Cl1	C1B	1.57(3)
C34	C33	1.388(10)	C1B	Cl1[2]	1.64(3)
C34	C37	1.474(10)	C1A	F6	1.39(3)
C6	C3	1.550(9)	C1A	F7	1.479(14)
C6	C7	1.540(10)	C1A	F14	1.296(12)
C41	C42	1.380(11)	C1A	F15	1.498(15)
C47	C48	1.391(9)	C1A	F16	1.229(14)
C42	C45	1.457(11)	C1A	F18	1.28(3)

Table 5: Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Co1	Br1	Co1[1]	94.03(4)	F24	C60	C56	111.7(7)
Br1	Co1	Br1[1]	85.97(4)	C16	C15	C14	117.8(7)
N3	Co1	Br1	91.64(15)	F21B	C53	C50	107.7(8)
N3	Co1	Br1[1]	162.67(16)	F22B	C53	C50	114.3(8)
N3	Co1	N1	84.7(2)	F22B	C53	F21B	112.5(12)
N2	Co1	Br1[1]	110.27(15)	F22B	C53	F20B	106.4(9)
N2	Co1	Br1	110.90(16)	F20B	C53	C50	111.8(8)
N2	Co1	N3	86.6(2)	F20B	C53	F21B	103.7(10)
N2	Co1	N1	85.3(2)	F22A	C53	C50	110.8(8)
N1	Co1	Br1[1]	92.65(15)	F20A	C53	C50	116.7(9)
N1	Co1	Br1	163.16(16)	F20A	C53	F22A	103.6(11)
C11	N3	Co1	123.0(4)	F21A	C53	C50	118.7(10)
C2	N3	Co1	118.5(4)	F21A	C53	F22A	98.0(14)
C2	N3	C11	118.3(5)	F21A	C53	F20A	106.5(9)
C6	N2	Co1	121.5(5)	C59	C58	C61	119.0(8)
C6	N2	C23	124.8(6)	C57	C58	C59	121.0(7)

C23	N2	Co1	113.5(4)	C57	C58	C61	119.9(8)
C4	N1	Co1	118.8(5)	C30	B1	C54	111.9(5)
C4	N1	C17	119.3(6)	C46	B1	C30	112.9(5)
C17	N1	Co1	121.5(4)	C46	B1	C54	102.2(5)
C35	C30	B1	122.2(6)	C46	B1	C38	113.1(6)
C31	C30	C35	116.0(6)	C38	B1	C30	103.0(5)
C31	C30	B1	121.1(6)	C38	B1	C54	114.3(5)
C55	C54	C59	115.0(6)	C14	C13	C12	118.4(8)
C55	C54	B1	120.5(6)	F11	C44	F12	102.6(6)
C59	C54	B1	124.0(6)	F11	C44	C40	113.5(6)
C12	C11	N3	121.2(6)	F13	C44	F11	106.0(6)
C16	C11	N3	121.5(6)	F13	C44	F12	107.5(7)
C16	C11	C12	117.3(6)	F13	C44	C40	113.0(7)
C51	C46	C47	115.6(6)	F12	C44	C40	113.4(6)
C51	C46	B1	122.4(6)	F4	C22	C17	117.4(8)
C47	C46	B1	121.0(5)	F4	C22	C21	120.6(9)
C34	C35	C30	122.6(6)	C21	C22	C17	122.0(9)
C56	C55	C54	123.6(6)	F10	C37	C34	112.6(7)
C50	C51	C46	123.0(6)	F8	C37	F10	102.8(7)
C30	C31	C32	122.6(6)	F8	C37	C34	112.9(6)
C43	C38	C39	115.6(6)	F9	C37	F10	105.8(7)
C43	C38	B1	122.7(6)	F9	C37	F8	106.9(7)
C39	C38	B1	121.1(6)	F9	C37	C34	114.8(7)
C58	C59	C54	122.2(7)	C13	C14	C15	122.4(7)
C51	C50	C49	121.8(6)	C58	C57	C56	118.0(8)
C51	C50	C53	120.0(7)	O1	C24	C23	113.3(7)
C49	C50	C53	118.1(6)	O1	C24	C25	124.2(9)
N3	C2	C3	117.4(6)	C23	C24	C25	122.4(9)
N3	C2	C1	125.2(6)	C23	C28	C27	117.9(9)
C1	C2	C3	117.4(5)	C26	C27	C28	119.4(10)
C31	C32	C36	119.0(6)	F3	C18	C17	115.9(7)
C33	C32	C31	120.4(6)	F3	C18	C19	121.1(9)
C33	C32	C36	120.5(6)	C17	C18	C19	123.0(9)
C42	C43	C38	121.6(7)	C24	C25	C26	118.2(9)
C41	C40	C39	119.9(7)	F16B	C45	C42	114.1(9)
C41	C40	C44	118.8(7)	F16B	C45	F15B	110.2(9)
C39	C40	C44	121.3(6)	F16B	C45	F14B	104.5(9)
C35	C34	C33	120.2(6)	F15B	C45	C42	115.8(8)
C35	C34	C37	120.4(6)	F15B	C45	F14B	101.2(10)
C33	C34	C37	119.4(6)	F14B	C45	C42	109.6(8)
N2	C6	C3	114.6(6)	F16A	C45	C42	113.5(9)
N2	C6	C7	130.8(6)	F15A	C45	C42	118.4(10)
C7	C6	C3	114.6(5)	F15A	C45	F16A	99.8(13)
C40	C41	C42	119.0(7)	F14A	C45	C42	117.2(11)
C32	C33	C34	118.2(6)	F14A	C45	F16A	102.7(12)
C48	C47	C46	122.0(6)	F14A	C45	F15A	102.6(13)
C43	C42	C45	118.2(8)	F26B	C61	C58	104.6(17)
C41	C42	C43	121.1(7)	F28B	C61	C58	111(2)
C41	C42	C45	120.7(7)	F28B	C61	F26B	105(4)
C2	C3	C6	111.6(6)	F28B	C61	F27B	103(3)
C4	C3	C2	112.3(5)	F27B	C61	C58	114.1(19)

C4	C3	C6	109.5(5)	F27B	C61	F26B	119(4)
C55	C56	C60	121.8(6)	F27A	C61	C58	115.0(8)
C55	C56	C57	120.2(7)	F27A	C61	F28A	107.3(11)
C57	C56	C60	118.0(7)	F26A	C61	C58	113.6(9)
C47	C48	C49	120.5(6)	F26A	C61	F27A	104.9(11)
C47	C48	C1A	119.3(7)	F26A	C61	F28A	103.3(10)
C49	C48	C1A	120.1(7)	F28A	C61	C58	111.8(9)
C40	C39	C38	122.8(6)	C20	C21	C22	119.1(9)
F1	C12	C11	118.6(6)	C25	C26	C27	121.5(9)
F1	C12	C13	120.2(7)	C20	C19	C18	118.9(10)
C11	C12	C13	121.2(7)	C21	C20	C19	120.9(10)
N1	C4	C3	116.9(6)	F5	C36	C32	114.2(7)
N1	C4	C5	125.6(7)	F5	C36	F6A	94.3(10)
C5	C4	C3	117.5(6)	F5	C36	F7B	97.0(9)
C22	C17	N1	121.5(7)	F6A	C36	C32	107.9(9)
C18	C17	N1	122.2(7)	F6A	C36	F7B	133.3(11)
C18	C17	C22	116.0(8)	F7A	C36	C32	117.2(12)
C50	C49	C48	117.1(6)	F7A	C36	F5	120.4(14)
C24	O1	C29	116.4(9)	F7A	C36	F6B	54.1(14)
C8	C7	C6	115.8(6)	F7B	C36	C32	108.1(8)
C10	C7	C6	107.7(6)	F6B	C36	C32	115.5(11)
C10	C7	C8	109.1(8)	F6B	C36	F5	122.5(13)
C9	C7	C6	108.2(7)	C1B	Cl1	C1B[2]	51(2)
C9	C7	C8	107.0(7)	Cl1	C1B	Cl1[2]	129(2)
C9	C7	C10	108.8(8)	C48	C1A	F7	104.4(8)
C24	C23	N2	121.0(7)	C48	C1A	F15	108.3(7)
C24	C23	C28	120.5(8)	F6	C1A	C48	109.8(9)
C28	C23	N2	118.4(7)	F6	C1A	F15	93.8(13)
F2	C16	C11	116.9(6)	F14	C1A	C48	111.0(7)
F2	C16	C15	120.2(7)	F14	C1A	F7	99.9(8)
C15	C16	C11	122.9(8)	F16	C1A	C48	123.8(10)
F25	C60	F24	105.8(8)	F16	C1A	F6	109.0(13)
F25	C60	C56	114.1(7)	F16	C1A	F15	107.9(9)
F23	C60	F25	106.0(7)	F18	C1A	C48	120.2(9)
F23	C60	F24	104.8(7)	F18	C1A	F7	101.0(12)
F23	C60	C56	113.6(7)	F18	C1A	F14	116.6(11)

Table 6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5.

Atom	*x*	*y*	*z*	U(eq)
H35	3717	6326	3605	32
H55	2647	6919	4865	35
H51	3385	9782	3701	31
H31	5868	7519	4301	39
H59	1822	8829	2994	41
H43	3170	7989	2251	39
H41	5377	9201	761	46

H33	6754	5025	4091	41
H47	4227	7647	5369	35
H3	8331	7884	7457	37
H39	5376	9010	3126	37
H49	3427	10000	5977	46
H1A	7867	6135	6765	58
H1B	7923	7130	6543	58
H1C	6964	6799	7130	58
H15	9933	3502	6978	62
H13	6898	3734	8045	57
H14	8291	3005	7351	63
H57	-525	7701	4375	56
H28	6678	6248	10028	68
H5A	10158	8619	7483	67
H5B	9980	8194	6776	67
H5C	11098	7926	7192	67
H8A	6416	8166	9777	94
H8B	6351	9158	9398	94
H8C	7437	8616	9769	94
H27	6045	6151	11394	82
H25	8504	7321	11738	79
H21	13088	7893	9140	85
H26	6937	6731	12211	87
H19	14012	5694	8357	93
H10A	6507	8280	7673	123
H10B	5709	8823	8224	123
H10C	5964	7806	8474	123
H20	14423	6766	8907	90
H29A	10534	8150	10437	209
H29B	10281	7387	11138	209
H29C	9497	8293	11033	209
H9A	8478	9120	8422	112
H9B	7319	9669	8202	112
H9C	7966	9060	7643	112
H1BA	10221	10517	5574	72
H1BB	9341	9920	5786	72

Table 7: Atomic Occupancy for 5.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F21B	0.540(15)	F22B	0.540(15)	F20B	0.540(15)
F26B	0.179(10)	F28B	0.179(10)	F16B	0.618(6)

F15B	0.618(6)	F14B	0.618(6)	F16A	0.382(6)
F15A	0.382(6)	F14A	0.382(6)	F27B	0.179(10)
F27A	0.821(10)	F26A	0.821(10)	F28A	0.821(10)
F6A	0.583(15)	F22A	0.460(15)	F20A	0.460(15)
F21A	0.460(15)	F7A	0.435(14)	F7B	0.565(14)
F6B	0.417(15)	C1B	0.26(3)	H1BA	0.22(18)
H1BB	0.74(17)	F6	0.458(7)	F7	0.542(7)
F14	0.542(7)	F15	0.458(7)	F16	0.458(7)
F18	0.542(7)				

8.3 Appendix C:

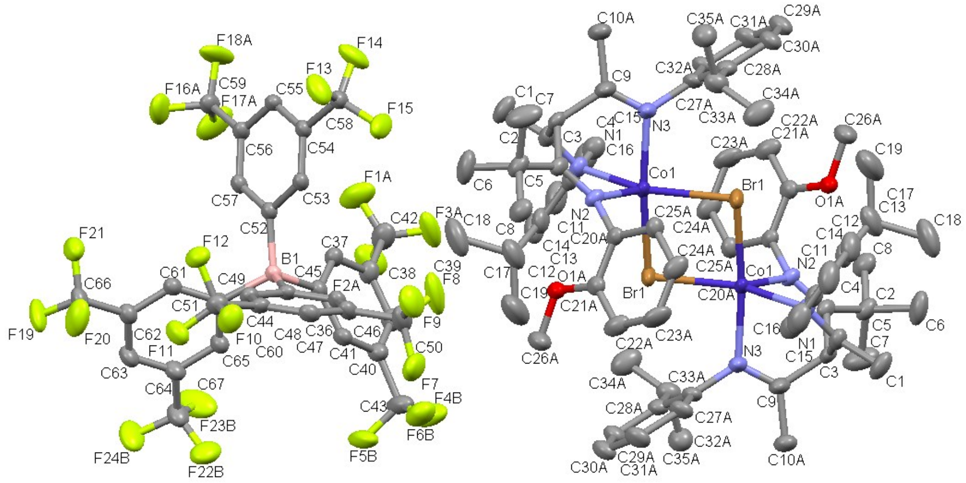


Figure A3: Thermal Ellipsoid plot (40% probability) of **6**, showing BArF anion. Hydrogen atoms and minor components of rotational disorder in CF_3 groups, and around aryl-N bonds, are removed.

Table 1 Crystal data and structure refinement for 6.

Identification code	**6**
Empirical formula	$C_{134}H_{114}B_2Br_2Co_2F_{48}N_6O_2$
Formula weight	3051.61
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.5422(8)
b/Å	16.3657(10)
c/Å	17.6818(10)
α/°	73.037(5)
β/°	87.555(5)
γ/°	76.085(6)
Volume/Å^3	3368.2(4)
Z	1
ρ_{calc}g/cm^3	1.504
μ/mm^{-1}	3.686
F(000)	1542.0
Crystal size/mm^3	0.1 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.228 to 136.494
Index ranges	$-15 \leq h \leq 15$, $-19 \leq k \leq 19$, $-21 \leq l \leq 21$
Reflections collected	41455
Independent reflections	11998 [R_{int} = 0.0578, R_{sigma} = 0.0402]
Data/restraints/parameters	11998/439/1132
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0587, wR_2 = 0.1470
Final R indexes [all data]	R_1 = 0.0706, wR_2 = 0.1559
Largest diff. peak/hole / e Å^{-3}	0.89/-0.54

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10611.2(4)	-997.5(2)	9896.8(2)	46.03(13)
Co1	9887.7(5)	458.3(3)	8913.6(3)	32.69(15)
N2	10988(2)	1172(2)	8325.7(16)	35.1(6)
N1	8641(3)	1431(2)	8169.1(17)	39.2(7)
N3	10091(4)	-139(2)	7974(2)	58.5(10)
C5	11617(3)	2089(3)	7031(2)	45.9(9)
C8	12570(4)	2261(3)	7436(2)	53.5(10)
C6	10830(4)	2982(3)	6623(3)	73.5(16)
C7	12108(4)	1629(5)	6411(3)	77.5(17)

