

Supporting Information

Unusual Coordination Mode for 1,3-Diphosphete Ligands Towards Cr-Cr Quintuple Bond Complex

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1. Experimental

All steps were performed under an atmosphere of dry Argon with standard schlenk techniques. All solvents were freshly collected from a Solvent Purification System by M. Braun and were degassed prior to use. All NMR spectra have been recorded using deuterated benzene, which was dried over Na/K alloy, refluxed for three hours and then distilled under inert atmosphere. $t\text{BuC}\equiv\text{P}$,^[1] $\text{MeC}\equiv\text{P}$,^[2] $\text{AdC}\equiv\text{P}$ ^[3] and **1**^[4] have been synthesised according to literature procedure.

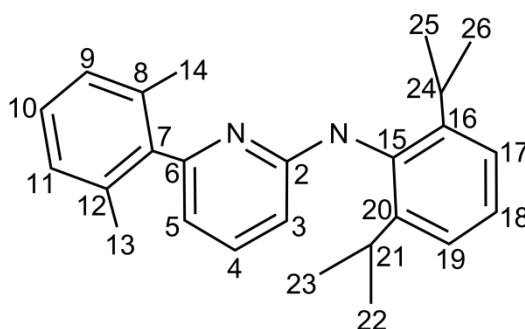


Fig. S1 Ligand numbering scheme.

1.1. Synthesis of 2:

To a solution of $1.22 \cdot 10^{-4}$ mol (100 mg) **1** in 10 ml hexane is added $2.5 \cdot 10^{-4}$ mol $t\text{BuC}\equiv\text{P}$. The colour of the solution instantly changes from dark violet to crimson red. After stirring overnight, the solution is filtered over silica and the solvent is removed under reduced pressure. The residue is taken up in 2 ml fresh hexane or pentane and stored at +5 °C. After some time, red crystals of **2** are formed on the solvent front while the rest of compound precipitated as a red solid. Yield (crystals + precipitate): 53 mg (43 %)

¹ H-NMR	δ [ppm] = 0.69 (d, 3H, $J = 6.6$ Hz, $\text{H}^{22,23/25,26}$), 0.95 (pt, 6H, $J = 7.4$ Hz, $\text{H}^{22,23/25,26}$), 1.05 (s, 6H, $\text{H}^{13,14}$), 1.06 (s, 18H, $(t\text{BuC})_2\text{P}_2$), 1.12 (d, 6H, $J = 6.6$ Hz, $\text{H}^{22,23/25,26}$), 1.28 (d, 6H, $J = 6.6$ Hz, $\text{H}^{22,23/25,26}$), 1.38 (s, 6H, $\text{H}^{13,14}$), 3.5 (dsept, 2H, $J = 6.6$ Hz, $\text{H}^{21/24}$), 4.12 (sept, 2H, $J = 6.6$ Hz, $\text{H}^{21,24}$), 5.54 (d, 2H, $J = 6.6$ Hz, H^3), 5.6 (d, 2H, $J = 7.5$ Hz, $\text{H}^{9,11/17,19}$), 6.24 (d, 2H, $J = 7.4$ Hz, H^5), 6.37 (d, 2H, $J = 7.8$ Hz, H^4), 6.70 (q, 4H, $J = 7.4$ Hz, $\text{H}^{9,11/17,19}$), 7.02 (m, 2H, $\text{H}^{9,11/17,19}$), 7.19 (m, 2H, $\text{H}^{10/18}$), 7.26 (m, 2H, $\text{H}^{10/18}$)
³¹ P-NMR	δ [ppm] = 106.7 (s)
³¹ P{ ¹ H}-NMR	δ [ppm] = 106.7 (s)
Elemental analysis	calculated for $\text{C}_{60}\text{H}_{76}\text{Cr}_2\text{N}_4\text{P}_2$ (1018.4 g/mol): C 70.69, H 7.52, N 5.49; found: C 69.55, H 7.81, N 5.06.
FD MS (toluene)	m/z [%] = 1019 (100) [M^+]

1.2. Synthesis of 3:

To a solution of $1.22 \cdot 10^{-4}$ mol (100 mg) **1** in 10 ml THF is added $2.5 \cdot 10^{-4}$ mol $\text{MeC}\equiv\text{P}$. The colour of the solution instantly changes from dark violet to crimson red. After stirring overnight, the solution is

filtered over silica and the solvent is removed under reduced pressure. The residue is taken up in 2 ml fresh hexane and stored at +5 °C.

^{31}P -NMR	δ [ppm] = 114.4 (s)
$^{31}\text{P}\{^1\text{H}\}$ -NMR	δ [ppm] = 114.4 (s)
FD MS (toluene)	m/z [%] = 934.4 (10) [M^+]; 876.4 (100) [M^+ -MeCP] in a scaled version from 800-1200 Da; m/z [%] = 876.4 (20) [M^+ -MeCP], 358.4 (100) [L]

1.3. Synthesis of 4:

To a solution of $4.88 \cdot 10^{-5}$ mol (40 mg) **1** in 10 ml hexane is added $9.76 \cdot 10^{-5}$ mol (17.4 mg) AdC \equiv P in 10 ml hexane. The colour of the solution instantly changes from dark violet to crimson red. After stirring overnight, the solution is filtered over silica and the solvent is removed under reduced pressure. The residue is taken up in 15 ml fresh pentane and stored at +5 °C. Fractionised crystallisation leads to a total yield of 32 mg (67%)

^1H -NMR	δ [ppm] = 0.75 (d, 6H, $J = 6.9$ Hz, $\text{H}^{22,23/25,26}$), 0.91 (d, 6H, $J = 7.4$ Hz, $\text{H}^{22,23/25,26}$), 1.07 (s, 6H, $\text{H}^{13,14}$), 1.12 (d, 6H, $J = 6.7$ Hz, $\text{H}^{22,23/25,26}$), 1.37 (d, 6H, $J = 6.9$ Hz, $\text{H}^{22,23/25,26}$), 1.70 (t, 2.6 Hz, 3H, AdCP), 1.38 (s, 6H, $\text{H}^{13,14}$), 1.94 (br, 6H, AdCP), 2.5 (br, 6H, AdCP), 3.45 (sept, 2H, $J = 6.7$ Hz, $\text{H}^{21/24}$), 3.98 (sept, 2H, $J = 6.7$ Hz, $\text{H}^{21,24}$), 5.54 (d, 2H, $J = 6.7$ Hz, H^3), 5.66 (d, 2H, $J = 7.2$ Hz, $\text{H}^{9,11/17,19}$), 6.24 (m, 2H, H^5), 6.37 (m, 2H, H^4), 6.70 (m, 4H, $\text{H}^{9,11/17,19}$), 7.02 (m, 2H, $\text{H}^{9,11/17,19}$), 7.19 (m, 2H, $\text{H}^{10/18}$), 7.26 (m, 2H, $\text{H}^{10/18}$)
^{31}P -NMR	δ [ppm] = 460.6 (s)
$^{31}\text{P}\{^1\text{H}\}$ -NMR	δ [ppm] = 460.6 (s)
FD MS (toluene)	m/z [%] = 996.4 (100) [M^+], 818.3 (20) [1^+], 714.4 (35) [L_2^+]

2. NMR Spectra

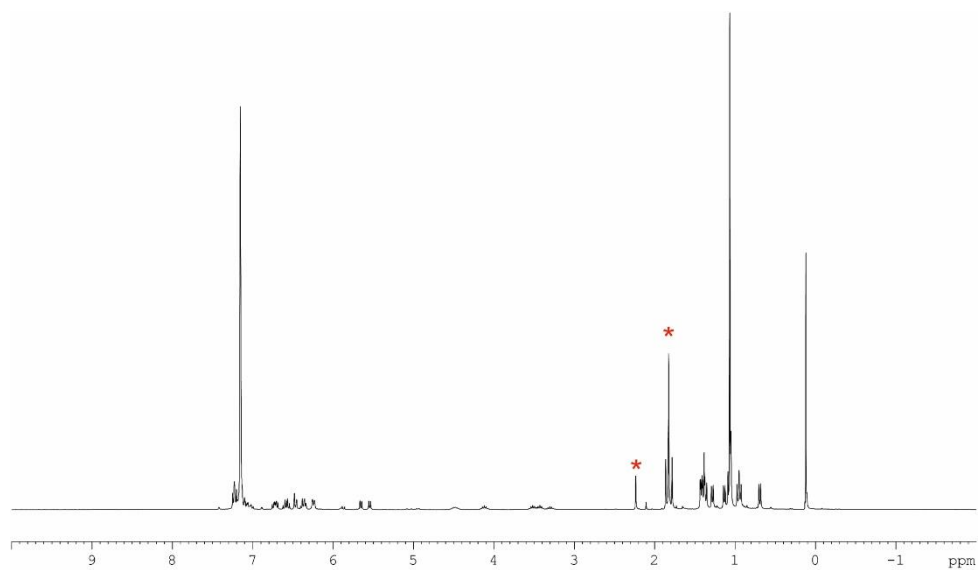


Fig. S2 ^1H NMR spectrum of **2** in C_6D_6 at r.t. * unidentified impurity.