C4	10920(3)	1524(2)	7580(2)	35.6(7)
C3	9987(3)	1343(2)	7159(2)	37.7(8)
C9	10102(5)	364(3)	7274(2)	60.5(12)
C2	8843(3)	1693(3)	7433(2)	42.0(8)
C1	8031(4)	2263(3)	6787(2)	57.5(12)
C11	7532(3)	1732(3)	8415(2)	44.3(9)
C16	6775(3)	1237(3)	8408(2)	51.5(10)
C15	5693(4)	1512(4)	8608(3)	67.6(14)
C14	5387(4)	2275(4)	8835(3)	70.2(14)
C13	6146(4)	2751(3)	8852(3)	62.9(12)
C12	7229(4)	2502(3)	8647(3)	54.4(11)
C17	8031(4)	3074(3)	8629(4)	70.8(15)
C18	7802(5)	3866(3)	7866(5)	90(2)
C19	7989(7)	3421(4)	9328(5)	111(3)
O1A	10961(6)	2383(4)	9040(4)	40.4(16)
C10A	9993(6)	86(4)	6538(3)	49.1(14)
C27A	9941(3)	-1042.1(18)	8124(2)	39.0(12)
C28A	10863(2)	-1728(2)	8174(2)	41.3(12)
C29A	10745(3)	-2584(2)	8321(3)	49(2)
C30A	9706(4)	-2753(2)	8419(3)	53.4(15)
C31A	8784(3)	-2067(3)	8370(3)	54.9(19)
C32A	8902(3)	-1211(3)	8222(3)	44(2)
C33A	12045(5)	-1580(7)	8045(5)	52(2)
C35A	12498(6)	-1748(5)	7278(4)	57.5(16)
C34A	12840(6)	-2114(6)	8730(4)	72(2)
C20A	11875(4)	1031(4)	8861(3)	31.1(18)
C21A	11824(4)	1655(3)	9261(3)	37.1(16)
C22A	12622(5)	1522(4)	9835(4)	50(2)
C23A	13471(5)	766(5)	10009(4)	59(3)
C24A	13522(4)	142(4)	9609(4)	53(2)
C25A	12724(5)	275(4)	9035(3)	37(2)
C26A	10802(9)	2992(6)	9498(5)	63(3)
O1B	12743(7)	11(5)	8953(5)	39.9(18)
C10B	10723(13)	149(10)	6488(7)	49.1(14)
C27B	10841(8)	-1048(5)	8023(6)	38(3)
C28B	10147(6)	-1614(6)	8110(7)	46(3)
C29B	10585(8)	-2506(6)	8218(8)	50(5)
C30B	11717(9)	-2833(5)	8241(8)	60(4)
C31B	12412(6)	-2268(7)	8154(8)	58(4)
C32B	11974(7)	-1375(6)	8046(8)	37(4)
C33B	8899(10)	-1283(12)	8068(12)	46(4)
C35B	8435(12)	-699(10)	7248(8)	49(3)
C34B	8295(16)	-2015(13)	8330(12)	56(4)
C20B	11705(8)	1411(6)	8849(5)	32(2)
C25B	11441(11)	2191(10)	9058(9)	49(3)
C24B	12059(9)	2305(6)	9620(6)	56(2)
C23B	12971(9)	1626(8)	9971(7)	52(3)
C22B	13226(9)	830(7)	9786(6)	41(2)
C21B	12577(7)	726(6)	9202(5)	33.0(17)
C26B	13494(8)	-771(6)	9436(6)	56(3)
F9	11828(2)	4632.1(19)	7502(2)	78.2(9)

F8	10318(3)	4353.4(18)	7898(3)	97.9(13)
F7	11092(3)	5095(2)	8439.0(19)	89.8(11)
F11	10462(2)	8607.4(16)	5630.2(16)	57.0(6)
F12	10725(2)	7765.6(18)	4887.9(13)	55.9(6)
F10	11931(2)	7557.4(19)	5778.0(17)	64.1(7)
F21	6628(3)	10013.2(17)	4156.0(15)	69.5(8)
F19	6107(3)	11058.2(16)	4665.1(19)	79.1(9)
F20	7760(2)	10310(2)	4836(2)	85.9(10)
F14	7683(2)	4285.6(18)	4615(2)	73.1(9)
F15	8671(3)	4234.3(18)	5581.2(17)	82.4(10)
F13	8987(2)	4933.4(17)	4429(2)	71.1(8)
C44	8496(3)	6810(2)	6622(2)	33.5(7)
C49	9117(3)	7365(2)	6159(2)	34.7(7)
C48	10258(3)	7159(2)	6206(2)	37.2(8)
C47	10843(3)	6387(2)	6726(2)	39.1(8)
C46	10248(3)	5826(2)	7191(2)	41.8(8)
C45	9101(3)	6029(2)	7141(2)	38.1(8)
C51	10845(3)	7770(3)	5642(2)	42.9(8)
C50	10850(4)	4985(3)	7770(3)	56.0(11)
C60	6616(3)	8082(2)	6334(2)	34.0(7)
C65	6086(3)	8419(2)	6926(2)	39.6(8)
C64	5747(4)	9322(3)	6833(2)	46.5(9)
C63	5941(4)	9927(2)	6146(2)	46.4(9)
C62	6445(3)	9614(2)	5540(2)	39.9(8)
C61	6752(3)	8712(2)	5631(2)	35.3(7)
C66	6730(4)	10247(2)	4804(3)	46.5(9)
C67	5183(5)	9622(3)	7496(3)	59.7(11)
C52	6935(3)	6692(2)	5711.3(19)	31.5(7)
C57	5986(3)	7066(2)	5222(2)	33.8(7)
C56	5752(3)	6702(2)	4645(2)	36.9(8)
C55	6448(3)	5953(2)	4530(2)	36.8(8)
C54	7399(3)	5576(2)	5005(2)	33.9(7)
C53	7633(3)	5944(2)	5577.8(19)	31.8(7)
C58	8174(3)	4759(2)	4900(2)	39.9(8)
C59	4704(3)	7112(3)	4156(2)	46.3(9)
C36	6553(3)	6466(2)	7242(2)	33.3(7)
C41	6841(3)	6389(2)	8019(2)	38.7(8)
C40	6277(4)	5990(3)	8670(2)	44.7(9)
C39	5412(3)	5643(3)	8566(2)	46.0(9)
C38	5118(3)	5702(3)	7802(2)	44.1(9)
C37	5680(3)	6104(2)	7158(2)	38.9(8)
C43	6617(5)	5963(4)	9481(3)	64.1(12)
C42	4196(4)	5330(3)	7674(3)	60.8(11)
B1	7142(3)	7020(2)	6477(2)	32.4(8)
F24B	4854(8)	10509(3)	7315(4)	92(2)
F23B	4307(6)	9337(7)	7698(5)	105(3)
F22B	5842(5)	9384(5)	8133(3)	83(2)
F18A	4549(5)	6691(4)	3662(4)	97(3)
F16A	4718(4)	7919(3)	3688(3)	79.7(18)
F17A	3837(4)	7242(6)	4583(3)	95(2)
F3A	4248(6)	4551(4)	8078(6)	81(3)

F1A	3856(8)	5493(7)	6961(4)	88(3)
F2A	3217(4)	5770(4)	7985(4)	78(2)
F4B	5970(20)	5635(19)	10024(8)	101(5)
F5B	6505(16)	6778(9)	9530(9)	87(4)
F6B	7675(17)	5610(14)	9635(15)	88(4)
F22A	5420(20)	10287(15)	7613(14)	80(6)
F24A	4095(18)	9783(16)	7480(15)	89(5)
F23A	5370(20)	9013(12)	8242(8)	79(6)
F18B	4833(9)	7323(11)	3404(6)	84(4)
F16B	4090(10)	7803(8)	4279(8)	70(4)
F17B	4047(8)	6563(7)	4270(8)	67(4)
F2B	3848(10)	4807(8)	8278(5)	94(4)
F3B	4618(6)	4657(6)	7264(5)	86(3)
F1B	3516(10)	5839(8)	7128(7)	93(4)
F4A	6489(9)	5216(7)	10039(4)	70(3)
F5A	6084(14)	6617(9)	9714(8)	122(4)
F6A	7686(10)	5927(10)	9564(8)	85(3)

Table 3: Anisotropic Displacement Parameters (Å^2×10^3) for xrepw504. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	76.1(3)	23.52(18)	29.44(19)	-1.96(13)	-3.90(17)	-1.05(17)
Co1	46.4(3)	23.6(3)	26.5(3)	-1.9(2)	-13.3(2)	-9.5(2)
N2	34.9(15)	41.2(16)	26.0(14)	-7.2(12)	-7.4(11)	-4.7(13)
N1	41.4(16)	38.6(16)	33.1(16)	-1.3(12)	-9.8(12)	-10.5(14)
N3	107(3)	34.8(17)	33.8(17)	-10.8(14)	-24.3(18)	-10.8(19)
C5	45(2)	55(2)	30.5(18)	-2.3(16)	-5.4(15)	-10.5(19)
C8	55(2)	65(3)	40(2)	-6.4(19)	0.2(18)	-25(2)
C6	68(3)	62(3)	67(3)	25(2)	-15(2)	-21(3)
C7	56(3)	138(6)	54(3)	-46(3)	11(2)	-32(3)
C4	35.6(17)	34.5(17)	30.0(17)	-8.1(13)	-7.9(13)	4.0(15)
C3	47(2)	37.4(18)	24.2(16)	-3.0(13)	-11.1(14)	-6.2(16)
C9	102(4)	45(2)	33(2)	-15.3(17)	-18(2)	-7(2)
C2	46(2)	40.0(19)	35.2(19)	0.7(15)	-12.1(15)	-13.0(17)
C1	49(2)	72(3)	37(2)	8.8(19)	-13.5(18)	-14(2)
C11	46(2)	45(2)	34.5(19)	3.0(15)	-10.5(16)	-13.5(18)
C16	50(2)	59(3)	46(2)	-6.6(19)	-5.8(18)	-23(2)
C15	55(3)	77(3)	60(3)	6(2)	-5(2)	-25(3)
C14	57(3)	60(3)	70(3)	8(2)	3(2)	-4(2)
C13	59(3)	45(2)	66(3)	1(2)	1(2)	0(2)
C12	60(3)	36(2)	53(2)	2.9(17)	-14(2)	-2.8(19)
C17	63(3)	36(2)	109(4)	-15(2)	-20(3)	-6(2)
C18	82(4)	41(3)	138(6)	-7(3)	16(4)	-20(3)
C19	143(7)	52(3)	141(7)	-29(4)	-50(5)	-16(4)
O1A	62(4)	34(3)	28(3)	-8(2)	-2(3)	-18(3)
C10A	66(4)	54(3)	35(2)	-17(2)	-7(3)	-22(3)
C27A	54(3)	38(3)	33(2)	-16(2)	-5(2)	-19(2)
C28A	54(3)	43(3)	33(3)	-18(2)	-3(2)	-12(2)
C29A	66(4)	38(3)	52(5)	-21(3)	-1(3)	-17(3)

C30A	77(4)	43(3)	54(3)	-24(2)	10(3)	-27(3)
C31A	63(4)	53(3)	65(4)	-27(3)	2(3)	-31(3)
C32A	50(3)	45(3)	51(4)	-24(3)	1(3)	-24(3)
C33A	51(3)	53(4)	58(4)	-24(3)	-4(3)	-15(3)
C35A	64(4)	60(4)	51(3)	-17(3)	4(3)	-18(3)
C34A	49(3)	106(6)	55(4)	-22(4)	-3(3)	-11(4)
C20A	33(4)	34(4)	27(3)	-3(3)	-2(3)	-16(3)
C21A	46(4)	37(3)	32(3)	-6(3)	2(3)	-21(3)
C22A	44(4)	78(6)	36(4)	-14(3)	0(3)	-32(4)
C23A	46(5)	93(6)	42(5)	-20(4)	-14(4)	-22(4)
C24A	36(4)	76(5)	42(4)	-8(3)	-7(3)	-13(3)
C25A	34(4)	33(5)	41(4)	-5(4)	-7(3)	-7(4)
C26A	102(7)	45(4)	50(5)	-22(4)	-2(4)	-21(4)
O1B	49(4)	28(3)	37(3)	-4(2)	-17(3)	-2(3)
C10B	66(4)	54(3)	35(2)	-17(2)	-7(3)	-22(3)
C27B	47(5)	40(6)	35(6)	-19(5)	-1(4)	-11(4)
C28B	50(5)	52(6)	44(7)	-22(5)	-3(4)	-18(4)
C29B	68(7)	47(7)	40(10)	-22(6)	3(6)	-12(5)
C30B	74(7)	39(6)	69(10)	-22(6)	6(6)	-11(5)
C31B	66(7)	38(6)	69(10)	-21(5)	-4(6)	-5(5)
C32B	50(6)	32(7)	29(8)	-9(5)	-1(5)	-9(4)
C33B	52(6)	51(7)	47(7)	-29(6)	1(5)	-18(5)
C35B	49(7)	67(8)	45(6)	-26(5)	1(5)	-30(6)
C34B	74(10)	65(9)	49(8)	-33(7)	12(7)	-36(8)
C20B	39(4)	29(4)	29(4)	-7(3)	-5(3)	-12(3)
C25B	57(7)	42(5)	51(6)	-22(4)	-8(5)	-8(5)
C24B	79(6)	46(4)	48(5)	-18(3)	-11(4)	-18(4)
C23B	57(6)	59(5)	47(5)	-15(4)	-9(4)	-24(4)
C22B	36(4)	52(5)	37(4)	-8(3)	-11(4)	-20(4)
C21B	34(4)	33(4)	31(3)	-3(3)	-4(3)	-12(3)
C26B	65(6)	35(4)	54(5)	-5(3)	-22(4)	6(4)
F9	58.4(17)	52.8(15)	109(2)	-15.1(16)	-20.0(16)	8.1(13)
F8	64.1(18)	37.7(14)	165(4)	18.7(18)	-40(2)	-14.2(13)
F7	126(3)	59.9(17)	60.9(18)	-1.5(14)	-38.6(18)	7.6(18)
F11	68.9(16)	46.1(13)	63.9(15)	-18.2(11)	13.6(12)	-27.5(12)
F12	69.6(16)	66.4(15)	37.7(12)	-13.9(11)	2.3(11)	-28.8(13)
F10	45.7(13)	75.0(18)	67.2(17)	-3.9(13)	-8.8(12)	-24.8(13)
F21	117(2)	46.1(13)	44.4(14)	-7.2(11)	4.8(14)	-25.0(15)
F19	111(2)	27.7(11)	74.7(19)	0.5(11)	23.0(17)	6.0(13)
F20	64.8(17)	89(2)	85(2)	22.1(17)	-7.8(15)	-39.6(17)
F14	62.2(16)	51.2(15)	122(3)	-53.1(17)	-13.0(16)	-6.5(13)
F15	121(3)	45.4(14)	56.3(16)	-14.0(12)	-28.6(16)	31.2(16)
F13	68.5(17)	44.9(13)	98(2)	-24.9(14)	21.1(16)	-7.3(13)
C44	39.8(18)	33.6(17)	32.1(17)	-13.8(13)	-7.0(14)	-11.2(15)
C49	40.3(18)	34.1(17)	30.9(17)	-9.3(13)	-8.3(14)	-9.8(15)
C48	44.4(19)	40.1(18)	32.4(17)	-14.6(14)	-7.0(14)	-13.5(16)
C47	37.2(18)	40.3(19)	45(2)	-18.1(16)	-8.0(15)	-10.5(16)
C46	45(2)	32.9(18)	49(2)	-11.9(16)	-15.9(16)	-9.5(16)
C45	46(2)	30.1(17)	40.0(19)	-7.3(14)	-9.4(15)	-14.2(16)
C51	43(2)	47(2)	42(2)	-12.6(16)	-5.8(16)	-16.4(18)
C50	49(2)	39(2)	74(3)	-3(2)	-23(2)	-12.0(19)