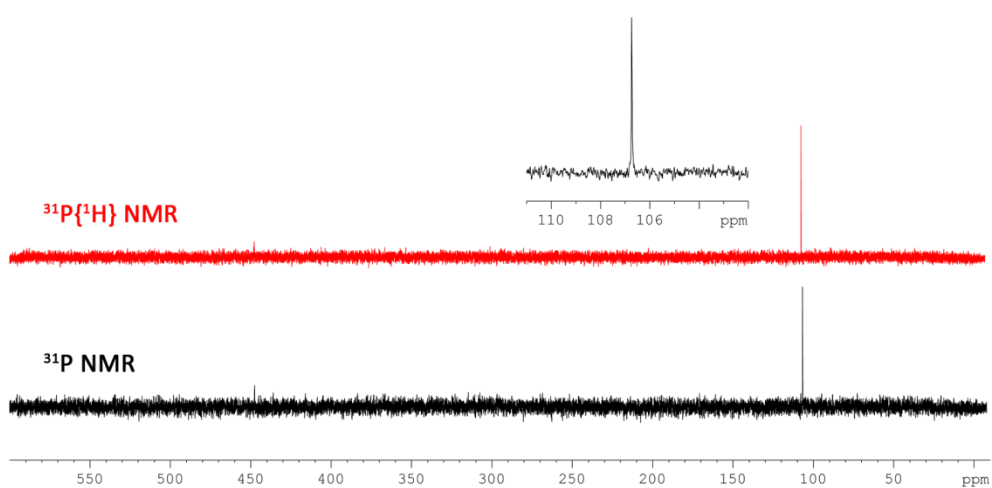


Fig. S3 ^{31}P (black) and $^{31}\text{P}\{^1\text{H}\}$ (red) NMR spectra of **2** in C_6D_6 at r.t. Main signal is the [2+2] cycloaddition product at $\delta = 106$ ppm, with minor impurities from the side-on product (3%) at $\delta = 450$ ppm.

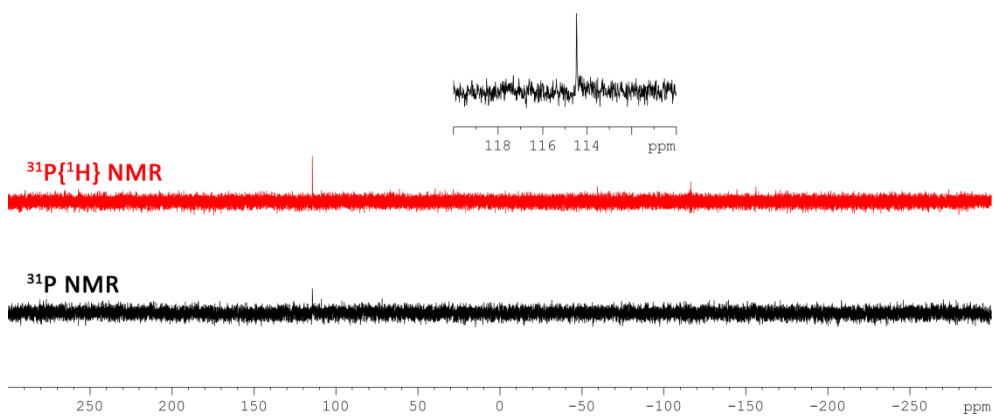


Fig. S4 ^{31}P (black) and $^{31}\text{P}\{^1\text{H}\}$ (red) NMR spectra of **3** in C_6D_6 at r.t.

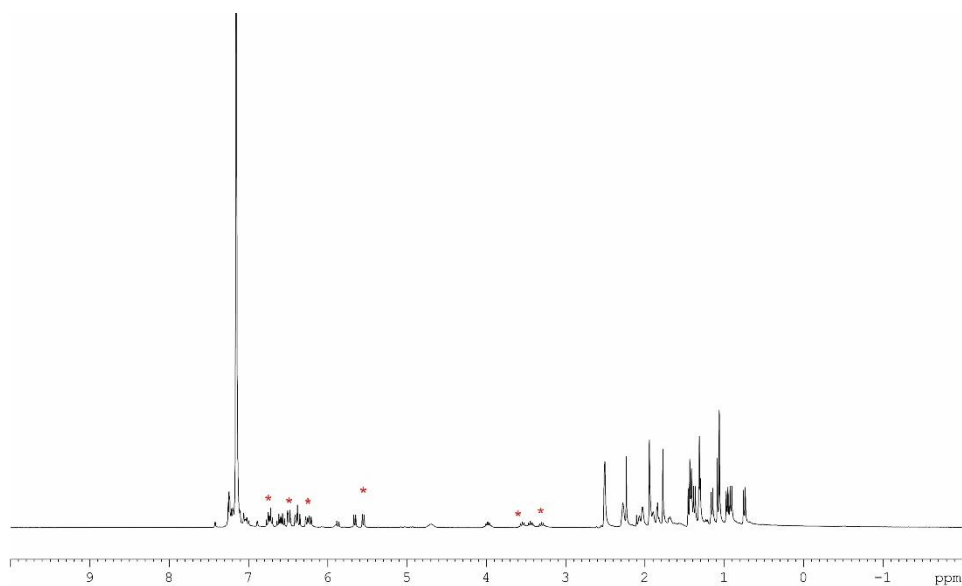


Fig. S5 ^1H NMR spectra of **4** in C_6D_6 at r.t. * signals arising from nonequivalent protons in the organic ligands.

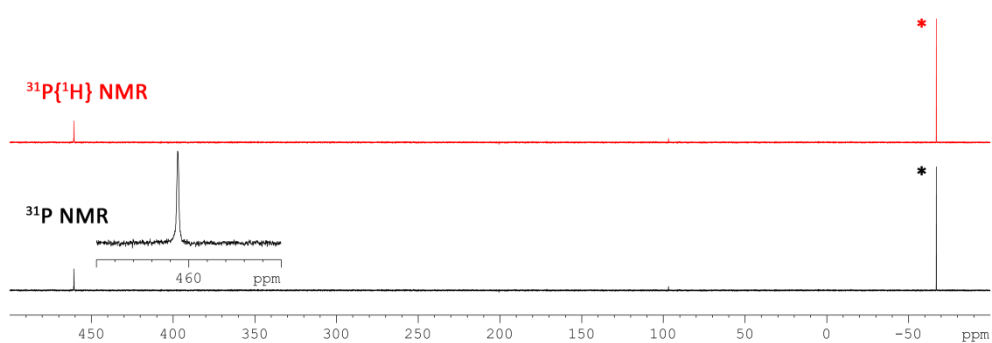


Fig. S6 ^{31}P (black) and $^{31}\text{P}\{^1\text{H}\}$ (red) NMR spectra of reaction mixtures of **4** in C_6D_6 at r.t. Signal marked with an asterisk is residual $\text{AdC}\equiv\text{P}$. Main product of the reaction is the side-on complex **4** at $\delta = 460$ ppm with minor impurities from the cycloaddition product at $\delta = 100$ ppm (5%).

3. Crystallographic Data

Using Olex2,^[5] all structures were solved with the ShelXT structure solution program,^[6] using the Direct Methods solution method. The model was refined with version 2014/6 of ShelXL using Least Squares minimisation.^[7] Experimental and crystal data created by ReportPlus in Olex2.