C60	36.9(18)	30.1(16)	37.7(18)	-11.7(14)	-6.3(14)	-9.6(14)
C65	48(2)	32.6(17)	39.6(19)	-10.9(15)	0.0(16)	-11.7(16)
C64	58(2)	37.8(19)	48(2)	-19.7(17)	3.2(18)	-9.9(18)
C63	59(2)	28.7(17)	52(2)	-14.5(16)	1.8(18)	-7.7(17)
C62	43(2)	32.3(17)	45(2)	-10.0(15)	-3.4(16)	-10.0(16)
C61	37.9(18)	31.4(17)	37.4(18)	-11.0(14)	-6.4(14)	-7.3(15)
C66	54(2)	26.9(17)	53(2)	-6.0(16)	-0.3(18)	-6.1(17)
C67	83(3)	42(2)	53(2)	-20.0(18)	15(2)	-9(2)
C52	36.1(17)	26.2(15)	32.1(16)	-5.8(13)	-4.4(13)	-9.7(14)
C57	37.4(18)	25.2(15)	37.9(18)	-6.7(13)	-6.6(14)	-7.7(14)
C56	41.8(19)	29.8(16)	38.3(18)	-5.3(14)	-13.9(15)	-10.0(15)
C55	50(2)	28.6(16)	34.0(17)	-9.0(13)	-10.8(15)	-10.6(15)
C54	41.5(18)	24.9(15)	34.9(17)	-6.3(13)	-7.2(14)	-8.5(14)
C53	35.6(17)	26.2(15)	32.8(16)	-5.3(13)	-9.1(13)	-8.0(14)
C58	49(2)	31.5(17)	38.7(19)	-10.4(14)	-8.3(16)	-7.2(16)
C59	49(2)	37.3(18)	50(2)	-11.0(15)	-22.9(16)	-2.7(16)
C36	38.3(18)	24.6(15)	36.5(18)	-8.3(13)	-5.0(14)	-6.1(14)
C41	49(2)	34.3(17)	37.5(18)	-11.6(14)	-2.7(15)	-17.8(16)
C40	61(2)	42(2)	36.3(19)	-12.7(16)	-0.1(17)	-18.6(19)
C39	50(2)	44(2)	45(2)	-8.5(17)	6.5(17)	-18.1(18)
C38	39(2)	43(2)	47(2)	-4.2(16)	-5.7(16)	-13.7(17)
C37	42.1(19)	35.8(18)	37.7(19)	-6.3(14)	-9.2(15)	-11.0(16)
C43	98(3)	77(3)	38(2)	-22(2)	7(2)	-53(3)
C42	54(2)	67(3)	61(2)	-1.5(19)	-12.7(19)	-32(2)
B1	39(2)	26.2(17)	33.0(19)	-7.4(14)	-7.6(15)	-9.9(16)
F24B	136(5)	49(2)	76(4)	-25(2)	32(3)	9(3)
F23B	109(4)	137(6)	113(6)	-83(5)	69(4)	-65(5)
F22B	103(4)	93(4)	53(2)	-38(2)	3(2)	-5(3)
F18A	95(4)	75(3)	125(5)	-66(3)	-82(4)	30(3)
F16A	82(3)	51(2)	85(3)	9(2)	-50(3)	-3(2)
F17A	43(2)	157(6)	66(3)	-17(3)	-20.8(18)	-2(3)
F3A	54(4)	36(2)	141(7)	1(3)	-43(4)	-16(2)
F1A	82(7)	143(9)	59(3)	-25(4)	-6(3)	-69(6)
F2A	39(3)	78(4)	130(6)	-44(4)	5(3)	-20(2)
F4B	156(11)	145(12)	43(5)	-29(7)	26(7)	-113(10)
F5B	157(10)	88(5)	48(6)	-33(4)	11(5)	-76(5)
F6B	115(6)	100(9)	58(7)	-15(8)	-25(5)	-43(6)
F22A	112(13)	65(8)	84(12)	-50(8)	29(9)	-29(8)
F24A	101(7)	98(13)	76(11)	-53(10)	21(6)	-9(6)
F23A	131(13)	59(7)	45(5)	-27(5)	19(6)	-8(7)
F18B	62(6)	126(11)	52(5)	-11(5)	-19(4)	-14(7)
F16B	65(7)	59(5)	85(8)	-35(6)	-43(6)	16(5)
F17B	46(5)	49(5)	92(8)	8(5)	-41(5)	-15(4)
F2B	105(9)	144(9)	58(4)	-21(5)	13(4)	-93(7)
F3B	79(5)	104(5)	108(6)	-44(4)	-6(4)	-64(4)
F1B	59(6)	86(6)	117(8)	8(5)	-44(6)	-23(4)
F4A	102(6)	87(5)	34(2)	-10(3)	-4(3)	-56(4)
F5A	178(9)	125(7)	77(6)	-66(6)	2(6)	-15(6)
F6A	116(4)	130(8)	35(3)	-15(5)	-4(3)	-88(5)

Table 4: Bond Lengths for 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Co1	2.4899(6)	F11	C51	1.333(5)
Br1	Co1[1]	2.5100(7)	F12	C51	1.350(4)
Co1	Br1[1]	2.5099(7)	F10	C51	1.337(5)
Co1	N2	2.072(3)	F21	C66	1.330(5)
Co1	N1	2.114(3)	F19	C66	1.327(5)
Co1	N3	2.138(3)	F20	C66	1.324(5)
N2	C4	1.274(4)	F14	C58	1.311(5)
N2	C20A	1.424(5)	F15	C58	1.334(4)
N2	C20B	1.506(10)	F13	C58	1.321(5)
N1	C2	1.281(5)	C44	C49	1.398(5)
N1	C11	1.452(5)	C44	C45	1.401(5)
N3	C9	1.274(6)	C44	B1	1.665(5)
N3	C27A	1.480(4)	C49	C48	1.389(5)
N3	C27B	1.537(8)	C48	C47	1.383(5)
C5	C8	1.541(6)	C48	C51	1.499(5)
C5	C6	1.543(6)	C47	C46	1.383(6)
C5	C7	1.532(7)	C46	C45	1.397(5)
C5	C4	1.534(5)	C46	C50	1.501(5)
C4	C3	1.543(5)	C60	C65	1.395(5)
C3	C9	1.525(6)	C60	C61	1.399(5)
C3	C2	1.527(6)	C60	B1	1.651(5)
C9	C10A	1.519(6)	C65	C64	1.398(5)
C9	C10B	1.650(12)	C64	C63	1.379(6)
C2	C1	1.494(5)	C64	C67	1.489(6)
C11	C16	1.391(6)	C63	C62	1.383(6)
C11	C12	1.400(6)	C62	C61	1.396(5)
C16	C15	1.388(7)	C62	C66	1.498(5)
C15	C14	1.384(8)	C67	F24B	1.354(6)
C14	C13	1.374(8)	C67	F23B	1.292(8)
C13	C12	1.386(7)	C67	F22B	1.331(7)
C12	C17	1.523(7)	C67	F22A	1.265(16)
C17	C18	1.554(8)	C67	F24A	1.33(2)
C17	C19	1.497(10)	C67	F23A	1.390(16)
O1A	C21A	1.374(8)	C52	C57	1.404(5)
O1A	C26A	1.431(10)	C52	C53	1.398(5)
C27A	C28A	1.3900	C52	B1	1.645(5)
C27A	C32A	1.3900	C57	C56	1.393(5)
C28A	C29A	1.3900	C56	C55	1.387(5)
C28A	C33A	1.556(7)	C56	C59	1.504(5)
C29A	C30A	1.3900	C55	C54	1.392(5)
C30A	C31A	1.3900	C54	C53	1.394(5)
C31A	C32A	1.3900	C54	C58	1.507(5)
C33A	C35A	1.521(9)	C59	F18A	1.307(6)
C33A	C34A	1.515(9)	C59	F16A	1.343(6)
C20A	C21A	1.3900	C59	F17A	1.307(6)
C20A	C25A	1.3900	C59	F18B	1.286(12)
C21A	C22A	1.3900	C59	F16B	1.275(11)
C22A	C23A	1.3900	C59	F17B	1.328(10)

C23A	C24A	1.3900	C36	C41	1.398(5)
C24A	C25A	1.3900	C36	C37	1.396(5)
O1B	C21B	1.336(11)	C36	B1	1.649(5)
O1B	C26B	1.450(11)	C41	C40	1.402(5)
C27B	C28B	1.3900	C40	C39	1.380(6)
C27B	C32B	1.3900	C40	C43	1.500(6)
C28B	C29B	1.3900	C39	C38	1.386(6)
C28B	C33B	1.526(13)	C38	C37	1.392(5)
C29B	C30B	1.3900	C38	C42	1.484(6)
C30B	C31B	1.3900	C43	F4B	1.308(13)
C31B	C32B	1.3900	C43	F5B	1.334(14)
C33B	C35B	1.533(14)	C43	F6B	1.32(2)
C33B	C34B	1.518(14)	C43	F4A	1.368(8)
C20B	C25B	1.392(16)	C43	F5A	1.284(10)
C20B	C21B	1.379(11)	C43	F6A	1.341(13)
C25B	C24B	1.367(16)	C42	F3A	1.255(7)
C24B	C23B	1.406(15)	C42	F1A	1.279(8)
C23B	C22B	1.394(15)	C42	F2A	1.441(7)
C22B	C21B	1.413(12)	C42	F2B	1.293(9)
F9	C50	1.354(6)	C42	F3B	1.473(8)
F8	C50	1.323(5)	C42	F1B	1.269(9)
F7	C50	1.305(6)			

Table 5: Bond Angles for 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Co1	Br1	Co1^{1}	95.12(2)	C46	C45	C44	121.9(3)
Br1	Co1	Br1^{1}	84.88(2)	F11	C51	F12	105.0(3)
N2	Co1	Br1^{1}	104.51(8)	F11	C51	F10	108.1(3)
N2	Co1	Br1	118.92(8)	F11	C51	C48	113.0(3)
N2	Co1	N1	87.14(11)	F12	C51	C48	111.8(3)
N2	Co1	N3	86.05(14)	F10	C51	F12	104.7(3)
N1	Co1	Br1^{1}	94.59(9)	F10	C51	C48	113.6(3)
N1	Co1	Br1	153.29(9)	F9	C50	C46	112.6(4)
N1	Co1	N3	84.96(13)	F8	C50	F9	103.3(4)
N3	Co1	Br1	90.78(9)	F8	C50	C46	112.5(3)
N3	Co1	Br1^{1}	169.41(12)	F7	C50	F9	104.8(4)
C4	N2	Co1	122.0(2)	F7	C50	F8	110.3(4)
C4	N2	C20A	128.8(4)	F7	C50	C46	112.7(4)
C4	N2	C20B	121.5(4)	C65	C60	C61	115.2(3)
C20A	N2	Co1	108.1(3)	C65	C60	B1	122.5(3)
C20B	N2	Co1	115.2(4)	C61	C60	B1	122.1(3)
C2	N1	Co1	117.2(3)	C60	C65	C64	122.3(4)
C2	N1	C11	117.9(3)	C65	C64	C67	118.6(4)
C11	N1	Co1	124.3(2)	C63	C64	C65	121.1(4)
C9	N3	Co1	117.1(3)	C63	C64	C67	120.3(4)
C9	N3	C27A	121.5(3)	C64	C63	C62	118.0(3)
C9	N3	C27B	108.8(5)	C63	C62	C61	120.5(4)
C27A	N3	Co1	119.7(3)	C63	C62	C66	119.6(3)
C27B	N3	Co1	124.6(4)	C61	C62	C66	119.8(3)

C8	C5	C6	108.5(4)	C62	C61	C60	122.8(3)
C7	C5	C8	107.8(4)	F21	C66	C62	112.9(3)
C7	C5	C6	109.9(4)	F19	C66	F21	105.5(4)
C7	C5	C4	108.2(4)	F19	C66	C62	113.6(4)
C4	C5	C8	115.7(3)	F20	C66	F21	106.3(4)
C4	C5	C6	106.7(3)	F20	C66	F19	106.3(4)
N2	C4	C5	130.8(3)	F20	C66	C62	111.7(3)
N2	C4	C3	114.4(3)	F24B	C67	C64	112.6(4)
C5	C4	C3	114.8(3)	F23B	C67	C64	112.7(5)
C9	C3	C4	112.8(3)	F23B	C67	F24B	105.6(6)
C9	C3	C2	106.4(3)	F23B	C67	F22B	108.6(6)
C2	C3	C4	113.6(3)	F22B	C67	C64	112.1(4)
N3	C9	C3	118.5(3)	F22B	C67	F24B	104.8(5)
N3	C9	C10A	123.3(4)	F22A	C67	C64	116.1(9)
N3	C9	C10B	129.8(6)	F22A	C67	F24A	106.0(11)
C3	C9	C10B	106.4(6)	F22A	C67	F23A	102.5(11)
C10A	C9	C3	117.0(4)	F24A	C67	C64	116.3(12)
N1	C2	C3	118.5(3)	F24A	C67	F23A	97.5(11)
N1	C2	C1	126.1(4)	F23A	C67	C64	116.1(7)
C1	C2	C3	115.2(3)	C57	C52	B1	122.5(3)
C16	C11	N1	118.2(4)	C53	C52	C57	116.0(3)
C16	C11	C12	120.8(4)	C53	C52	B1	121.0(3)
C12	C11	N1	121.0(4)	C56	C57	C52	121.6(3)
C15	C16	C11	120.5(5)	C57	C56	C59	119.3(3)
C14	C15	C16	119.0(5)	C55	C56	C57	121.5(3)
C13	C14	C15	120.0(5)	C55	C56	C59	119.2(3)
C14	C13	C12	122.7(5)	C56	C55	C54	117.8(3)
C11	C12	C17	121.8(4)	C55	C54	C53	120.6(3)
C13	C12	C11	117.0(4)	C55	C54	C58	119.5(3)
C13	C12	C17	121.1(4)	C53	C54	C58	119.9(3)
C12	C17	C18	109.2(4)	C54	C53	C52	122.5(3)
C19	C17	C12	114.6(6)	F14	C58	F15	106.8(3)
C19	C17	C18	108.5(5)	F14	C58	F13	107.3(3)
C21A	O1A	C26A	117.3(7)	F14	C58	C54	112.9(3)
C28A	C27A	N3	118.9(3)	F15	C58	C54	112.0(3)
C28A	C27A	C32A	120.0	F13	C58	F15	104.5(3)
C32A	C27A	N3	121.1(3)	F13	C58	C54	112.8(3)
C27A	C28A	C29A	120.0	F18A	C59	C56	113.8(4)
C27A	C28A	C33A	122.6(4)	F18A	C59	F16A	103.8(5)
C29A	C28A	C33A	117.4(4)	F16A	C59	C56	110.7(4)
C30A	C29A	C28A	120.0	F17A	C59	C56	113.0(4)
C31A	C30A	C29A	120.0	F17A	C59	F18A	110.4(5)
C30A	C31A	C32A	120.0	F17A	C59	F16A	104.2(5)
C31A	C32A	C27A	120.0	F18B	C59	C56	114.6(6)
C35A	C33A	C28A	111.1(6)	F18B	C59	F17B	103.5(8)
C34A	C33A	C28A	113.7(6)	F16B	C59	C56	117.1(5)
C34A	C33A	C35A	110.4(6)	F16B	C59	F18B	104.6(8)
C21A	C20A	N2	117.2(4)	F16B	C59	F17B	103.7(8)
C21A	C20A	C25A	120.0	F17B	C59	C56	111.8(5)
C25A	C20A	N2	122.6(4)	C41	C36	B1	121.7(3)
O1A	C21A	C20A	115.5(5)	C37	C36	C41	115.5(3)

O1A	C21A	C22A	124.5(5)	C37	C36	B1	122.6(3)
C22A	C21A	C20A	120.0	C36	C41	C40	122.2(4)
C21A	C22A	C23A	120.0	C41	C40	C43	118.7(4)
C22A	C23A	C24A	120.0	C39	C40	C41	120.8(4)
C25A	C24A	C23A	120.0	C39	C40	C43	120.5(4)
C24A	C25A	C20A	120.0	C40	C39	C38	118.1(4)
C21B	O1B	C26B	116.1(8)	C39	C38	C37	120.7(4)
C28B	C27B	N3	105.9(6)	C39	C38	C42	119.2(4)
C28B	C27B	C32B	120.0	C37	C38	C42	120.0(4)
C32B	C27B	N3	134.0(6)	C38	C37	C36	122.7(3)
C27B	C28B	C29B	120.0	F4B	C43	C40	112.2(8)
C27B	C28B	C33B	122.0(10)	F4B	C43	F5B	103.6(10)
C29B	C28B	C33B	118.0(10)	F4B	C43	F6B	114.8(14)
C30B	C29B	C28B	120.0	F5B	C43	C40	110.3(8)
C29B	C30B	C31B	120.0	F6B	C43	C40	112.2(12)
C32B	C31B	C30B	120.0	F6B	C43	F5B	102.9(11)
C31B	C32B	C27B	120.0	F4A	C43	C40	111.8(5)
C28B	C33B	C35B	113.9(14)	F5A	C43	C40	114.1(7)
C34B	C33B	C28B	113.6(14)	F5A	C43	F4A	106.9(7)
C34B	C33B	C35B	107.8(14)	F5A	C43	F6A	106.4(8)
C25B	C20B	N2	124.1(8)	F6A	C43	C40	114.1(7)
C21B	C20B	N2	113.2(7)	F6A	C43	F4A	102.7(7)
C21B	C20B	C25B	122.0(10)	F3A	C42	C38	115.7(5)
C24B	C25B	C20B	120.3(12)	F3A	C42	F1A	113.0(7)
C25B	C24B	C23B	118.6(10)	F3A	C42	F2A	99.8(5)
C22B	C23B	C24B	121.7(9)	F1A	C42	C38	117.5(6)
C23B	C22B	C21B	118.7(9)	F1A	C42	F2A	99.3(6)
O1B	C21B	C20B	116.3(8)	F2A	C42	C38	108.4(4)
O1B	C21B	C22B	125.1(9)	F2B	C42	C38	118.2(6)
C20B	C21B	C22B	118.6(9)	F2B	C42	F3B	95.4(7)
C49	C44	C45	115.5(3)	F3B	C42	C38	108.2(4)
C49	C44	B1	121.2(3)	F1B	C42	C38	113.9(7)
C45	C44	B1	122.9(3)	F1B	C42	F2B	119.3(9)
C48	C49	C44	122.5(3)	F1B	C42	F3B	96.1(7)
C49	C48	C51	118.1(3)	C60	B1	C44	108.8(3)
C47	C48	C49	121.2(3)	C52	B1	C44	107.1(3)
C47	C48	C51	120.6(3)	C52	B1	C60	112.7(3)
C46	C47	C48	117.4(3)	C52	B1	C36	107.7(3)
C47	C46	C45	121.4(3)	C36	B1	C44	111.8(3)
C47	C46	C50	119.2(4)	C36	B1	C60	108.7(3)
C45	C46	C50	119.4(4)				

Table 6: Torsion Angles for 6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co1	N2	C4	C5	178.5(3)	C49	C48	C51	F12	-67.3(4)
Co1	N2	C4	C3	-2.3(4)	C49	C48	C51	F10	174.6(3)
Co1	N2	C20A	C21A	-96.0(4)	C48	C47	C46	C45	-0.1(5)
Co1	N2	C20A	C25A	79.1(4)	C48	C47	C46	C50	-179.3(4)
Co1	N2	C20B	C25B	-91.7(11)	C47	C48	C51	F11	-132.8(4)
Co1	N2	C20B	C21B	79.0(7)	C47	C48	C51	F12	109.0(4)
Co1	N1	C2	C3	-4.6(5)	C47	C48	C51	F10	-9.2(5)
Co1	N1	C2	C1	169.8(4)	C47	C46	C45	C44	-0.4(6)
Co1	N1	C11	C16	-82.7(4)	C47	C46	C50	F9	-34.4(5)
Co1	N1	C11	C12	97.7(4)	C47	C46	C50	F8	-150.6(4)
Co1	N3	C9	C3	0.9(7)	C47	C46	C50	F7	83.8(5)
Co1	N3	C9	C10A	-166.4(5)	C45	C44	C49	C48	0.1(5)
Co1	N3	C9	C10B	151.2(8)	C45	C44	B1	C60	144.9(3)
Co1	N3	C27A	C28A	-106.3(4)	C45	C44	B1	C52	-93.0(4)
Co1	N3	C27A	C32A	73.1(3)	C45	C44	B1	C36	24.8(4)
Co1	N3	C27B	C28B	104.4(6)	C45	C46	C50	F9	146.3(4)
Co1	N3	C27B	C32B	-71.0(9)	C45	C46	C50	F8	30.1(6)
N2	C4	C3	C9	-59.8(4)	C45	C46	C50	F7	-95.4(5)
N2	C4	C3	C2	61.4(4)	C51	C48	C47	C46	-175.6(3)
N2	C20A	C21A	O1A	-5.5(6)	C50	C46	C45	C44	178.9(4)
N2	C20A	C21A	C22A	175.2(5)	C60	C65	C64	C63	-1.1(6)
N2	C20A	C25A	C24A	-174.9(6)	C60	C65	C64	C67	179.8(4)
N2	C20B	C25B	C24B	171.0(10)	C65	C60	C61	C62	3.9(5)
N2	C20B	C21B	O1B	8.6(12)	C65	C60	B1	C44	-101.3(4)
N2	C20B	C21B	C22B	-171.8(8)	C65	C60	B1	C52	140.1(3)
N1	C11	C16	C15	-177.5(4)	C65	C60	B1	C36	20.7(4)
N1	C11	C12	C13	178.4(4)	C65	C64	C63	C62	2.3(6)
N1	C11	C12	C17	1.9(6)	C65	C64	C67	F24B	-177.1(6)
N3	C27A	C28A	C29A	179.4(3)	C65	C64	C67	F23B	-57.8(8)
N3	C27A	C28A	C33A	-2.5(6)	C65	C64	C67	F22B	65.1(7)
N3	C27A	C32A	C31A	-179.4(4)	C65	C64	C67	F22A	142.1(16)
N3	C27B	C28B	C29B	-176.2(7)	C65	C64	C67	F24A	-92.2(14)
N3	C27B	C28B	C33B	5.4(13)	C65	C64	C67	F23A	21.6(15)
N3	C27B	C32B	C31B	174.9(10)	C64	C63	C62	C61	-0.5(6)
C5	C4	C3	C9	119.5(4)	C64	C63	C62	C66	-176.3(4)
C5	C4	C3	C2	-119.3(3)	C63	C64	C67	F24B	3.7(8)
C8	C5	C4	N2	0.6(6)	C63	C64	C67	F23B	123.0(7)
C8	C5	C4	C3	-178.6(3)	C63	C64	C67	F22B	-114.1(6)
C6	C5	C4	N2	-120.2(5)	C63	C64	C67	F22A	-37.1(17)
C6	C5	C4	C3	60.6(5)	C63	C64	C67	F24A	88.7(14)
C7	C5	C4	N2	121.6(4)	C63	C64	C67	F23A	-157.6(14)
C7	C5	C4	C3	-57.7(4)	C63	C62	C61	C60	-2.8(6)
C4	N2	C20A	C21A	96.2(5)	C63	C62	C66	F21	-145.3(4)
C4	N2	C20A	C25A	-88.7(5)	C63	C62	C66	F19	-25.3(6)
C4	N2	C20B	C25B	75.5(12)	C63	C62	C66	F20	95.0(5)
C4	N2	C20B	C21B	-113.8(7)	C61	C60	C65	C64	-2.0(5)
C4	C3	C9	N3	60.7(6)	C61	C60	B1	C44	73.3(4)
C4	C3	C9	C10A	-131.2(5)	C61	C60	B1	C52	-45.4(4)
C4	C3	C9	C10B	-96.0(6)	C61	C60	B1	C36	-164.7(3)

C4	C3	C2	N1	-57.3(5)	C61	C62	C66	F21	38.8(5)
C4	C3	C2	C1	127.6(4)	C61	C62	C66	F19	158.9(4)
C9	N3	C27A	C28A	89.2(5)	C61	C62	C66	F20	-80.9(5)
C9	N3	C27A	C32A	-91.4(5)	C66	C62	C61	C60	173.0(4)
C9	N3	C27B	C28B	-110.6(6)	C67	C64	C63	C62	-178.5(4)
C9	N3	C27B	C32B	74.0(8)	C52	C57	C56	C55	0.1(6)
C9	C3	C2	N1	67.4(4)	C52	C57	C56	C59	177.9(3)
C9	C3	C2	C1	-107.7(4)	C57	C52	C53	C54	-1.1(5)
C2	N1	C11	C16	88.7(4)	C57	C52	B1	C44	-153.1(3)
C2	N1	C11	C12	-90.9(5)	C57	C52	B1	C60	-33.4(4)
C2	C3	C9	N3	-64.5(6)	C57	C52	B1	C36	86.5(4)
C2	C3	C9	C10A	103.6(5)	C57	C56	C55	C54	-0.6(6)
C2	C3	C9	C10B	138.9(6)	C57	C56	C59	F18A	-176.9(6)
C11	N1	C2	C3	-176.7(3)	C57	C56	C59	F16A	66.6(6)
C11	N1	C2	C1	-2.2(6)	C57	C56	C59	F17A	-49.9(6)
C11	C16	C15	C14	-1.8(7)	C57	C56	C59	F18B	125.6(9)
C11	C12	C17	C18	99.4(5)	C57	C56	C59	F16B	2.4(10)
C11	C12	C17	C19	-138.7(5)	C57	C56	C59	F17B	-117.0(8)
C16	C11	C12	C13	-1.2(6)	C56	C55	C54	C53	0.3(5)
C16	C11	C12	C17	-177.6(4)	C56	C55	C54	C58	179.8(3)
C16	C15	C14	C13	0.7(7)	C55	C56	C59	F18A	1.0(7)
C15	C14	C13	C12	0.2(8)	C55	C56	C59	F16A	-115.5(5)
C14	C13	C12	C11	0.0(7)	C55	C56	C59	F17A	128.0(6)
C14	C13	C12	C17	176.5(5)	C55	C56	C59	F18B	-56.5(10)
C13	C12	C17	C18	-76.9(6)	C55	C56	C59	F16B	-179.7(9)
C13	C12	C17	C19	45.0(6)	C55	C56	C59	F17B	60.8(9)
C12	C11	C16	C15	2.1(6)	C55	C54	C53	C52	0.7(5)
O1A	C21A	C22A	C23A	-179.2(6)	C55	C54	C58	F14	-26.6(5)
C27A	N3	C9	C3	165.8(4)	C55	C54	C58	F15	-147.2(4)
C27A	N3	C9	C10A	-1.6(8)	C55	C54	C58	F13	95.2(4)
C27A	C28A	C29A	C30A	0.0	C53	C52	C57	C56	0.8(5)
C27A	C28A	C33A	C35A	-110.4(7)	C53	C52	B1	C44	35.6(4)
C27A	C28A	C33A	C34A	124.3(7)	C53	C52	B1	C60	155.3(3)
C28A	C27A	C32A	C31A	0.0	C53	C52	B1	C36	-84.8(4)
C28A	C29A	C30A	C31A	0.0	C53	C54	C58	F14	152.9(4)
C29A	C28A	C33A	C35A	67.7(7)	C53	C54	C58	F15	32.3(5)
C29A	C28A	C33A	C34A	-57.5(8)	C53	C54	C58	F13	-85.3(4)
C29A	C30A	C31A	C32A	0.0	C58	C54	C53	C52	-178.8(3)
C30A	C31A	C32A	C27A	0.0	C59	C56	C55	C54	-178.4(4)
C32A	C27A	C28A	C29A	0.0	C36	C41	C40	C39	0.8(6)
C32A	C27A	C28A	C33A	178.1(5)	C36	C41	C40	C43	-177.9(4)
C33A	C28A	C29A	C30A	-178.2(5)	C41	C36	C37	C38	0.8(5)
C20A	N2	C4	C5	-15.2(7)	C41	C36	B1	C44	43.2(4)
C20A	N2	C4	C3	164.0(4)	C41	C36	B1	C60	-76.9(4)
C20A	C21A	C22A	C23A	0.0	C41	C36	B1	C52	160.6(3)
C21A	C20A	C25A	C24A	0.0	C41	C40	C39	C38	-0.1(6)
C21A	C22A	C23A	C24A	0.0	C41	C40	C43	F4B	175.0(16)
C22A	C23A	C24A	C25A	0.0	C41	C40	C43	F5B	60.1(11)
C23A	C24A	C25A	C20A	0.0	C41	C40	C43	F6B	-54.0(12)
C25A	C20A	C21A	O1A	179.3(5)	C41	C40	C43	F4A	-146.5(7)
C25A	C20A	C21A	C22A	0.0	C41	C40	C43	F5A	92.1(12)

C26A	O1A	C21A	C20A	172.9(6)	C41	C40	C43	F6A	-30.5(9)
C26A	O1A	C21A	C22A	-7.9(9)	C40	C39	C38	C37	-0.3(6)
C27B	N3	C9	C3	-147.2(5)	C40	C39	C38	C42	179.6(4)
C27B	N3	C9	C10B	3.1(10)	C39	C40	C43	F4B	-3.7(18)
C27B	C28B	C29B	C30B	0.0	C39	C40	C43	F5B	-118.6(10)
C27B	C28B	C33B	C35B	67(2)	C39	C40	C43	F6B	127.3(12)
C27B	C28B	C33B	C34B	-169.0(12)	C39	C40	C43	F4A	34.8(9)
C28B	C27B	C32B	C31B	0.0	C39	C40	C43	F5A	-86.6(12)
C28B	C29B	C30B	C31B	0.0	C39	C40	C43	F6A	150.8(8)
C29B	C28B	C33B	C35B	-111.3(13)	C39	C38	C37	C36	-0.1(6)
C29B	C28B	C33B	C34B	12.6(19)	C39	C38	C42	F3A	-51.1(8)
C29B	C30B	C31B	C32B	0.0	C39	C38	C42	F1A	171.3(7)
C30B	C31B	C32B	C27B	0.0	C39	C38	C42	F2A	59.9(6)
C32B	C27B	C28B	C29B	0.0	C39	C38	C42	F2B	-14.2(10)
C32B	C27B	C28B	C33B	-178.4(13)	C39	C38	C42	F3B	-120.9(6)
C33B	C28B	C29B	C30B	178.5(13)	C39	C38	C42	F1B	133.5(8)
C20B	N2	C4	C5	12.1(7)	C37	C36	C41	C40	-1.1(5)
C20B	N2	C4	C3	-168.6(5)	C37	C36	B1	C44	-142.0(3)
C20B	C25B	C24B	C23B	1(2)	C37	C36	B1	C60	97.9(4)
C25B	C20B	C21B	O1B	179.6(11)	C37	C36	B1	C52	-24.6(4)
C25B	C20B	C21B	C22B	-0.8(15)	C37	C38	C42	F3A	128.8(7)
C25B	C24B	C23B	C22B	-2.9(18)	C37	C38	C42	F1A	-8.8(8)
C24B	C23B	C22B	C21B	3.0(16)	C37	C38	C42	F2A	-120.2(5)
C23B	C22B	C21B	O1B	178.3(10)	C37	C38	C42	F2B	165.7(8)
C23B	C22B	C21B	C20B	-1.1(13)	C37	C38	C42	F3B	58.9(6)
C21B	C20B	C25B	C24B	1(2)	C37	C38	C42	F1B	-46.6(9)
C26B	O1B	C21B	C20B	-167.0(8)	C43	C40	C39	C38	178.6(4)
C26B	O1B	C21B	C22B	13.6(15)	C42	C38	C37	C36	180.0(4)
C44	C49	C48	C47	-0.5(5)	B1	C44	C49	C48	-172.8(3)
C44	C49	C48	C51	175.7(3)	B1	C44	C45	C46	173.1(3)
C49	C44	C45	C46	0.3(5)	B1	C60	C65	C64	172.9(4)
C49	C44	B1	C60	-42.7(4)	B1	C60	C61	C62	-171.0(3)
C49	C44	B1	C52	79.4(4)	B1	C52	C57	C56	-171.0(3)
C49	C44	B1	C36	-162.8(3)	B1	C52	C53	C54	170.7(3)
C49	C48	C47	C46	0.5(5)	B1	C36	C41	C40	174.0(3)
C49	C48	C51	F11	50.9(4)	B1	C36	C37	C38	-174.3(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6.