3.1. Compound 2

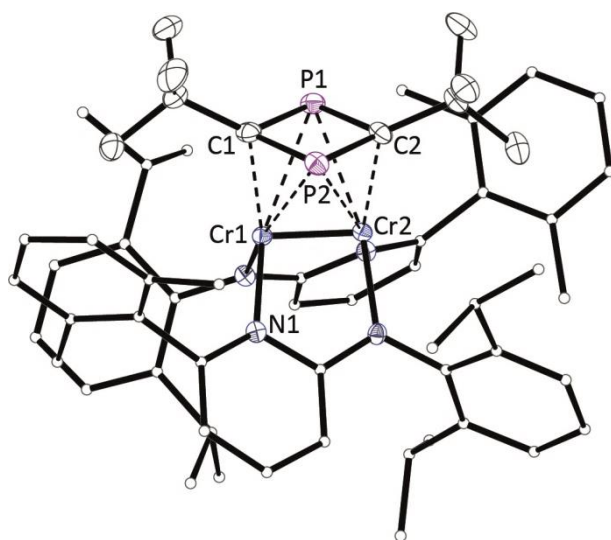


Fig. S7 Molecular structure of **2** in the solid state. Hydrogen atoms are omitted, carbon atoms of the ligand are shown in a ball-and-stick representation for clarity. Thermal ellipsoids are shown at 50% probability level. Selected bond lengths [Å] and angles [°]: Cr1-Cr2 1.8694(3), P1-P2 2.6708(6), P1-C1 1.8076(17), P1-C6 1.8195(16), P2-C1 1.8184(16), P2-C6 1.8051(17), C1-P1-C6 85.03(8), C6-P2-C1 85.13(8), P1-C1-P2 94.88(8), P2-C6-P1 94.93(8).

Single red block-shaped crystals of **2** were obtained by recrystallisation from hexane. A suitable crystal (0.21×0.12×0.09) was selected and mounted on a mylar loop on a SuperNova, Single source at offset, Atlas diffractometer. The crystal was kept at $T = 123.01(10)$ K during data collection.

3.2. Compound 4

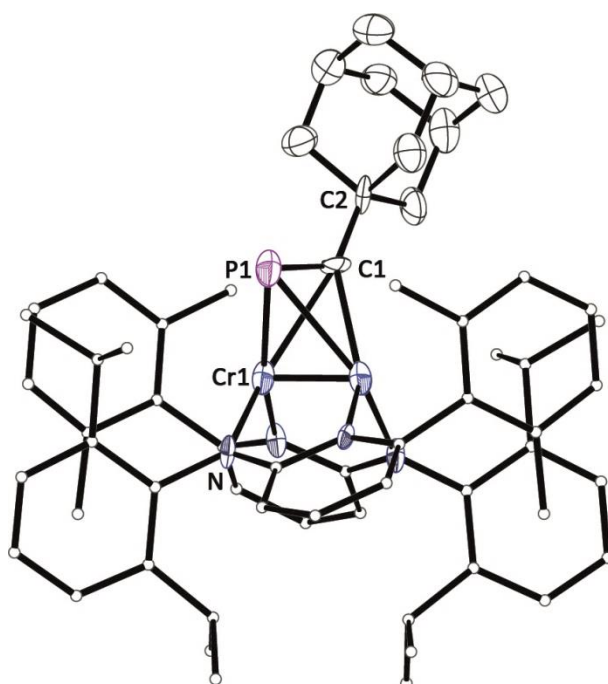


Fig. S8 Molecular structure of **4** in the solid state. Hydrogen atoms are omitted, carbon atoms of the ligand are shown in a ball-and-stick representation for clarity. Thermal ellipsoids are shown at 50% probability level. Selected bond lengths [Å] and angles [°]: Cr1-Cr1' 1.8054(13), Cr1-P1 2.674(3), Cr1-C1 2.117(8), Cr1-C1' 2.388(9), C1-P1 1.731(16), Cr1'-Cr1-C1 74.5(3), Cr1'-Cr1-P1 58.42(6), C2-C1-P1 121.9(7).

Single clear red plate-shaped crystals of **4** were obtained by recrystallisation from hexane. A suitable crystal (0.10×0.07×0.02) was selected and mounted on a mitogen holder on a GV50, TitanS2 diffractometer. The crystal was kept at $T = 123.1(3)$ K during data collection.

CCDC reference numbers 2247228 (**2**) and, 2247229 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for compounds **2** and **4**.

Compound	2	4
Empirical formula	C ₆₆ H ₉₀ Cr ₂ N ₄ P ₂	C ₆₁ H ₇₃ Cr ₂ N ₄ P
Formula weight	1105.35	997.20
Temperature/K	123.01	123.1
Crystal system	triclinic	monoclinic
Space group	P-1	P2/c
a/Å	12.8677(2)	10.2784(6)
b/Å	13.10453(19)	22.2038(13)
c/Å	18.2132(3)	12.5344(5)
α/°	99.9375(13)	90
β/°	90.7104(13)	105.268(5)
γ/°	92.7071(12)	90
Volume/Å ³	3021.09(8)	2759.6(3)
Z	2	2
ρ _{calc} /cm ³	1.215	1.200
μ/mm ⁻¹	3.776	3.820
F(000)	1184.0	1060.0
Crystal size/mm ³	0.2143 × 0.1185 × 0.0946	0.1008 × 0.0728 × 0.0211
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/°	6.856 to 147.522	8.326 to 148.754
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 15, -20 ≤ l ≤ 22	-12 ≤ h ≤ 7, -26 ≤ k ≤ 18, -14 ≤ l ≤ 15
Reflections collected	43882	9570
Independent reflections	11915 [R _{int} = 0.0237, R _{sigma} = 0.0205]	5342 [R _{int} = 0.0423, R _{sigma} = 0.0596]
Data/restraints/parameters	11915/0/687	5342/0/367
Goodness-of-fit on F ²	1.046	1.067
Final R indexes [I > 2σ(I)]	R ₁ = 0.0313, wR ₂ = 0.0832	R ₁ = 0.0835, wR ₂ = 0.2358
Final R indexes [all data]	R ₁ = 0.0360, wR ₂ = 0.0874	R ₁ = 0.1074, wR ₂ = 0.2465
Largest diff. peak/hole / e Å ⁻³	0.48/-0.35	1.36/-0.76

4. Computational Data

The DFT calculations have been performed with the TURBOMOLE program package^{[8][9]} at the RI^[10]-B3LYP^[11]/def2-TZVP^[12] level of theory. To speed up the geometry optimization the Multipole Accelerated Resolution-of-the-Identity (MARI-J)^[13] approximation has been used. The final energy of the molecules was determined by single point calculations without using the RI formalism. For the calculation of the reaction energies the SCF energies were used without corrections.

Table S2. Calculated reaction energies (kJ·mol⁻¹) of different transformations at the B3LYP/def2-TZVP level of theory.

Transformation	Reaction Energy (kJ·mol ⁻¹)
2 MeCP = 1,3-(MeCP) ₂	-6.56
2 MeCP = 1,2-(MeCP) ₂	-54.91
2 tBuCP = 1,3-(tBuCP) ₂	-1.42
2 tBuCP = 1,2-(tBuCP) ₂	0.28
2 AdCP = 1,3-(AdCP) ₂	0.16
2 AdCP = 1,2-(AdCP) ₂	5.28
L ₂ Cr ₂ + 2 MeCP = L ₂ Cr ₂ {1,3-(MeCP) ₂ }	-208.09
L ₂ Cr ₂ + 2 MeCP = L ₂ Cr ₂ {1,2-(MeCP) ₂ }	-228.86
L ₂ Cr ₂ + MeCP = L ₂ Cr ₂ (MeCP)	-81.63
L ₂ Cr ₂ (MeCP) + MeCP = L ₂ Cr ₂ {1,3-(MeCP) ₂ }	-126.45
L ₂ Cr ₂ (MeCP) + MeCP = L ₂ Cr ₂ {1,2-(MeCP) ₂ }	-147.23
L ₂ Cr ₂ + 2 tBuCP = L ₂ Cr ₂ {1,3-(tBuCP) ₂ }	-76.35
L ₂ Cr ₂ + 2 tBuCP = L ₂ Cr ₂ {1,2-(tBuCP) ₂ }	-43.39
L ₂ Cr ₂ + tBuCP = L ₂ Cr ₂ (tBuCP)	-39.69
L ₂ Cr ₂ + 2 AdCP = L ₂ Cr ₂ {1,3-(AdCP) ₂ }	-47.08
L ₂ Cr ₂ + AdCP = L ₂ Cr ₂ (AdCP)	-33.07
L ₂ Cr ₂ (AdCP) + AdCP = L ₂ Cr ₂ {1,3-(AdCP) ₂ }	-14.01
L ₂ Cr ₂ (AdCP) + AdCP = L ₂ Cr ₂ {1,2-(AdCP) ₂ }	17.01

Table S3. Total energy (a.u.) of different compounds at the B3LYP/def2-TZVP level of theory.

Compound	Total Energy (a.u.)
tBuCP	-537.16779293930
AdCP	-769.35557890561
MeCP	-419.27076490598
L ₂ Cr ₂	-4247.51261321978
L ₂ Cr ₂ {1,3-(tBuCP) ₂ }	-5321.87727905913
L ₂ Cr ₂ {1,2-(tBuCP) ₂ }	-5321.86472391464
L ₂ Cr ₂ (tBuCP)	-4784.69552154092
L ₂ Cr ₂ {1,3-(AdCP) ₂ }	-5786.24170203342
L ₂ Cr ₂ {1,2-(AdCP) ₂ }	-5786.22988912358
L ₂ Cr ₂ (AdCP)	-5016.88078836213
L ₂ Cr ₂ {1,3-(MeCP) ₂ }	-5086.13339933761
L ₂ Cr ₂ {1,2-(MeCP) ₂ }	-5086.14131258771

$L_2Cr_2(MeCP)$	-4666.81447104862
$1,3-(tBuCP)_2$	-1074.33612601004
$1,2-(tBuCP)_2$	-1074.33548041351
$1,3-(AdCP)_2$	-1538.71109812696
$1,2-(AdCP)_2$	-1538.70914737324
$1,3-(MeCP)_2$	-838.54402751377
$1,2-(MeCP)_2$	-838.56244330990

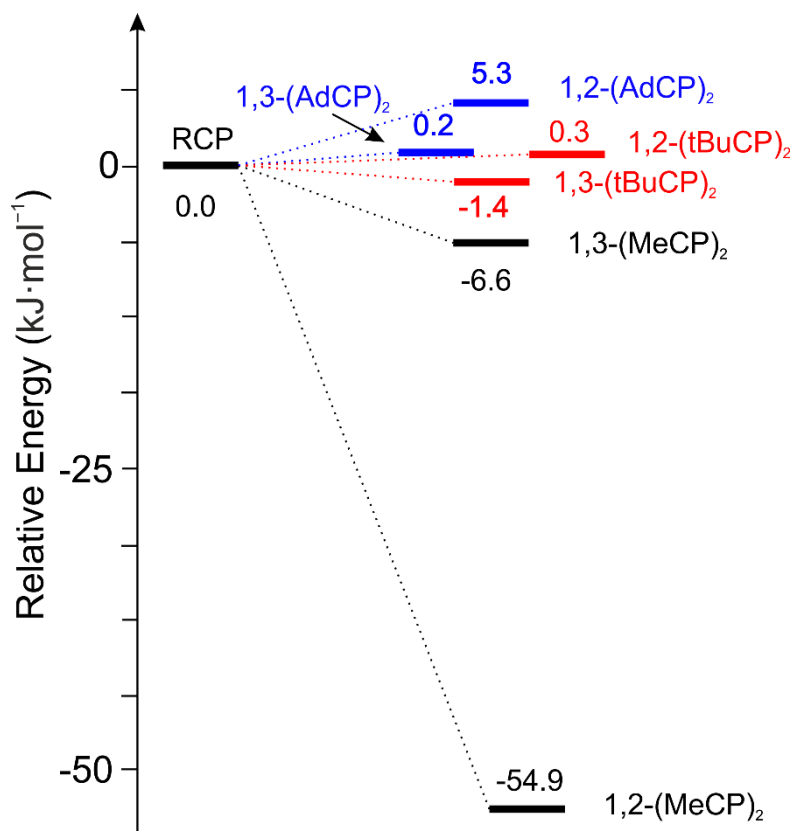


Fig. S9 Reaction energy diagram of the dimerization of different phosphalkynes.

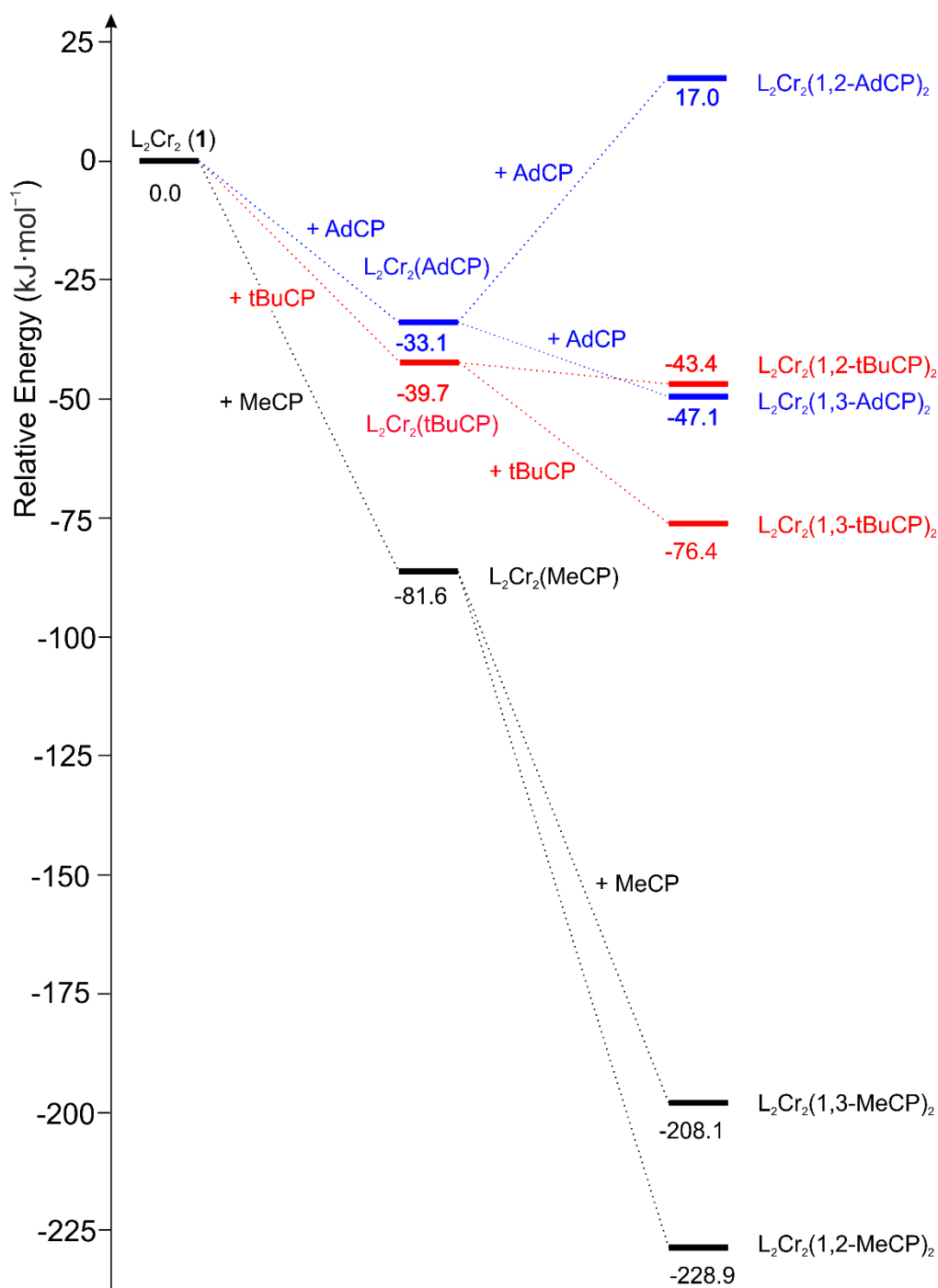
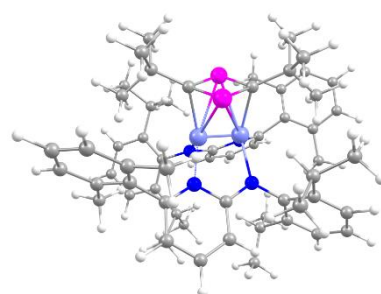


Fig. S10 Reaction energy diagram of the reaction of **1** with different phosphalkynes.