Atom	*x*	*y*	*z*	U(eq)
H8A	12982	2605	7036	80
H8B	13060	1699	7718	80
H8C	12274	2589	7813	80
H6A	10484	3256	7025	110
H6B	10262	2889	6316	110
H6C	11245	3368	6270	110
H7A	12568	1974	6060	116
H7B	11513	1576	6100	116
H7C	12556	1041	6678	116
H3	10014	1637	6579	45

H1A	7932	1927	6429	86
H1B	8303	2776	6491	86
H1C	7326	2460	7017	86
H16	7000	705	8266	62
H15	5171	1183	8589	81
H14	4651	2470	8979	84
H13	5920	3271	9011	76
H17	8792	2714	8606	85
H18A	7831	3649	7402	136
H18B	8359	4205	7827	136
H18C	7072	4243	7888	136
H19A	7268	3817	9335	167
H19B	8563	3743	9290	167
H19C	8109	2929	9815	167
H10A	9937	-527	6694	74
H10B	10640	144	6215	74
H10C	9331	463	6232	74
H29A	11375	-3052	8355	59
H30A	9625	-3337	8520	64
H31A	8074	-2182	8437	66
H32A	8272	-742	8188	53
H33A	11991	-946	7990	62
H35A	12468	-2341	7279	86
H35B	13263	-1696	7232	86
H35C	12057	-1314	6829	86
H34A	12606	-1922	9200	108
H34B	13579	-2027	8593	108
H34C	12851	-2739	8841	108
H22A	12587	1949	10109	60
H23A	14016	676	10401	71
H24A	14103	-374	9728	64
H25A	12759	-151	8762	45
H26A	10168	3480	9280	95
H26B	11460	3219	9479	95
H26C	10668	2692	10047	95
H10D	11467	245	6474	74
H10E	10306	538	6009	74
H10F	10767	-465	6515	74
H29B	10110	-2893	8277	60
H30B	12017	-3443	8315	72
H31B	13186	-2491	8170	69
H32B	12448	-989	7987	44
H33B	8705	-916	8440	55
H35D	8813	-222	7064	73
H35E	7647	-451	7281	73
H35F	8547	-1053	6877	73
H34D	8422	-2366	7956	83
H34E	7505	-1759	8345	83
H34F	8566	-2393	8859	83
H25B	10827	2646	8808	59
H24B	11876	2833	9770	67

H23B	13426	1710	10344	63
H22B	13824	367	10047	49
H26D	13546	-1257	9208	83
H26E	13221	-930	9974	83
H26F	14222	-654	9452	83
H49	8745	7904	5798	42
H47	11623	6247	6762	47
H45	8721	5625	7468	46
H65	5951	8021	7411	48
H63	5734	10539	6090	56
H61	7067	8518	5196	42
H57	5490	7579	5285	41
H55	6281	5705	4139	44
H53	8292	5677	5890	38
H41	7439	6615	8109	46
H39	5030	5372	9006	55
H37	5459	6133	6642	47

Table 8: Atomic Occupancy for 6.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O1A	0.530(6)	C10A	0.686(8)	H10A	0.686(8)
H10B	0.686(8)	H10C	0.686(8)	C27A	0.715(6)
C28A	0.715(6)	C29A	0.715(6)	H29A	0.715(6)
C30A	0.715(6)	H30A	0.715(6)	C31A	0.715(6)
H31A	0.715(6)	C32A	0.715(6)	H32A	0.715(6)
C33A	0.715(6)	H33A	0.715(6)	C35A	0.715(6)
H35A	0.715(6)	H35B	0.715(6)	H35C	0.715(6)
C34A	0.715(6)	H34A	0.715(6)	H34B	0.715(6)
H34C	0.715(6)	C20A	0.530(6)	C21A	0.530(6)
C22A	0.530(6)	H22A	0.530(6)	C23A	0.530(6)
H23A	0.530(6)	C24A	0.530(6)	H24A	0.530(6)
C25A	0.530(6)	H25A	0.530(6)	C26A	0.530(6)
H26A	0.530(6)	H26B	0.530(6)	H26C	0.530(6)
O1B	0.470(6)	C10B	0.314(8)	H10D	0.314(8)
H10E	0.314(8)	H10F	0.314(8)	C27B	0.285(6)
C28B	0.285(6)	C29B	0.285(6)	H29B	0.285(6)
C30B	0.285(6)	H30B	0.285(6)	C31B	0.285(6)
H31B	0.285(6)	C32B	0.285(6)	H32B	0.285(6)
C33B	0.285(6)	H33B	0.285(6)	C35B	0.285(6)
H35D	0.285(6)	H35E	0.285(6)	H35F	0.285(6)

C34B	0.285(6)	H34D	0.285(6)	H34E	0.285(6)
H34F	0.285(6)	C20B	0.470(6)	C25B	0.470(6)
H25B	0.470(6)	C24B	0.470(6)	H24B	0.470(6)
C23B	0.470(6)	H23B	0.470(6)	C22B	0.470(6)
H22B	0.470(6)	C21B	0.470(6)	C26B	0.470(6)
H26D	0.470(6)	H26E	0.470(6)	H26F	0.470(6)
F24B	0.780(15)	F23B	0.780(15)	F22B	0.780(15)
F18A	0.724(9)	F16A	0.724(9)	F17A	0.724(9)
F3A	0.545(8)	F1A	0.545(8)	F2A	0.545(8)
F4B	0.39(2)	F5B	0.39(2)	F6B	0.39(2)
F22A	0.220(15)	F24A	0.220(15)	F23A	0.220(15)
F18B	0.276(9)	F16B	0.276(9)	F17B	0.276(9)
F2B	0.455(8)	F3B	0.455(8)	F1B	0.455(8)
F4A	0.61(2)	F5A	0.61(2)	F6A	0.61(2)

8.4 Appendix D:

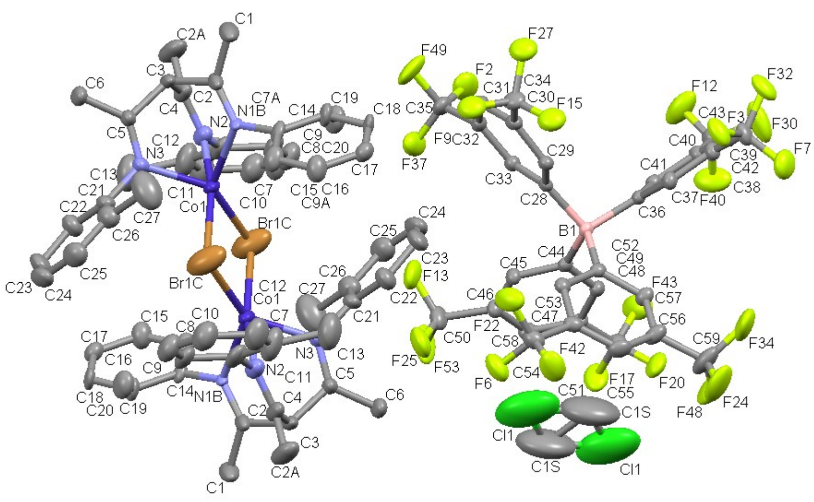


Figure A4: Thermal Ellipsoid plot (40% probability) of **7**, showing BArF anion. Hydrogen atoms and minor components of rotational disorder in CF_3 groups, and around aryl-N bonds, and in Bromine atom position, are removed.

Table 1: Crystal data and structure refinement for 7.

Identification code	**7**
Empirical formula	$C_{122}H_{90}B_2Br_2Cl_2Co_2F_{48}N_6$
Formula weight	2916.65
Temperature/K	150.03(16)
Crystal system	triclinic
Space group	P-1
a/Å	12.8325(6)
b/Å	15.0886(7)
c/Å	17.1355(7)
α/°	75.314(4)
β/°	83.402(4)
γ/°	71.836(4)
Volume/Å^3	3047.2(2)
Z	1
ρ_{calc}g/cm^3	1.589
μ/mm^{-1}	1.075
F(000)	1462.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.274 to 52.746
Index ranges	$-10 \le h \le 16$, $-14 \le k \le 18$, $-21 \le l \le 21$
Reflections collected	18523
Independent reflections	12273 [R_{int} = 0.0250, R_{sigma} = 0.0464]
Data/restraints/parameters	12273/371/985
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0691, wR_2 = 0.1811
Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.1967
Largest diff. peak/hole / e Å^{-3}	1.29/-1.23

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Co1	5562.3(5)	251.5(4)	5792.5(3)	36.28(17)
N2	4742(4)	1050(3)	6618(2)	53.1(11)
N3	6300(3)	-834(2)	6743.0(19)	37.5(8)
C1	7999(6)	1230(5)	6708(4)	86(2)
C2	7130(5)	840(3)	6532(3)	57.9(15)
C2A	4813(7)	1540(5)	7879(4)	91(2)
C3	6475(5)	434(3)	7265(2)	52.1(14)
C4	5267(5)	1027(3)	7219(3)	59.8(15)
C5	6623(4)	-619(3)	7329(2)	40.7(10)
C6	7167(5)	-1307(3)	8059(3)	54.1(13)
C21	6423(4)	-1818(3)	6750(2)	40.4(10)

C22	5595(5)	-2207(3)	7096(3)	52.8(12)
C23	5695(5)	-3147(4)	7061(3)	60.0(14)
C24	6614(6)	-3661(4)	6700(3)	64.2(16)
C25	7415(5)	-3263(4)	6361(3)	63.8(14)
C26	7346(4)	-2323(4)	6368(3)	53.3(12)
C27	8270(6)	-1859(6)	5979(6)	107(3)
Br1A	3866.6(18)	-147(3)	5576(2)	48.6(6)
N1B	7140(19)	643(19)	5821(15)	23(4)
C7	3716(14)	1607(10)	6475(10)	58(4)
C8	3448(15)	2483(10)	5915(10)	54(4)
C9	2360(16)	3047(10)	5846(9)	70(4)
C10	1542(15)	2736(13)	6335(9)	75(5)
C11	1811(15)	1861(14)	6894(9)	77(5)
C12	2898(16)	1296(12)	6964(9)	78(5)
C13	2990(30)	286(18)	7530(20)	94(4)
C18	8024(16)	2184(8)	3981(8)	38(5)
C19	7536(16)	1883(9)	4727(8)	41(4)
C14	7771(13)	911(10)	5089(7)	33(4)
C15	8494(13)	240(9)	4704(9)	47(5)
C16	8982(13)	542(10)	3958(9)	55(6)
C17	8747(13)	1514(11)	3597(7)	41(5)
C20	6371(19)	2458(18)	4834(16)	59.7(19)
Br1C	6154(5)	-918(5)	4948(4)	45(3)
Br1B	4187(11)	-519(10)	5694(3)	71(2)
N1A	6788(8)	898(7)	5857(6)	48(2)
C7A	3506(11)	1542(11)	6627(11)	48(4)
C8A	3174(13)	2460(11)	6135(12)	69(4)
C9A	2064(14)	2920(11)	6011(11)	76(5)
C10A	1287(11)	2462(15)	6380(10)	82(5)
C11A	1620(12)	1545(15)	6872(9)	71(4)
C12A	2729(12)	1085(12)	6996(9)	58(3)
C13A	3100(30)	21(18)	7500(20)	94(4)
C14A	7402(5)	1239(4)	5145(3)	51(2)
C15A	8420(4)	663(5)	4937(4)	79(3)
C16A	8977(4)	977(6)	4228(5)	96(4)
C17A	8516(5)	1869(5)	3727(3)	71(3)
C18A	7498(5)	2446(4)	3935(3)	58(2)
C19A	6941(5)	2131(4)	4644(3)	42.5(17)
C20A	5745(7)	2732(5)	4846(4)	59.7(19)
F2	1218(3)	6870(2)	4648.0(17)	67.2(9)
F3	4648(2)	8572.9(18)	289.4(18)	53.3(7)
F6	3588(2)	3153.9(19)	750(2)	61.0(8)
F7	3642(3)	9575(2)	-654.5(17)	65.5(8)
F13	-293(3)	4612(3)	3617.0(17)	74.4(10)
F17	-3031(2)	7240(2)	829(2)	69.2(9)
F20	-1893(3)	7772(2)	-25.4(16)	61.4(8)
F22	4918(3)	3549(2)	1036(2)	65.2(8)
F25	35(3)	3823(2)	2724(2)	77.6(10)
F32	3918(2)	10032.3(19)	358.2(19)	56.1(7)
F37	1278(3)	5453(3)	4651.4(16)	71.7(10)
F42	4764(3)	3473(2)	-173.7(19)	66.2(9)

F43	-2502(3)	8415(2)	953(2)	77.2(10)
F49	2531(3)	5723(3)	5207.2(15)	80.9(11)
F53	-1604(3)	4551(3)	2994(2)	98.0(15)
C28	2529(3)	6369(2)	2319.4(19)	23.0(7)
C29	3674(3)	6135(2)	2310(2)	25.2(7)
C30	4242(3)	5899(3)	3015(2)	29.9(8)
C31	3683(3)	5859(3)	3768(2)	32.5(8)
C32	2556(3)	6085(3)	3789(2)	31.8(8)
C33	1993(3)	6353(2)	3079(2)	26.5(7)
C34	5457(4)	5642(3)	2984(2)	41.8(9)
C35	1915(4)	6022(3)	4577(2)	42.4(10)
C36	1780(3)	7878(2)	1196.4(18)	23.2(7)
C37	2701(3)	8132(3)	794(2)	27.1(7)
C38	2736(3)	9067(3)	573(2)	29.3(8)
C39	1837(3)	9810(3)	722(2)	30.8(8)
C40	924(3)	9575(3)	1121(2)	28.9(7)
C41	909(3)	8626(3)	1360.3(19)	25.3(7)
C42	3735(4)	9303(3)	144(3)	39.3(9)
C43	-53(3)	10361(3)	1303(3)	38.9(9)
C44	649(3)	6531(2)	1629.6(19)	23.6(7)
C45	495(3)	5712(3)	2178(2)	26.6(7)
C46	-496(3)	5502(3)	2273(2)	31.9(8)
C47	-1378(3)	6086(3)	1818(2)	32.2(8)
C48	-1233(3)	6879(3)	1254(2)	29.6(8)
C49	-242(3)	7097(3)	1166.9(19)	27.0(7)
C50	-602(4)	4629(4)	2894(3)	48.0(11)
C51	-2166(4)	7556(3)	758(3)	43.3(10)
C52	2459(3)	6186(3)	775.1(19)	24.0(7)
C53	3101(3)	5229(3)	913(2)	26.2(7)
C54	3522(3)	4770(3)	283(2)	29.9(8)
C55	3306(3)	5253(3)	-509(2)	38.4(9)
C56	2673(3)	6197(3)	-663(2)	38.8(9)
C57	2256(3)	6645(3)	-34(2)	30.8(8)
C58	4193(3)	3745(3)	468(3)	39.8(9)
C59	2413(5)	6737(4)	-1508(3)	64.8(14)
B1	1849(3)	6732(3)	1488(2)	22.3(7)
F9	5944(4)	4739(4)	3336(4)	59.7(7)
F12	-215(5)	10343(5)	2053(2)	80(2)
F15	5913(5)	5774(4)	2221(3)	59.7(7)
F24	3093(6)	6372(4)	-2055(2)	91(2)
F27	5816(4)	6194(5)	3341(4)	59.7(7)
F30	-2(5)	11223(3)	892(5)	86(2)
F34	2584(6)	7631(4)	-1648(2)	93(2)
F40	-969(3)	10300(4)	1055(4)	77.3(19)
F48	1401(5)	6949(6)	-1670(5)	100(3)
F9A	5881(7)	5726(8)	3629(6)	59.7(7)
F12A	228(11)	10849(12)	1769(12)	74(5)
F15A	5865(7)	4681(6)	2995(7)	59.7(7)
F24A	2220(16)	6123(11)	-1929(8)	79(5)
F27A	5871(8)	6097(8)	2312(6)	59.7(7)
F30A	-467(14)	11014(11)	706(8)	64(4)

F34A	3159(14)	7018(16)	-1931(10)	93(5)
F40A	-898(10)	10081(9)	1695(12)	70(5)
F48A	1490(14)	7397(13)	-1618(13)	76(5)
Cl1	703(4)	4340(4)	544(3)	229(2)
C1S	363(14)	5359(11)	-185(10)	216(6)

Table 3: Anisotropic Displacement Parameters (Å^2×10^3) for 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	52.8(4)	41.1(3)	23.0(3)	-1.8(2)	-11.3(2)	-26.3(3)
N2	89(3)	35(2)	35.8(19)	-4.8(15)	-20(2)	-15(2)
N3	57(2)	32.4(18)	30.2(16)	-3.6(13)	-7.5(15)	-24.3(16)
C1	134(6)	75(4)	72(4)	26(3)	-65(4)	-75(4)
C2	95(4)	42(3)	48(3)	18(2)	-44(3)	-44(3)
C2A	159(7)	59(4)	53(3)	-23(3)	-43(4)	-8(4)
C3	102(4)	33(2)	32(2)	3.9(17)	-34(2)	-34(3)
C4	115(5)	31(2)	36(2)	-0.4(18)	-31(3)	-21(3)
C5	67(3)	31(2)	29.7(19)	0.1(15)	-12.8(19)	-24(2)
C6	91(4)	36(2)	38(2)	6.3(18)	-25(2)	-26(2)
C21	58(3)	35(2)	37(2)	-7.3(16)	-12.7(19)	-22(2)
C22	69(3)	39(3)	56(3)	-6(2)	-4(2)	-27(2)
C23	85(4)	43(3)	62(3)	0(2)	-15(3)	-39(3)
C24	103(5)	32(3)	64(3)	-11(2)	-31(3)	-20(3)
C25	81(4)	42(3)	63(3)	-15(2)	-17(3)	-3(3)
C26	59(3)	44(3)	56(3)	-9(2)	-12(2)	-13(2)
C27	76(5)	83(5)	150(8)	-2(5)	-1(5)	-26(4)
Br1A	43.8(8)	89.7(13)	33.6(10)	-29.7(8)	12.5(5)	-42.2(8)
N1B	29(10)	25(10)	18(6)	1(6)	-11(6)	-13(8)
C7	91(9)	58(6)	22(5)	-10(4)	-7(5)	-13(6)
C8	84(8)	49(5)	23(6)	-7(4)	-13(5)	-9(5)
C9	85(9)	68(7)	45(6)	-2(5)	-14(6)	-11(6)
C10	82(9)	78(9)	57(7)	-7(6)	-7(6)	-14(6)
C11	85(8)	81(9)	50(6)	-8(6)	13(5)	-15(6)
C12	90(8)	79(8)	42(7)	6(6)	3(6)	-8(6)
C13	100(7)	89(7)	71(5)	10(7)	7(5)	-22(7)
C18	59(11)	25(8)	21(6)	9(5)	-5(7)	-9(7)
C19	54(7)	29(6)	28(6)	8(5)	-6(6)	-4(5)
C14	27(8)	35(6)	24(6)	10(4)	-8(5)	-4(5)
C15	37(8)	47(8)	42(7)	1(6)	-3(6)	-1(6)
C16	54(11)	50(9)	51(8)	0(6)	3(7)	-11(7)
C17	48(9)	45(9)	29(7)	-5(6)	-6(6)	-13(6)
C20	68(5)	41(4)	53(3)	-1(3)	-12(3)	2(3)
Br1C	31(4)	58(5)	35(4)	-27(3)	-18(2)	19(3)
Br1B	93(4)	132(5)	19.8(11)	10(2)	-13.6(17)	-97(4)
N1A	60(6)	40(5)	46(3)	17(3)	-31(4)	-28(4)
C7A	59(6)	52(6)	22(6)	-12(4)	9(4)	-3(5)
C8A	74(7)	58(6)	55(9)	-4(6)	18(6)	-3(5)
C9A	68(7)	61(8)	67(9)	7(6)	12(6)	1(5)
C10A	73(7)	75(9)	75(8)	-12(7)	26(6)	-6(6)

C11A	70(6)	78(9)	56(7)	-14(6)	16(5)	-16(5)
C12A	69(6)	71(7)	25(5)	-8(4)	17(4)	-16(5)
C13A	100(7)	89(7)	71(5)	10(7)	7(5)	-22(7)
C14A	49(4)	49(4)	52(3)	19(3)	-28(3)	-27(3)
C15A	48(4)	69(5)	91(6)	34(4)	-14(4)	-14(4)
C16A	49(4)	87(6)	112(7)	40(5)	-1(4)	-15(4)
C17A	64(5)	68(6)	69(5)	18(4)	-11(4)	-28(4)
C18A	73(5)	55(4)	42(3)	15(3)	-22(3)	-25(4)
C19A	60(5)	29(3)	36(3)	2(2)	-18(3)	-10(3)
C20A	68(5)	41(4)	53(3)	-1(3)	-12(3)	2(3)
F2	84(2)	74(2)	41.9(15)	-23.2(14)	21.1(14)	-22.5(18)
F3	34.5(13)	35.1(14)	85(2)	-6.2(13)	12.0(13)	-13.0(11)
F6	58.1(18)	37.4(15)	86(2)	-7.4(14)	5.2(15)	-20.1(13)
F7	70(2)	77(2)	45.6(15)	0.9(14)	14.6(14)	-35.1(17)
F13	94(2)	86(2)	40.8(15)	21.9(15)	-9.5(15)	-50(2)
F17	43.2(16)	82(2)	79(2)	13.4(16)	-30.8(14)	-29.5(15)
F20	66.2(19)	70.7(19)	41.8(14)	10.9(13)	-26.9(13)	-22.8(16)
F22	55.5(18)	44.4(16)	92(2)	-24.6(15)	-29.9(16)	8.0(13)
F25	102(3)	42.0(18)	85(2)	9.0(16)	-6(2)	-32.8(18)
F32	44.3(15)	39.8(15)	91(2)	-15.6(14)	10.5(14)	-25.7(12)
F37	107(3)	92(2)	37.3(14)	-12.5(14)	18.7(15)	-69(2)
F42	77(2)	44.3(16)	69.0(19)	-27.3(14)	27.4(16)	-5.2(15)
F43	73(2)	52.6(19)	97(2)	-20.6(17)	-44.7(19)	11.6(16)
F49	80(2)	135(3)	20.7(12)	-2.5(15)	-10.9(13)	-32(2)
F53	58(2)	110(3)	111(3)	55(2)	-22.9(19)	-60(2)
C28	29.2(18)	19.2(16)	22.4(15)	-3.6(12)	-3.5(13)	-10.0(14)
C29	30.2(18)	23.3(17)	24.7(16)	-5.2(13)	-3.9(13)	-10.8(15)
C30	34(2)	26.1(19)	31.8(18)	-5.0(14)	-9.4(15)	-11.2(16)
C31	44(2)	30(2)	27.2(17)	-4.7(14)	-13.7(15)	-12.8(17)
C32	47(2)	31(2)	21.3(16)	-3.9(14)	-3.8(15)	-17.7(17)
C33	31.2(19)	26.4(18)	23.3(16)	-4.8(13)	-1.5(13)	-10.9(15)
C34	35(2)	45(2)	45(2)	-9.7(16)	-16.0(16)	-8.4(17)
C35	59(3)	52(3)	21.4(18)	-6.8(17)	-1.1(17)	-25(2)
C36	28.1(18)	24.5(17)	17.7(14)	-2.7(12)	-3.1(12)	-9.6(14)
C37	26.8(18)	27.7(18)	24.8(16)	-1.4(13)	-0.9(13)	-9.2(15)
C38	29.4(19)	29.1(19)	29.8(17)	-1.1(14)	-1.8(14)	-13.4(16)
C39	37(2)	22.3(18)	32.9(18)	0.4(14)	-6.4(15)	-11.6(16)
C40	30.2(19)	26.1(18)	29.4(17)	-4.0(14)	-7.5(14)	-6.8(15)
C41	26.3(17)	30.4(18)	20.2(15)	-4.2(13)	-2.2(13)	-10.6(15)
C42	38(2)	30(2)	46(2)	0.0(17)	5.3(17)	-15.8(18)
C43	38(2)	28.6(19)	46(2)	-7.1(15)	-3.8(16)	-4.6(16)
C44	27.3(18)	26.4(18)	18.5(14)	-5.7(12)	-0.1(12)	-9.8(14)
C45	27.0(18)	27.2(18)	24.3(16)	-0.6(13)	-4.3(13)	-9.5(15)
C46	33(2)	36(2)	28.1(17)	-0.7(15)	-1.2(14)	-18.4(17)
C47	26.3(19)	40(2)	33.4(19)	-6.8(16)	-2.0(14)	-15.5(17)
C48	27.2(18)	36(2)	27.9(17)	-8.2(15)	-5.2(14)	-9.9(16)
C49	32.7(19)	29.0(19)	20.7(15)	-2.5(13)	-2.9(13)	-12.8(15)
C50	46(3)	48(3)	49(3)	9(2)	-7(2)	-27(2)
C51	42(2)	45(3)	46(2)	-5.2(19)	-17.7(19)	-14(2)
C52	23.5(17)	29.1(18)	23.0(16)	-7.4(13)	-0.2(12)	-11.9(14)
C53	25.6(17)	28.2(18)	27.2(16)	-5.3(13)	-0.7(13)	-12.0(15)

C54	25.1(18)	33(2)	36.1(19)	-15.1(15)	1.1(14)	-10.5(15)
C55	34(2)	52(3)	32.9(19)	-24.9(18)	4.3(16)	-9.1(19)
C56	35(2)	50(3)	27.6(19)	-13.6(17)	-4.3(16)	-2.3(19)
C57	27.3(18)	37(2)	25.1(17)	-7.7(15)	-2.0(14)	-4.5(16)
C58	37(2)	36(2)	50(2)	-16.5(18)	1.7(18)	-11.8(18)
C59	72(3)	79(3)	27(2)	-16(2)	-10(2)	9(3)
B1	25.6(19)	24.0(19)	17.7(16)	-4.1(13)	0.9(14)	-8.8(16)
F9	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F12	79(4)	87(4)	41(2)	-26(2)	-5(2)	33(3)
F15	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F24	117(5)	96(4)	25.3(18)	-15(2)	11(2)	13(3)
F27	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F30	69(4)	31(2)	129(5)	1(3)	35(3)	-4(2)
F34	155(6)	78(3)	30(2)	10.6(19)	-15(3)	-25(3)
F40	34(2)	88(4)	112(5)	-53(3)	-19(2)	9(2)
F48	88(3)	140(7)	56(3)	2(4)	-41(3)	-15(4)
F9A	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F12A	52(7)	73(9)	106(9)	-66(8)	-8(6)	5(6)
F15A	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F24A	111(12)	89(8)	25(6)	-17(5)	-30(7)	2(7)
F27A	41.5(11)	71.5(18)	69.2(16)	-19.9(13)	-13.3(10)	-14.3(12)
F30A	69(9)	46(7)	55(5)	-4(4)	-18(5)	12(6)
F34A	97(8)	118(14)	48(8)	-12(8)	-5(6)	-14(9)
F40A	49(6)	42(6)	109(11)	-19(6)	19(6)	-5(5)
F48A	88(8)	81(10)	29(7)	-11(7)	-16(6)	20(7)
Cl1	195(4)	291(5)	232(4)	-189(4)	-31(3)	-4(3)
C1S	182(9)	269(9)	287(9)	-147(6)	-25(7)	-121(7)

Table 4: Bond Lengths for 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N2	2.072(4)	F13	C50	1.336(6)
Co1	N3	2.065(3)	F17	C51	1.321(5)
Co1	Br1A	2.519(2)	F20	C51	1.331(5)
Co1	Br1A[1]	2.405(2)	F22	C58	1.338(5)
Co1	N1B	2.29(3)	F25	C50	1.318(6)
Co1	Br1C[1]	2.467(6)	F32	C42	1.337(5)
Co1	Br1C	2.448(6)	F37	C35	1.333(5)
Co1	Br1B	2.437(5)	F42	C58	1.330(5)
Co1	Br1B[1]	2.475(5)	F43	C51	1.348(6)
Co1	N1A	2.119(11)	F49	C35	1.313(5)
N2	C4	1.280(6)	F53	C50	1.315(5)
N2	C7	1.334(15)	C28	C29	1.400(5)
N2	C7A	1.528(14)	C28	C33	1.398(5)
N3	C5	1.277(5)	C28	B1	1.638(5)
N3	C21	1.441(5)	C29	C30	1.392(5)
C1	C2	1.503(6)	C30	C31	1.398(5)
C2	C3	1.532(7)	C30	C34	1.483(6)
C2	N1B	1.32(3)	C31	C32	1.377(6)
C2	N1A	1.257(12)	C32	C33	1.392(5)

C2A	C4	1.494(8)	C32	C35	1.495(5)
C3	C4	1.528(8)	C34	F9	1.323(6)
C3	C5	1.518(6)	C34	F15	1.363(7)
C5	C6	1.490(5)	C34	F27	1.357(6)
C21	C22	1.376(6)	C34	F9A	1.336(8)
C21	C26	1.387(7)	C34	F15A	1.376(9)
C22	C23	1.399(7)	C34	F27A	1.329(10)
C23	C24	1.371(9)	C36	C37	1.408(5)
C24	C25	1.352(9)	C36	C41	1.380(5)
C25	C26	1.395(7)	C36	B1	1.650(5)
C26	C27	1.562(9)	C37	C38	1.379(5)
Br1A	$Co1^{1}$	2.405(2)	C38	C39	1.387(6)
N1B	C14	1.45(2)	C38	C42	1.498(5)
C7	C8	1.3900	C39	C40	1.385(5)
C7	C12	1.3900	C40	C41	1.391(5)
C8	C9	1.3900	C40	C43	1.499(6)
C9	C10	1.3900	C43	F12	1.272(6)
C10	C11	1.3900	C43	F30	1.331(6)
C11	C12	1.3900	C43	F40	1.332(6)
C12	C13	1.563(11)	C43	F12A	1.356(11)
C18	C19	1.3900	C43	F30A	1.260(11)
C18	C17	1.3900	C43	F40A	1.334(11)
C19	C14	1.3900	C44	C45	1.404(5)
C19	C20	1.493(14)	C44	C49	1.386(5)
C14	C15	1.3900	C44	B1	1.640(5)
C15	C16	1.3900	C45	C46	1.386(5)
C16	C17	1.3900	C46	C47	1.378(5)
Br1C	$Co1^{1}$	2.467(6)	C46	C50	1.502(5)
Br1C	$Br1B^{1}$	2.100(14)	C47	C48	1.383(5)
Br1B	$Co1^{1}$	2.475(5)	C48	C49	1.393(5)
Br1B	$Br1C^{1}$	2.100(14)	C48	C51	1.494(5)
N1A	C14A	1.445(10)	C52	C53	1.396(5)
C7A	C8A	1.3900	C52	C57	1.397(5)
C7A	C12A	1.3900	C52	B1	1.634(5)
C8A	C9A	1.3900	C53	C54	1.397(5)
C9A	C10A	1.3900	C54	C55	1.381(6)
C10A	C11A	1.3900	C54	C58	1.490(6)
C11A	C12A	1.3900	C55	C56	1.377(6)
C12A	C13A	1.570(11)	C56	C57	1.384(5)
C14A	C15A	1.3900	C56	C59	1.488(6)
C14A	C19A	1.3900	C59	F24	1.310(7)
C15A	C16A	1.3900	C59	F34	1.392(8)
C16A	C17A	1.3900	C59	F48	1.283(8)
C17A	C18A	1.3900	C59	F24A	1.399(13)
C18A	C19A	1.3900	C59	F34A	1.249(14)
C19A	C20A	1.571(8)	C59	F48A	1.285(15)
F2	C35	1.340(6)	Cl1	C1S	1.687(14)
F3	C42	1.331(5)	Cl1	$C1S^{2}$	1.456(16)
F6	C58	1.326(5)	C1S	$Cl1^{2}$	1.456(16)
F7	C42	1.333(5)			