Table S4. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,3-(tBuCP)_2\}]$ (**2**) at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	0.7291518	-0.8175046	-0.0094435
Cr	0.6206466	0.9028264	0.0371586
P	2.8232989	0.0536988	-1.2743259
P	2.7513220	0.2952350	1.3915693
N	-0.3462659	-1.2095284	-1.7806221
N	-0.7573726	1.0670606	-1.4919444
N	-0.5684614	1.1527808	1.7609772
N	-0.6803024	-1.1565078	1.4608943
C	2.8354175	-1.0424021	0.1535293
C	3.5830668	-2.3859207	0.3231275
C	4.5751254	-2.5836699	-0.8400182
H	4.0645003	-2.6107638	-1.8024277

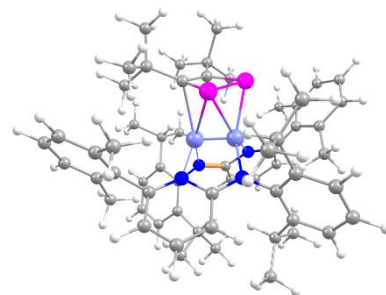


H	5.1078156	-3.5312732	-0.7204877
H	5.3120093	-1.7788917	-0.8678405
C	2.6407852	-3.5961716	0.3610090
H	1.8773263	-3.4889619	1.1297842
H	3.1975767	-4.5135793	0.5709407
H	2.1430734	-3.7272502	-0.5938669
C	4.4043550	-2.3573369	1.6282006
H	5.1426549	-1.5536409	1.6120159
H	4.9348975	-3.3048941	1.7543217
H	3.7725911	-2.2104596	2.5044450
C	2.6879909	1.3882852	-0.0374058
C	3.2706817	2.8143401	-0.1783315
C	4.1407634	2.8921845	-1.4493357
H	4.9718033	2.1861333	-1.4023996
H	4.5544639	3.8985944	-1.5556091
H	3.5675733	2.6712114	-2.3499623
C	2.1891907	3.8996370	-0.2559883
H	1.4784752	3.7037719	-1.0573116
H	2.6372553	4.8797100	-0.4414032
H	1.6384121	3.9631439	0.6763989
C	4.1835323	3.1284529	1.0235959
H	3.6351792	3.0898133	1.9645713
H	4.6005396	4.1345428	0.9237087
H	5.0118900	2.4200313	1.0827093
C	-1.0340433	-0.0729701	-2.1630525
C	-1.9668916	-0.1294786	-3.2349831
H	-2.4977184	0.7667265	-3.5080910
C	-2.1633638	-1.2923174	-3.9197979
H	-2.8838071	-1.3397433	-4.7274239
C	-1.3722834	-2.4005369	-3.6061061
H	-1.4226482	-3.3057972	-4.1942984
C	-0.4499090	-2.3212799	-2.5826678
C	0.5320345	-3.4638500	-2.5571861
C	1.6669744	-3.3419411	-3.3882910
C	2.5208360	-4.4350772	-3.5356197
H	3.3978266	-4.3341324	-4.1638811
C	2.2511046	-5.6444294	-2.9145929
H	2.9219264	-6.4852145	-3.0425436
C	1.1085073	-5.7736462	-2.1421444
H	0.8817664	-6.7206208	-1.6670427
C	0.2347085	-4.7013185	-1.9584194
C	1.9371555	-2.0970118	-4.1945163
H	1.2216373	-2.0107265	-5.0173270
H	2.9375485	-2.1309094	-4.6264162
H	1.8604183	-1.1880015	-3.6001545
C	-1.0108784	-4.9163120	-1.1462734
H	-1.1483553	-4.1423673	-0.3949980
H	-0.9732576	-5.8756208	-0.6306894
H	-1.9022574	-4.9134996	-1.7781716
C	-1.4228027	2.2640509	-1.9507472
C	-0.7513781	3.1432398	-2.8431422
C	-1.3848606	4.3283728	-3.2191810
H	-0.8759395	5.0134909	-3.8824445
C	-2.6605712	4.6452340	-2.7830868
H	-3.1286780	5.5730444	-3.0887301
C	-3.3394257	3.7478274	-1.9815055
H	-4.3526868	3.9747151	-1.6743338
C	-2.7554254	2.5510556	-1.5626236
C	0.5897017	2.8032868	-3.4918217
H	1.1578061	2.1927249	-2.7889041
C	1.4362189	4.0329551	-3.8547116
H	1.0121805	4.5755992	-4.7024165
H	2.4363762	3.7145684	-4.1533163
H	1.5395196	4.7318360	-3.0251847
C	0.3958241	1.9590345	-4.7668441
H	-0.1147771	1.0198402	-4.5682538
H	1.3662647	1.7264916	-5.2120418
H	-0.1896858	2.5125675	-5.5058550
C	-3.6382383	1.5828016	-0.7804680
H	-3.0429229	0.7013077	-0.5532341
C	-4.1436726	2.1580908	0.5501676
H	-3.3272569	2.3965350	1.2261981
H	-4.7881779	1.4327468	1.0503560
H	-4.7307598	3.0660462	0.3937589
C	-4.8486150	1.1370353	-1.6240270
H	-5.5096364	1.9798047	-1.8377757
H	-5.4338807	0.3934132	-1.0794738
H	-4.5508234	0.6963623	-2.5745672

C	-1.1245096	-0.0617283	2.1172016
C	-2.1007503	-0.1250595	3.1494638
H	-2.5264993	-1.0812370	3.4024152
C	-2.4683884	1.0021566	3.8233159
H	-3.2217213	0.9571390	4.6004606
C	-1.8091870	2.2011824	3.5400775
H	-1.9959616	3.0913718	4.1237048
C	-0.8428991	2.2405769	2.5555882
C	-0.0115149	3.4971037	2.5673725
C	-0.4363438	4.6888143	1.9528181
C	0.2881300	5.8616621	2.1687740
H	-0.0356056	6.7738193	1.6817968
C	1.4052385	5.8748542	2.9878448
H	1.9598346	6.7926904	3.1405691
C	1.7982762	4.7075655	3.6233477
H	2.6544543	4.7160329	4.2874287
C	1.0945244	3.5164985	3.4447241
C	-1.6641970	4.7473798	1.0892308
H	-1.6682869	3.9680737	0.3309587
H	-1.7299115	5.7076309	0.5782813
H	-2.5733115	4.6236672	1.6824375
C	1.4847363	2.3134933	4.2651465
H	0.7524915	2.1369944	5.0583158
H	2.4544647	2.4711342	4.7376375
H	1.5463532	1.4032815	3.6709131
C	-1.2097532	-2.4284003	1.8951162
C	-2.4780617	-2.8796419	1.4514783
C	-2.9249135	-4.1410037	1.8491566
H	-3.8877634	-4.4922666	1.4998120
C	-2.1740323	-4.9477434	2.6821918
H	-2.5348155	-5.9274406	2.9709205
C	-0.9679105	-4.4741938	3.1712156
H	-0.4058768	-5.0912312	3.8579716
C	-0.4724531	-3.2183106	2.8185239
C	-3.4416441	-2.0283190	0.6295951
H	-2.9515489	-1.0794627	0.4225580
C	-3.8173291	-2.6614361	-0.7176479
H	-2.9506648	-2.7978566	-1.3582700
H	-4.5248528	-2.0207103	-1.2472796
H	-4.2947624	-3.6345729	-0.5807899
C	-4.7312249	-1.7366916	1.4216912
H	-5.2892522	-2.6554972	1.6144421
H	-5.3827696	-1.0731252	0.8496711
H	-4.5292024	-1.2606980	2.3803513
C	0.7864179	-2.7145552	3.5231201
H	1.3020902	-2.0341322	2.8443184
C	1.7651902	-3.8293507	3.9232319
H	1.3779529	-4.4233443	4.7539636
H	2.7042225	-3.3887159	4.2620651
H	1.9896648	-4.5073718	3.1003716
C	0.4339959	-1.9071733	4.7880106
H	-0.1823674	-1.0390431	4.5674829
H	1.3478625	-1.5559784	5.2733703
H	-0.1072851	-2.5335311	5.5021969

Table S5. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,2-(tBuCP)_2\}]$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	0.6708634	-0.3817063	-0.3821380
Cr	0.2617009	1.1938429	0.0755019
P	2.2799290	1.2772372	-1.6029738
P	2.3938841	2.1740867	0.4104493
C	3.1157576	0.4998364	0.6787874
N	-0.6037541	-0.5910943	-2.0675761
N	-1.2145297	1.5165389	-1.2849663
N	-0.5772660	0.9299992	1.9598344
N	-0.5505619	-1.2637527	1.1628817
C	3.0835801	-0.0709794	-0.6078215
C	4.0137364	-1.1103221	-1.2899993
C	3.8859958	-0.9754793	-2.8152296
H	2.8537298	-1.0527910	-3.1340133
H	4.4448094	-1.7762419	-3.3036401
H	4.2820650	-0.0212251	-3.1651310
C	3.6680273	-2.5611700	-0.9134173
H	3.7126864	-2.7303371	0.1581231

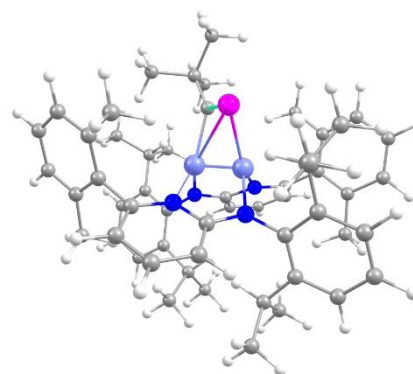


H	4.3675401	-3.2529490	-1.3904469
H	2.6667156	-2.8242497	-1.2592710
C	5.5011747	-0.8173175	-0.9925395
H	5.7418952	0.2217783	-1.2253265
H	6.1243680	-1.4524208	-1.6278590
H	5.7899897	-1.0081615	0.0356731
C	-1.4197214	0.5202374	-2.1744655
C	-2.4101304	0.6001003	-3.1904767
H	-3.0142307	1.4896337	-3.2563075
C	-2.5939283	-0.4391722	-4.0543144
H	-3.3709540	-0.3992036	-4.8079691
C	-1.7250749	-1.5303905	-3.9845778
H	-1.7786806	-2.3301679	-4.7093955
C	-0.7152381	-1.5545253	-3.0434455
C	0.3339158	-2.6040847	-3.3099486
C	1.2353799	-2.3310331	-4.3634145
C	2.1244748	-3.3233603	-4.7720561
H	2.8237570	-3.1051920	-5.5705630
C	2.1283870	-4.5737636	-4.1728776
H	2.8320689	-5.3313512	-4.4959333
C	1.2103614	-4.8529705	-3.1748019
H	1.1802887	-5.8392152	-2.7265280
C	0.2886795	-3.8923971	-2.7523085
C	1.2337321	-1.0129936	-5.1010218
H	0.4114419	-0.9700518	-5.8198627
H	2.1640867	-0.8859460	-5.6546819
H	1.1190481	-0.1586013	-4.4339640
C	-0.7955294	-4.3052643	-1.8015557
H	-1.1030083	-3.4988935	-1.1465590
H	-0.4805298	-5.1424789	-1.1802802
H	-1.6828424	-4.6250763	-2.3571320
C	-1.9482987	2.7434112	-1.5040489
C	-1.3518095	3.7882635	-2.2493631
C	-2.0412979	4.9921819	-2.4024447
H	-1.5794877	5.7945752	-2.9642242
C	-3.3026430	5.1794787	-1.8668362
H	-3.8203114	6.1223883	-1.9942707
C	-3.9039644	4.1354380	-1.1855104
H	-4.9031231	4.2707449	-0.7904201
C	-3.2612852	2.9117010	-0.9996643
C	-0.0042332	3.6544112	-2.9411192
H	0.3942118	2.6708321	-2.7067681
C	1.0136463	4.6929726	-2.4456655
H	0.7033231	5.7108125	-2.6942930
H	1.9866411	4.5192133	-2.9095395
H	1.1472407	4.6398392	-1.3636847
C	-0.1482504	3.7233503	-4.4709983
H	-0.8467956	2.9695365	-4.8385726
H	0.8193504	3.5483919	-4.9473269
H	-0.5083938	4.7017718	-4.7984099
C	-4.0438420	1.8083385	-0.2974565
H	-3.4073821	0.9267371	-0.2574867
C	-4.4297434	2.1732380	1.1453051
H	-3.5570248	2.3528953	1.7701420
H	-4.9991571	1.3601511	1.5994926
H	-5.0548129	3.0687634	1.1742730
C	-5.3120946	1.4420767	-1.0908747
H	-6.0057095	2.2843474	-1.1381643
H	-5.8367334	0.6145418	-0.6092723
H	-5.0806154	1.1428179	-2.1132938
C	-0.9707489	-0.3913254	2.1004794
C	-1.7810680	-0.7634013	3.2148250
H	-2.0761560	-1.7934509	3.3263550
C	-2.1808020	0.1758749	4.1179830
H	-2.8249597	-0.1014402	4.9440102
C	-1.6902482	1.4844827	4.0141608
H	-1.9049724	2.2172868	4.7780949
C	-0.8321995	1.8154635	2.9903852
C	-0.0657818	3.1054921	3.1604762
C	-0.2830566	4.2473903	2.3734653
C	0.4752376	5.3978589	2.5901876
H	0.3052309	6.2625341	1.9593316
C	1.4204386	5.4491093	3.5986111
H	2.0144845	6.3419856	3.7505497
C	1.5797535	4.3525221	4.4309276
H	2.2913987	4.3963415	5.2471050
C	0.8379041	3.1853230	4.2487808
C	-1.3924521	4.3069802	1.3701932

H	-1.1303756	4.9229224	0.5111602
H	-2.2854993	4.7468094	1.8244843
H	-1.6739730	3.3252472	1.0122878
C	1.0129718	2.0954745	5.2819641
H	0.2869817	2.2163780	6.0911828
H	2.0055673	2.1573234	5.7287816
H	0.8794141	1.0942348	4.8835966
C	-1.0596857	-2.6089421	1.2905320
C	-2.4024554	-2.9233365	0.9545566
C	-2.8545462	-4.2338281	1.1118622
H	-3.8783524	-4.4703234	0.8509426
C	-2.0349399	-5.2376231	1.5931269
H	-2.4092497	-6.2476026	1.7076478
C	-0.7313644	-4.9274437	1.9357292
H	-0.0931399	-5.7058842	2.3315487
C	-0.2271843	-3.6333671	1.8022329
C	-3.4162089	-1.9061306	0.4457347
H	-2.9170926	-0.9414585	0.3822834
C	-3.9325537	-2.2597295	-0.9581071
H	-3.1244728	-2.3316805	-1.6828199
H	-4.6283468	-1.4957860	-1.3084221
H	-4.4658242	-3.2132382	-0.9543493
C	-4.6109808	-1.7674338	1.4072062
H	-5.1624566	-2.7068000	1.4863608
H	-5.3072895	-1.0118928	1.0393658
H	-4.2979522	-1.4753635	2.4086705
C	1.1816278	-3.3596571	2.3000966
H	1.5180918	-2.4441096	1.8138799
C	2.1760154	-4.4772693	1.9548624
H	1.9673765	-5.3926113	2.5118613
H	3.1915058	-4.1750569	2.2170626
H	2.1594324	-4.7186254	0.8912456
C	1.1789132	-3.1060175	3.8189532
H	0.5278031	-2.2732124	4.0862112
H	2.1856697	-2.8783419	4.1768186
H	0.8253756	-3.9914575	4.3534772
C	3.8634080	0.2004050	1.9892226
C	5.1450907	1.0734739	2.0209454
H	5.6753061	0.9013409	2.9615074
H	4.8980438	2.1333578	1.9579107
C	4.2554677	-1.2592776	2.2591106
H	3.3870766	-1.9102140	2.2365039
H	4.6900765	-1.3262419	3.2596053
C	2.9805345	0.6422612	3.1634866
H	2.6765356	1.6827543	3.0627128
H	3.5301601	0.5422617	4.1020384
H	2.0818547	0.0290682	3.2269534
H	5.8236587	0.8372784	1.2031108
H	4.9924875	-1.6498432	1.5649777