Table 5: Bond Angles for 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Co1	Br1A	92.38(13)	C29	C30	C31	120.8(3)
N2	Co1	Br1A[1]	150.18(14)	C29	C30	C34	120.4(3)
N2	Co1	N1B	92.8(6)	C31	C30	C34	118.7(3)
N2	Co1	Br1C[1]	86.11(18)	C32	C31	C30	118.2(3)
N2	Co1	Br1C	164.4(2)	C31	C32	C33	120.6(3)
N2	Co1	Br1B	99.1(4)	C31	C32	C35	120.7(3)
N2	Co1	Br1B[1]	136.9(4)	C33	C32	C35	118.7(4)
N2	Co1	N1A	82.5(3)	C32	C33	C28	122.7(3)
N3	Co1	N2	88.72(14)	F9	C34	C30	114.0(4)
N3	Co1	Br1A[1]	120.20(14)	F9	C34	F15	105.3(5)
N3	Co1	Br1A	104.32(13)	F9	C34	F27	106.8(4)
N3	Co1	N1B	80.5(6)	F15	C34	C30	113.9(4)
N3	Co1	Br1C	87.74(18)	F27	C34	C30	111.8(4)
N3	Co1	Br1C[1]	141.4(2)	F27	C34	F15	104.3(4)
N3	Co1	Br1B	92.8(3)	F9A	C34	C30	114.5(5)
N3	Co1	Br1B[1]	133.9(4)	F9A	C34	F15A	103.9(6)
N3	Co1	N1A	87.1(3)	F15A	C34	C30	107.9(5)
Br1A[1]	Co1	Br1A	87.48(6)	F27A	C34	C30	113.6(5)
N1B	Co1	Br1A[1]	85.6(6)	F27A	C34	F9A	110.0(6)
N1B	Co1	Br1A	173.0(6)	F27A	C34	F15A	106.2(7)
Br1C	Co1	Br1C[1]	87.2(2)	F2	C35	C32	112.4(3)
Br1C[1]	Co1	Br1B[1]	65.1(3)	F37	C35	F2	104.5(4)
Br1C	Co1	Br1B[1]	50.5(4)	F37	C35	C32	111.7(3)
Br1B	Co1	Br1C[1]	50.7(4)	F49	C35	F2	105.6(4)
Br1B	Co1	Br1C	66.0(4)	F49	C35	F37	108.6(4)
Br1B	Co1	Br1B[1]	87.16(17)	F49	C35	C32	113.5(4)
N1A	Co1	Br1C	112.5(4)	C37	C36	B1	118.8(3)
N1A	Co1	Br1C[1]	129.8(3)	C41	C36	C37	115.7(3)
N1A	Co1	Br1B[1]	91.8(3)	C41	C36	B1	125.4(3)
N1A	Co1	Br1B	178.4(5)	C38	C37	C36	122.5(3)
C4	N2	Co1	118.2(4)	C37	C38	C39	120.7(3)
C4	N2	C7	123.1(8)	C37	C38	C42	120.6(4)
C4	N2	C7A	117.3(8)	C39	C38	C42	118.7(3)
C7	N2	Co1	118.6(8)	C40	C39	C38	117.7(3)
C7A	N2	Co1	123.7(8)	C39	C40	C41	121.1(4)
C5	N3	Co1	119.2(3)	C39	C40	C43	118.9(3)
C5	N3	C21	120.6(3)	C41	C40	C43	120.0(3)
C21	N3	Co1	120.2(2)	C36	C41	C40	122.3(3)
C1	C2	C3	116.2(4)	F3	C42	F7	107.0(4)
N1B	C2	C1	119.8(12)	F3	C42	F32	106.4(3)
N1B	C2	C3	121.9(12)	F3	C42	C38	113.1(3)
N1A	C2	C1	128.1(6)	F7	C42	F32	105.5(3)
N1A	C2	C3	115.2(6)	F7	C42	C38	112.3(3)
C4	C3	C2	109.9(4)	F32	C42	C38	112.1(4)
C5	C3	C2	110.8(4)	F12	C43	C40	113.4(4)
C5	C3	C4	112.0(4)	F12	C43	F30	110.2(5)
N2	C4	C2A	126.0(6)	F12	C43	F40	106.3(5)
N2	C4	C3	117.7(5)	F30	C43	C40	112.1(4)

C2A	C4	C3	116.3(5)	F30	C43	F40	103.3(5)
N3	C5	C3	117.0(3)	F40	C43	C40	111.0(4)
N3	C5	C6	126.2(4)	F12A	C43	C40	110.5(6)
C6	C5	C3	116.7(3)	F30A	C43	C40	116.1(8)
C22	C21	N3	118.9(4)	F30A	C43	F12A	102.8(11)
C22	C21	C26	122.3(4)	F30A	C43	F40A	104.7(11)
C26	C21	N3	118.7(4)	F40A	C43	C40	115.6(6)
C21	C22	C23	118.5(5)	F40A	C43	F12A	105.9(11)
C24	C23	C22	119.8(5)	C45	C44	B1	121.4(3)
C25	C24	C23	120.7(5)	C49	C44	C45	115.5(3)
C24	C25	C26	121.8(6)	C49	C44	B1	122.8(3)
C21	C26	C25	116.9(5)	C46	C45	C44	122.3(3)
C21	C26	C27	121.0(5)	C45	C46	C50	118.8(3)
C25	C26	C27	122.0(6)	C47	C46	C45	121.1(3)
Co1[1]	Br1A	Co1	92.52(6)	C47	C46	C50	120.0(3)
C2	N1B	Co1	106.5(13)	C46	C47	C48	117.6(3)
C2	N1B	C14	129(2)	C47	C48	C49	121.2(3)
C14	N1B	Co1	121.8(18)	C47	C48	C51	120.3(3)
N2	C7	C8	124.0(10)	C49	C48	C51	118.5(3)
N2	C7	C12	115.9(10)	C44	C49	C48	122.2(3)
C8	C7	C12	120.0	F13	C50	C46	111.8(4)
C9	C8	C7	120.0	F25	C50	F13	104.4(4)
C10	C9	C8	120.0	F25	C50	C46	112.9(4)
C9	C10	C11	120.0	F53	C50	F13	107.0(4)
C12	C11	C10	120.0	F53	C50	F25	106.3(4)
C7	C12	C13	128.3(15)	F53	C50	C46	113.8(4)
C11	C12	C7	120.0	F17	C51	F20	107.4(3)
C11	C12	C13	111.0(16)	F17	C51	F43	107.4(4)
C19	C18	C17	120.0	F17	C51	C48	113.5(4)
C18	C19	C14	120.0	F20	C51	F43	103.3(4)
C18	C19	C20	114.0(12)	F20	C51	C48	113.0(4)
C14	C19	C20	115.0(13)	F43	C51	C48	111.5(3)
C19	C14	N1B	116.9(12)	C53	C52	C57	115.4(3)
C15	C14	N1B	122.7(13)	C53	C52	B1	124.2(3)
C15	C14	C19	120.0	C57	C52	B1	120.0(3)
C14	C15	C16	120.0	C52	C53	C54	122.0(3)
C17	C16	C15	120.0	C53	C54	C58	119.6(3)
C16	C17	C18	120.0	C55	C54	C53	120.6(4)
Co1	Br1C	Co1[1]	92.8(2)	C55	C54	C58	119.8(3)
Br1B[1]	Br1C	Co1[1]	63.9(3)	C56	C55	C54	118.6(3)
Br1B[1]	Br1C	Co1	65.4(3)	C55	C56	C57	120.3(4)
Co1	Br1B	Co1[1]	92.84(17)	C55	C56	C59	120.1(4)
Br1C[1]	Br1B	Co1	65.4(3)	C57	C56	C59	119.6(4)
Br1C[1]	Br1B	Co1[1]	64.1(2)	C56	C57	C52	123.0(4)
C2	N1A	Co1	119.8(6)	F6	C58	F22	105.2(4)
C2	N1A	C14A	117.6(9)	F6	C58	F42	106.5(4)
C14A	N1A	Co1	121.5(7)	F6	C58	C54	112.6(3)
C8A	C7A	N2	115.3(8)	F22	C58	C54	112.6(3)
C8A	C7A	C12A	120.0	F42	C58	F22	106.6(4)
C12A	C7A	N2	124.0(8)	F42	C58	C54	112.8(4)
C9A	C8A	C7A	120.0	F24	C59	C56	114.1(5)

C8A	C9A	C10A	120.0	F24	C59	F34	100.6(6)
C11A	C10A	C9A	120.0	F34	C59	C56	110.2(4)
C10A	C11A	C12A	120.0	F48	C59	C56	114.2(6)
C7A	C12A	C13A	120.3(15)	F48	C59	F24	113.3(6)
C11A	C12A	C7A	120.0	F48	C59	F34	102.8(6)
C11A	C12A	C13A	119.6(15)	F24A	C59	C56	108.6(7)
C15A	C14A	N1A	120.4(4)	F34A	C59	C56	116.8(9)
C15A	C14A	C19A	120.0	F34A	C59	F24A	102.7(10)
C19A	C14A	N1A	119.5(4)	F34A	C59	F48A	110.4(11)
C14A	C15A	C16A	120.0	F48A	C59	C56	117.2(10)
C15A	C16A	C17A	120.0	F48A	C59	F24A	98.4(9)
C16A	C17A	C18A	120.0	C28	B1	C36	103.3(3)
C19A	C18A	C17A	120.0	C28	B1	C44	112.3(3)
C14A	C19A	C20A	119.3(4)	C44	B1	C36	114.0(3)
C18A	C19A	C14A	120.0	C52	B1	C28	114.0(3)
C18A	C19A	C20A	120.5(3)	C52	B1	C36	109.6(3)
C29	C28	B1	122.1(3)	C52	B1	C44	104.0(3)
C33	C28	C29	115.8(3)	C1S[2]	Cl1	C1S	61.0(9)
C33	C28	B1	121.8(3)	Cl1[2]	C1S	Cl1	119.0(9)
C30	C29	C28	121.9(3)				

Table 6: Torsion Angles for 7.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co1	N2	C4	C2A	-179.1(5)	C31	C30	C34	F15	-175.3(4)
Co1	N2	C4	C3	1.9(6)	C31	C30	C34	F27	-57.4(5)
Co1	N2	C7	C8	-76.4(13)	C31	C30	C34	F9A	-22.8(7)
Co1	N2	C7	C12	107.9(10)	C31	C30	C34	F15A	92.3(6)
Co1	N2	C7A	C8A	-87.3(10)	C31	C30	C34	F27A	-150.3(6)
Co1	N2	C7A	C12A	83.5(14)	C31	C32	C33	C28	2.8(6)
Co1	N3	C5	C3	-2.1(6)	C31	C32	C35	F2	118.6(4)
Co1	N3	C5	C6	179.9(4)	C31	C32	C35	F37	-124.3(4)
Co1	N3	C21	C22	-89.4(4)	C31	C32	C35	F49	-1.2(6)
Co1	N3	C21	C26	87.1(4)	C33	C28	C29	C30	0.2(5)
Co1	N1B	C14	C19	92.8(18)	C33	C28	B1	C36	93.6(3)
Co1	N1B	C14	C15	-80.3(18)	C33	C28	B1	C44	-29.6(4)
Co1	N1A	C14A	C15A	-95.2(6)	C33	C28	B1	C52	-147.6(3)
Co1	N1A	C14A	C19A	81.4(7)	C33	C32	C35	F2	-63.0(5)
N2	C7	C8	C9	-175.5(15)	C33	C32	C35	F37	54.1(5)
N2	C7	C12	C11	175.9(14)	C33	C32	C35	F49	177.2(4)
N2	C7	C12	C13	-15(2)	C34	C30	C31	C32	-179.0(3)
N2	C7A	C8A	C9A	171.1(15)	C35	C32	C33	C28	-175.6(3)
N2	C7A	C12A	C11A	-170.3(16)	C36	C37	C38	C39	-1.6(5)
N2	C7A	C12A	C13A	5(2)	C36	C37	C38	C42	-179.9(3)
N3	C21	C22	C23	176.6(4)	C37	C36	C41	C40	2.0(5)
N3	C21	C26	C25	-177.6(4)	C37	C36	B1	C28	79.6(3)
N3	C21	C26	C27	3.5(7)	C37	C36	B1	C44	-158.2(3)
C1	C2	C3	C4	116.5(5)	C37	C36	B1	C52	-42.2(4)
C1	C2	C3	C5	-119.3(5)	C37	C38	C39	C40	1.8(5)

C1	C2	N1B	Co1	-173.3(6)	C37	C38	C42	F3	-25.0(5)
C1	C2	N1B	C14	-13(3)	C37	C38	C42	F7	96.3(4)
C1	C2	N1A	Co1	178.9(6)	C37	C38	C42	F32	-145.2(4)
C1	C2	N1A	C14A	10.9(12)	C38	C39	C40	C41	-0.1(5)
C2	C3	C4	N2	62.1(5)	C38	C39	C40	C43	179.0(3)
C2	C3	C4	C2A	-117.0(5)	C39	C38	C42	F3	156.7(4)
C2	C3	C5	N3	-61.6(6)	C39	C38	C42	F7	-82.0(5)
C2	C3	C5	C6	116.5(5)	C39	C38	C42	F32	36.5(5)
C2	N1B	C14	C19	-65(3)	C39	C40	C41	C36	-1.9(5)
C2	N1B	C14	C15	122(2)	C39	C40	C43	F12	-111.3(6)
C2	N1A	C14A	C15A	72.6(10)	C39	C40	C43	F30	14.2(7)
C2	N1A	C14A	C19A	-110.8(8)	C39	C40	C43	F40	129.1(5)
C3	C2	N1B	Co1	24.2(16)	C39	C40	C43	F12A	-59.1(12)
C3	C2	N1B	C14	-175.3(15)	C39	C40	C43	F30A	57.4(12)
C3	C2	N1A	Co1	-9.6(10)	C39	C40	C43	F40A	-179.3(11)
C3	C2	N1A	C14A	-177.6(6)	C41	C36	C37	C38	-0.3(5)
C4	N2	C7	C8	99.4(11)	C41	C36	B1	C28	-95.8(4)
C4	N2	C7	C12	-76.2(11)	C41	C36	B1	C44	26.4(4)
C4	N2	C7A	C8A	102.4(8)	C41	C36	B1	C52	142.4(3)
C4	N2	C7A	C12A	-86.9(12)	C41	C40	C43	F12	67.8(6)
C4	C3	C5	N3	61.5(6)	C41	C40	C43	F30	-166.7(6)
C4	C3	C5	C6	-120.4(5)	C41	C40	C43	F40	-51.8(6)
C5	N3	C21	C22	89.2(5)	C41	C40	C43	F12A	120.0(11)
C5	N3	C21	C26	-94.3(5)	C41	C40	C43	F30A	-123.4(11)
C5	C3	C4	N2	-61.5(5)	C41	C40	C43	F40A	-0.2(12)
C5	C3	C4	C2A	119.4(5)	C42	C38	C39	C40	-179.9(3)
C21	N3	C5	C3	179.2(4)	C43	C40	C41	C36	179.0(3)
C21	N3	C5	C6	1.2(8)	C44	C45	C46	C47	1.2(6)
C21	C22	C23	C24	1.2(7)	C44	C45	C46	C50	-177.9(4)
C22	C21	C26	C25	-1.3(7)	C45	C44	C49	C48	1.5(5)
C22	C21	C26	C27	179.9(6)	C45	C44	B1	C28	-35.3(4)
C22	C23	C24	C25	-1.5(8)	C45	C44	B1	C36	-152.3(3)
C23	C24	C25	C26	0.4(8)	C45	C44	B1	C52	88.4(4)
C24	C25	C26	C21	1.0(8)	C45	C46	C47	C48	1.0(6)
C24	C25	C26	C27	179.9(6)	C45	C46	C50	F13	51.9(6)
C26	C21	C22	C23	0.2(7)	C45	C46	C50	F25	-65.5(5)
N1B	C2	C3	C4	-80.4(13)	C45	C46	C50	F53	173.2(4)
N1B	C2	C3	C5	43.8(13)	C46	C47	C48	C49	-1.9(6)
N1B	C14	C15	C16	172.8(19)	C46	C47	C48	C51	-178.3(4)
C7	N2	C4	C2A	5.1(13)	C47	C46	C50	F13	-127.2(4)
C7	N2	C4	C3	-173.9(11)	C47	C46	C50	F25	115.5(5)
C7	C8	C9	C10	0.0	C47	C46	C50	F53	-5.9(7)
C8	C7	C12	C11	0.0	C47	C48	C49	C44	0.6(6)
C8	C7	C12	C13	170(2)	C47	C48	C51	F17	-9.6(6)
C8	C9	C10	C11	0.0	C47	C48	C51	F20	-132.2(4)
C9	C10	C11	C12	0.0	C47	C48	C51	F43	111.9(4)
C10	C11	C12	C7	0.0	C49	C44	C45	C46	-2.4(5)
C10	C11	C12	C13	-171.3(19)	C49	C44	B1	C28	151.3(3)
C12	C7	C8	C9	0.0	C49	C44	B1	C36	34.2(4)
C18	C19	C14	N1B	-173.2(18)	C49	C44	B1	C52	-85.0(4)
C18	C19	C14	C15	0.0	C49	C48	C51	F17	173.9(4)