Table S6. Cartesian coordinates of the optimized geometry of $[L_2Cr_2(tBuCP)]$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	0.3400064	-0.7583549	0.9699413
N	-1.4225663	0.1077478	1.5686520
N	-1.6620978	0.2992605	-0.7308078
C	-1.9263213	0.1739750	2.8338058
C	-3.1625885	0.7252387	3.0922607
H	-3.5267150	0.7672833	4.1090399
C	-3.9309283	1.2056678	2.0229090
H	-4.9082851	1.6356603	2.2062609
C	-3.4583334	1.1030930	0.7406475
H	-4.0515187	1.4352651	-0.0973428
C	-2.1876732	0.5216798	0.4977795
C	-1.1239008	-0.4186899	3.9558385
C	-1.1846890	-1.8104261	4.1787291
C	-0.4633534	-2.3612066	5.2358831
H	-0.5033267	-3.4315883	5.3997166
C	0.2884042	-1.5580989	6.0818345
H	0.8507846	-2.0009768	6.8947606
C	0.3057657	-0.1872165	5.8883768
H	0.8782159	0.4460399	6.5557876
C	-0.4045637	0.4029183	4.8411098
C	-2.0803061	-2.6973498	3.3559891
H	-3.1281511	-2.5512300	3.6354238

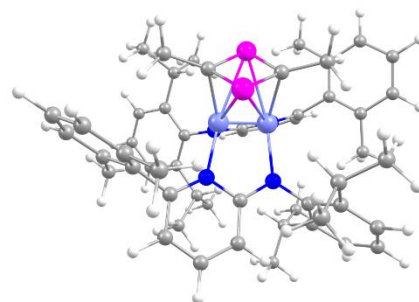


H	-1.8365443	-3.7476440	3.5164890
H	-2.0015140	-2.4883529	2.2918419
C	-0.4197139	1.9038952	4.7349782
H	-0.6461934	2.2407176	3.7284591
H	0.5424706	2.3234140	5.0276140
H	-1.1822191	2.3265729	5.3969162
C	-2.3053363	0.9395381	-1.8509234
C	-2.1527131	2.3335496	-2.0607401
C	-2.7652001	2.9266835	-3.1651877
H	-2.6452695	3.9909136	-3.3242976
C	-3.5228442	2.1949840	-4.0604554
H	-3.9879048	2.6771410	-4.9117082
C	-3.6892672	0.8392643	-3.8423249
H	-4.3020228	0.2678393	-4.5266223
C	-3.1054239	0.1945245	-2.7514903
C	-1.3838056	3.2569889	-1.1229075
H	-0.9705805	2.6570804	-0.3134542
C	-0.2087986	3.9492373	-1.8327980
H	0.5382451	3.2301515	-2.1694425
H	0.2838696	4.6495795	-1.1572463
H	-0.5443081	4.5170450	-2.7030331
C	-2.3209623	4.3096156	-0.5023139
H	-1.7805416	4.9283840	0.2150424
H	-3.1560650	3.8430127	0.0204370
H	-2.7321237	4.9727872	-1.2664868
C	-3.4384092	-1.2708851	-2.5281647
H	-2.6786796	-1.6730822	-1.8604954
C	-4.8014438	-1.4125159	-1.8255468
H	-4.8134045	-0.9036086	-0.8611356
H	-5.0406213	-2.4647189	-1.6548025
H	-5.5963313	-0.9841889	-2.4414986
C	-3.4234404	-2.1089371	-3.8137746
H	-4.2348346	-1.8323418	-4.4901444
H	-3.5581923	-3.1649515	-3.5718500
H	-2.4823833	-2.0021514	-4.3549078
C	-0.2851518	-2.8891383	-0.1271630
P	1.2845120	-2.8603249	0.4958617
C	-1.1011167	-4.1210786	-0.5187025
C	-0.5674665	-5.4051749	0.1480045
H	0.4602702	-5.6111289	-0.1537519
H	-0.5856435	-5.3182885	1.2361370
C	-0.9793609	-4.2924618	-2.0474713
H	-1.3264327	-3.4127101	-2.5860536
H	0.0583860	-4.4697027	-2.3326713
C	-2.5830932	-3.9741792	-0.1273462
H	-3.0022931	-3.0275284	-0.4562811
H	-2.7077313	-4.0359975	0.9532975
Cr	-0.0005856	-0.9251533	-0.6840285
N	1.6158036	0.1451855	-1.4169520
N	1.8231275	0.6103573	0.8403420
C	2.1353123	0.1247651	-2.6778550
C	3.3001865	0.7896430	-2.9976291
H	3.6674573	0.7576532	-4.0137960
C	4.0126497	1.4494326	-1.9882691
H	4.9419794	1.9563106	-2.2183121
C	3.5494167	1.4127554	-0.6996998
H	4.1085733	1.8609734	0.1068128
C	2.3314630	0.7527242	-0.4043277
C	1.4817742	-0.7266853	-3.7262630
C	1.8822504	-2.0737565	-3.8398294
C	1.3287648	-2.8590061	-4.8507461
H	1.6278114	-3.8971146	-4.9345868
C	0.4198734	-2.3263571	-5.7526221
H	-0.0024427	-2.9498627	-6.5313472
C	0.0674051	-0.9884144	-5.6639313
H	-0.6246119	-0.5625822	-6.3806944
C	0.5969291	-0.1694073	-4.6659852
C	2.9505075	-2.6613338	-2.9529808
H	3.9352852	-2.2712432	-3.2253194
H	2.9829131	-3.7460366	-3.0556477
H	2.7948799	-2.4276373	-1.9001067
C	0.2594361	1.2964661	-4.6565088
H	0.0197203	1.6524167	-3.6580057
H	-0.5969101	1.5014478	-5.2974383
H	1.1020353	1.8924772	-5.0188269
C	2.5225015	1.2048871	1.9504888
C	2.3707251	2.5797459	2.2574380
C	2.9749165	3.0837393	3.4095322

H	2.8545267	4.1325089	3.6514889
C	3.7364783	2.2843599	4.2444300
H	4.1882980	2.6973710	5.1381895
C	3.9443354	0.9611522	3.8987454
H	4.5807996	0.3443132	4.5209664
C	3.3736394	0.4060195	2.7531528
C	1.6603761	3.5738177	1.3452562
H	1.2403698	3.0207203	0.5071973
C	0.5097375	4.3174821	2.0388192
H	-0.3169042	3.6501773	2.2771800
H	0.1246006	5.1052865	1.3892926
H	0.8364475	4.7928301	2.9656796
C	2.6640287	4.5983191	0.7806522
H	2.1730165	5.2584909	0.0623387
H	3.4965120	4.1131064	0.2718558
H	3.0759731	5.2238871	1.5756728
C	3.7653150	-1.0183094	2.3865668
H	3.2413409	-1.2807091	1.4713045
C	5.2705287	-1.1212161	2.0836527
H	5.5654405	-0.4259788	1.2955836
H	5.5184112	-2.1323190	1.7514667
H	5.8762297	-0.9033488	2.9664818
C	3.3583606	-2.0365180	3.4607507
H	3.8894723	-1.8618809	4.3996547
H	3.5926055	-3.0506803	3.1295516
H	2.2895005	-1.9908223	3.6740026
H	-3.1691232	-4.7830543	-0.5719365
H	-1.1855604	-6.2625800	-0.1332833
H	-1.5741342	-5.1493343	-2.3760991

Table S7. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,3-(MeCP)_2\}]$ (**3**) at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	1.1305324	-0.7931301	-0.0109818
Cr	1.0267337	0.9228845	0.0570993
P	3.2269888	0.1454463	-1.2786153
P	3.1628874	0.2311330	1.4168300
N	0.1126960	-1.1611199	-1.7602289
N	-0.3415756	1.0937568	-1.4774076
N	-0.1050875	1.1617982	1.7576313
N	-0.2682627	-1.1313807	1.4653485
C	3.2005643	-1.0165735	0.0967911
C	3.7473502	-2.4171168	0.1617776
C	3.0598757	1.3860791	0.0381160
C	3.4471569	2.8396902	-0.0096971
C	-0.5734995	-0.0380651	-2.1754346
C	-1.4364035	-0.1209894	-3.3020879
H	-1.9777549	0.7582579	-3.6119903
C	-1.5548630	-1.2966170	-3.9888137
H	-2.2232684	-1.3660052	-4.8385453
C	-0.7544938	-2.3886163	-3.6284115
H	-0.7459358	-3.2942242	-4.2184317
C	0.1013444	-2.2772904	-2.5543769
C	1.1539746	-3.3427508	-2.4047853
C	2.3065019	-3.2111984	-3.2115815
C	3.2750285	-4.2140052	-3.1764840
H	4.1647015	-4.1058264	-3.7853460
C	3.1114448	-5.3412005	-2.3850573
H	3.8757755	-6.1084582	-2.3646821
C	1.9570260	-5.4859928	-1.6331442
H	1.8099145	-6.3767156	-1.0339347
C	0.9606745	-4.5075622	-1.6434357
C	2.4926355	-2.0550029	-4.1619304
H	1.8445079	-2.1657204	-5.0358092
H	3.5232653	-2.0139869	-4.5145901
H	2.2602380	-1.0954309	-3.7026738
C	-0.3196107	-4.7644742	-0.9000834
H	-0.6462777	-3.9010385	-0.3285377
H	-0.2076237	-5.5977883	-0.2074455
H	-1.1270761	-5.0145379	-1.5940664
C	-0.9946571	2.2925256	-1.9357101
C	-0.2748014	3.2175794	-2.7329317
C	-0.9099068	4.3898949	-3.1438664
H	-0.3657217	5.1025510	-3.7490101
C	-2.2270198	4.6584388	-2.8112199