C19	C18	C17	C16	0.0	C49	C48	C51	F20	51.3(5)
C19	C14	C15	C16	0.0	C49	C48	C51	F43	-64.6(5)
C14	C15	C16	C17	0.0	C50	C46	C47	C48	-179.9(4)
C15	C16	C17	C18	0.0	C51	C48	C49	C44	177.0(4)
C17	C18	C19	C14	0.0	C52	C53	C54	C55	-0.5(5)
C17	C18	C19	C20	-142.3(18)	C52	C53	C54	C58	-179.3(3)
C20	C19	C14	N1B	-31(2)	C53	C52	C57	C56	-1.0(5)
C20	C19	C14	C15	142.0(17)	C53	C52	B1	C28	33.4(4)
N1A	C2	C3	C4	-56.1(7)	C53	C52	B1	C36	148.6(3)
N1A	C2	C3	C5	68.1(8)	C53	C52	B1	C44	-89.2(4)
N1A	C14A	C15A	C16A	176.6(7)	C53	C54	C55	C56	0.4(6)
N1A	C14A	C19A	C18A	-176.6(7)	C53	C54	C58	F6	75.6(5)
N1A	C14A	C19A	C20A	-2.3(8)	C53	C54	C58	F22	-43.2(5)
C7A	N2	C4	C2A	-8.2(10)	C53	C54	C58	F42	-163.9(3)
C7A	N2	C4	C3	172.8(8)	C54	C55	C56	C57	-0.6(6)
C7A	C8A	C9A	C10A	0.0	C54	C55	C56	C59	-179.3(4)
C8A	C7A	C12A	C11A	0.0	C55	C54	C58	F6	-103.3(4)
C8A	C7A	C12A	C13A	176(2)	C55	C54	C58	F22	137.9(4)
C8A	C9A	C10A	C11A	0.0	C55	C54	C58	F42	17.2(5)
C9A	C10A	C11A	C12A	0.0	C55	C56	C57	C52	1.0(6)
C10A	C11A	C12A	C7A	0.0	C55	C56	C59	F24	-21.3(8)
C10A	C11A	C12A	C13A	-176(2)	C55	C56	C59	F34	-133.5(5)
C12A	C7A	C8A	C9A	0.0	C55	C56	C59	F48	111.4(7)
C14A	C15A	C16A	C17A	0.0	C55	C56	C59	F24A	38.6(10)
C15A	C14A	C19A	C18A	0.0	C55	C56	C59	F34A	-76.8(13)
C15A	C14A	C19A	C20A	174.3(6)	C55	C56	C59	F48A	148.9(11)
C15A	C16A	C17A	C18A	0.0	C57	C52	C53	C54	0.8(5)
C16A	C17A	C18A	C19A	0.0	C57	C52	B1	C28	-153.6(3)
C17A	C18A	C19A	C14A	0.0	C57	C52	B1	C36	-38.4(4)
C17A	C18A	C19A	C20A	-174.3(6)	C57	C52	B1	C44	83.8(4)
C19A	C14A	C15A	C16A	0.0	C57	C56	C59	F24	160.0(6)
C28	C29	C30	C31	1.9(5)	C57	C56	C59	F34	47.8(7)
C28	C29	C30	C34	179.1(3)	C57	C56	C59	F48	-67.3(8)
C29	C28	C33	C32	-2.6(5)	C57	C56	C59	F24A	-140.1(9)
C29	C28	B1	C36	-80.7(4)	C57	C56	C59	F34A	104.5(13)
C29	C28	B1	C44	156.0(3)	C57	C56	C59	F48A	-29.8(13)
C29	C28	B1	C52	38.1(4)	C58	C54	C55	C56	179.3(4)
C29	C30	C31	C32	-1.7(5)	C59	C56	C57	C52	179.7(4)
C29	C30	C34	F9	-113.4(5)	B1	C28	C29	C30	174.9(3)
C29	C30	C34	F15	7.4(6)	B1	C28	C33	C32	-177.2(3)
C29	C30	C34	F27	125.3(5)	B1	C36	C37	C38	-176.1(3)
C29	C30	C34	F9A	159.9(6)	B1	C36	C41	C40	177.5(3)
C29	C30	C34	F15A	-85.0(6)	B1	C44	C45	C46	-176.3(3)
C29	C30	C34	F27A	32.4(7)	B1	C44	C49	C48	175.3(3)
C30	C31	C32	C33	-0.5(5)	B1	C52	C53	C54	174.0(3)
C30	C31	C32	C35	177.8(4)	B1	C52	C57	C56	-174.6(3)
C31	C30	C34	F9	63.8(5)	C1S[1]	Cl1	C1S	Cl1[1]	0.002(3)

Table 7: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7.

Atom	*x*	*y*	*z*	U(eq)
H1A	7687	1677	7044	129
H1B	8282	1551	6211	129
H1C	8584	713	6981	129
H2AA	4081	1946	7759	137
H2AB	5268	1924	7921	137
H2AC	4800	1081	8381	137
H3	6760	490	7752	62
H6A	6714	-1193	8531	81
H6B	7867	-1221	8102	81
H6C	7269	-1951	8016	81
H22	4983	-1854	7348	63
H23	5140	-3421	7282	72
H24	6686	-4291	6689	77
H25	8029	-3625	6118	77
H27A	8584	-1703	6389	161
H27B	7964	-1286	5579	161
H27C	8829	-2303	5729	161
H8	3995	2691	5588	65
H9	2180	3633	5471	84
H10	814	3114	6288	90
H11	1263	1653	7222	92
H13A	3742	-89	7567	141
H13B	2683	358	8056	141
H13C	2585	-30	7310	141
H18	7867	2835	3740	46
H15	8652	-410	4945	56
H16	9466	93	3700	66
H17	9074	1715	3097	50
H20A	6088	2211	5360	89
H20B	6336	3115	4781	89
H20C	5940	2417	4429	89
H8A	3693	2766	5889	83
H9A	1842	3534	5682	91
H10A	545	2770	6297	98
H11A	1100	1239	7118	86
H13D	3886	-192	7532	141
H13E	2772	-13	8036	141
H13F	2874	-381	7245	141
H15A	8728	66	5273	95
H16A	9658	591	4089	115
H17A	8889	2080	3253	86
H18A	7190	3043	3600	70
H20D	5486	2412	5354	89
H20E	5748	3357	4877	89
H20F	5269	2792	4430	89
H29	4068	6138	1819	30
H31	4062	5684	4240	39
H33	1230	6528	3110	32
H37	3310	7651	673	32

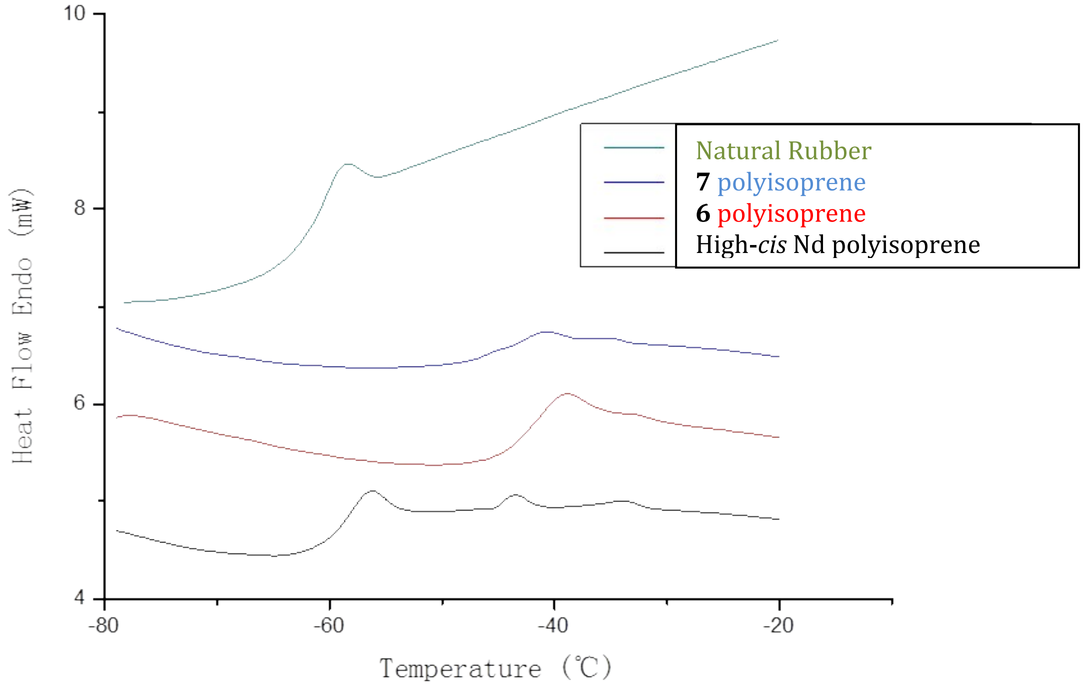
H39	1848	10444	561	37
H41	291	8491	1641	30
H45	1077	5296	2489	32
H47	-2046	5951	1887	39
H49	-175	7639	785	32
H53	3254	4887	1442	31
H55	3582	4947	-929	46
H57	1822	7280	-155	37
H1SA	408	5876	37	259
H1SB	919	5293	-617	259

Table 8: Atomic Occupancy for 7.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Br1A	0.656(11)	N1B	0.237(11)	C7	0.51(4)
C8	0.51(4)	H8	0.51(4)	C9	0.51(4)
H9	0.51(4)	C10	0.51(4)	H10	0.51(4)
C11	0.51(4)	H11	0.51(4)	C12	0.51(4)
C13	0.51(4)	H13A	0.51(4)	H13B	0.51(4)
H13C	0.51(4)	C18	0.237(11)	H18	0.237(11)
C19	0.237(11)	C14	0.237(11)	C15	0.237(11)
H15	0.237(11)	C16	0.237(11)	H16	0.237(11)
C17	0.237(11)	H17	0.237(11)	C20	0.237(11)
H20A	0.237(11)	H20B	0.237(11)	H20C	0.237(11)
Br1C	0.064(2)	Br1B	0.245(11)	N1A	0.763(11)
C7A	0.49(4)	C8A	0.49(4)	H8A	0.49(4)
C9A	0.49(4)	H9A	0.49(4)	C10A	0.49(4)
H10A	0.49(4)	C11A	0.49(4)	H11A	0.49(4)
C12A	0.49(4)	C13A	0.49(4)	H13D	0.49(4)
H13E	0.49(4)	H13F	0.49(4)	C14A	0.763(11)
C15A	0.763(11)	H15A	0.763(11)	C16A	0.763(11)
H16A	0.763(11)	C17A	0.763(11)	H17A	0.763(11)
C18A	0.763(11)	H18A	0.763(11)	C19A	0.763(11)
C20A	0.763(11)	H20D	0.763(11)	H20E	0.763(11)
H20F	0.763(11)	F9	0.639(6)	F12	0.743(10)
F15	0.639(6)	F24	0.773(9)	F27	0.639(6)
F30	0.743(10)	F34	0.773(9)	F40	0.743(10)
F48	0.773(9)	F9A	0.361(6)	F12A	0.257(10)
F15A	0.361(6)	F24A	0.227(9)	F27A	0.361(6)
F30A	0.257(10)	F34A	0.227(9)	F40A	0.257(10)
F48A	0.227(9)				

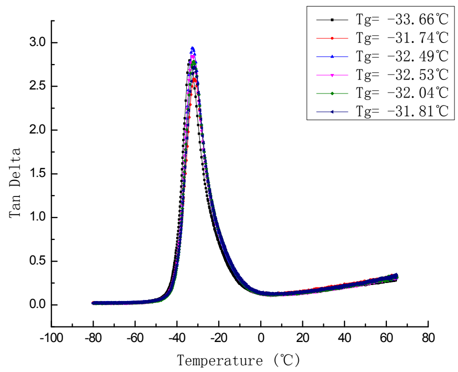
8.5 Appendix E:
Thermal Analysis Data

Differential Scanning Calorimetry Data

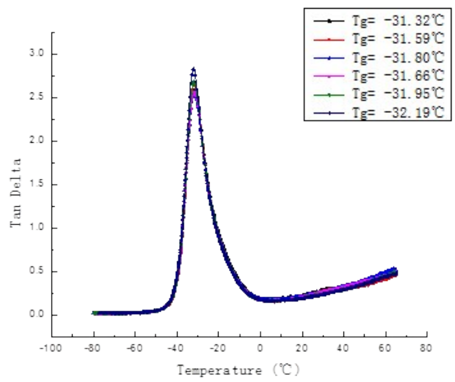


Dynamic Mechanical Thermal Analysis Data (DMTA)

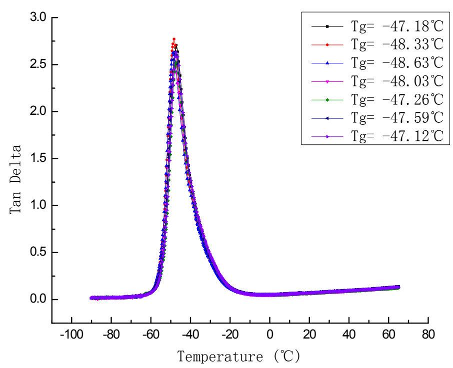
For Polyisoprene from catalyst **6** (24 h, 150 equivalents DEAC, 35 °C), Tan δ



For Polyisoprene from catalyst **7**(24 h, 150 equivalents DEAC, 35 °C), Tan δ



And for comparison, High-*Cis* Nd polyisoprene:



high-*cis*-Nd Polyisoprene

Note: DMTA T_g values are systematically higher by ca. 10 °C, but more precise, than DSC ones.