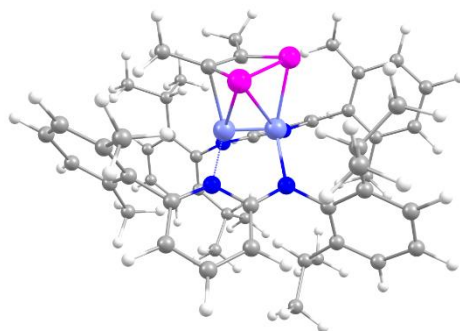


H	-2.6997720	5.5748080	-3.1431581
C	-2.9354084	3.7355227	-2.0635271
H	-3.9704007	3.9377573	-1.8173324
C	-2.3509225	2.5488673	-1.6192596
C	1.1402348	2.9450221	-3.2275007
H	1.6020534	2.2361187	-2.5410409
C	2.0266548	4.1979334	-3.2745630
H	1.7304452	4.8765882	-4.0774038
H	3.0630076	3.9115310	-3.4650657
H	1.9956799	4.7564106	-2.3375524
C	1.1201900	2.2735391	-4.6131237
H	0.5602266	1.3388512	-4.6019811
H	2.1385079	2.0524378	-4.9417818
H	0.6607281	2.9329122	-5.3544107
C	-3.2306284	1.5763308	-0.8423002
H	-2.6306132	0.6969445	-0.6177885
C	-3.7155264	2.1606532	0.4940873
H	-2.8855521	2.4064077	1.1538856
H	-4.3496927	1.4394137	1.0130676
H	-4.3042450	3.0680031	0.3401438
C	-4.4410617	1.1218209	-1.6776483
H	-5.1060720	1.9589962	-1.9007387
H	-5.0238765	0.3806410	-1.1270966
H	-4.1378345	0.6735866	-2.6238117
C	-0.6656799	-0.0371307	2.1485846
C	-1.5786020	-0.0618571	3.2379770
H	-2.0203014	-1.0012177	3.5289327
C	-1.8682441	1.0897052	3.9146265
H	-2.5746450	1.0760450	4.7358222
C	-1.1940143	2.2721704	3.5824743
H	-1.3222222	3.1718702	4.1676622
C	-0.2876789	2.2680646	2.5446070
C	0.6279575	3.4569790	2.4292803
C	0.3179503	4.5879571	1.6559792
C	1.1844827	5.6830567	1.6757201
H	0.9491906	6.5479064	1.0667355
C	2.3196308	5.6845510	2.4695963
H	2.9825250	6.5412242	2.4723540
C	2.5933685	4.5876072	3.2731084
H	3.4663392	4.5923167	3.9148965
C	1.7574192	3.4715755	3.2780745
C	-0.9582362	4.6839458	0.8691094
H	-1.1643065	3.7809381	0.3026890
H	-0.9216277	5.5155898	0.1665545
H	-1.8112322	4.8477858	1.5340547
C	2.0511712	2.3475542	4.2395491
H	1.3528782	2.3662759	5.0809206
H	3.0599630	2.4436743	4.6412468
H	1.9713846	1.3675289	3.7715600
C	-0.7835417	-2.4028848	1.9036338
C	-2.0795268	-2.8320211	1.5273085
C	-2.5261263	-4.0840557	1.9519930
H	-3.5140040	-4.4179404	1.6598694
C	-1.7403036	-4.9075693	2.7373784
H	-2.1059344	-5.8771672	3.0529254
C	-0.4859488	-4.4708139	3.1293267
H	0.1167502	-5.1066449	3.7638750
C	0.0111834	-3.2265835	2.7405091
C	-3.0421468	-1.9805812	0.7078178
H	-2.5492623	-1.0336553	0.4977944
C	-3.4000797	-2.6262815	-0.6400835
H	-2.5214014	-2.7792491	-1.2636266
H	-4.0918171	-1.9871326	-1.1920410
H	-3.8863152	-3.5945626	-0.4994025
C	-4.3313321	-1.6775973	1.4928334
H	-4.8923939	-2.5910601	1.7016276
H	-4.9823605	-1.0207770	0.9123829
H	-4.1239227	-1.1873688	2.4440578
C	1.3543073	-2.7734826	3.2997769
H	1.7537926	-2.0110401	2.6318154
C	2.3916261	-3.9015902	3.3968019
H	2.1503350	-4.6106943	4.1918121
H	3.3730168	-3.4833039	3.6297447
H	2.4746252	-4.4623107	2.4644305
C	1.1818264	-2.1103173	4.6788376
H	0.5027117	-1.2593757	4.6361717
H	2.1454144	-1.7547894	5.0515875
H	0.7815421	-2.8252250	5.4027615

H	3.3671100	-2.9659748	1.0244365
H	4.8384442	-2.4021009	0.2524131
H	3.5066324	-2.9933653	-0.7311091
H	3.0856116	3.3914492	0.8576622
H	4.5364362	2.9488214	-0.0310377
H	3.0634803	3.3348151	-0.9027454

Table S8. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,2-(MeCP)_2\}]$ at the RI-B3LYP/def2-TZVP level of theory.

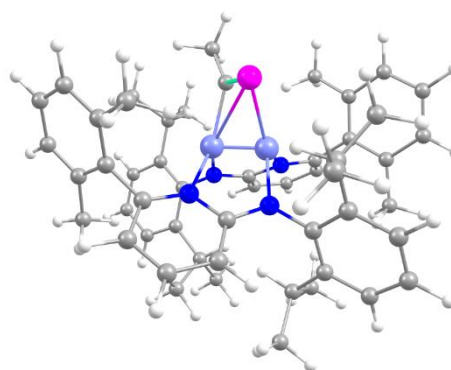
Atom	x	y	z
Cr	1.1719898	-0.5394407	-0.3613328
Cr	0.8880429	1.0740702	0.1185639
P	2.9863798	0.8274691	-1.6157649
P	3.1000645	1.8811611	0.3489817
C	3.3019371	0.1342830	0.8008944
N	0.0072479	-0.5913456	-2.0733070
N	-0.5394351	1.5107364	-1.2617646
N	0.1625087	0.7742085	2.0141443
N	0.1592445	-1.4133750	1.2317562
C	3.3297275	-0.5360549	-0.4481109
C	4.0535290	-1.8185369	-0.7619721
C	-0.6579570	0.6059844	-2.2563400
C	-1.3580419	0.8539228	-3.4651466
H	-1.8290546	1.8135426	-3.6040420
C	-1.4093578	-0.1041783	-4.4373756
H	-1.9515435	0.0781285	-5.3573396
C	-0.7124120	-1.3039631	-4.2524671
H	-0.6905198	-2.0614003	-5.0231330
C	0.0168543	-1.4994484	-3.0997584
C	0.9072567	-2.7097297	-3.0652102
C	2.1258645	-2.6633249	-3.7756252
C	2.9168418	-3.8109934	-3.8342693
H	3.8592383	-3.7722650	-4.3679194
C	2.5133933	-4.9925310	-3.2299328
H	3.1428653	-5.8726724	-3.2811168
C	1.2904003	-5.0459338	-2.5808123
H	0.9520687	-5.9744277	-2.1362555
C	0.4667606	-3.9214419	-2.5069935
C	2.5721439	-1.4356494	-4.5294177
H	2.0421400	-1.3546355	-5.4827284
H	3.6389310	-1.4881350	-4.7490965
H	2.3870412	-0.5133603	-3.9809656
C	-0.9110605	-4.0580066	-1.9253269
H	-1.2129152	-3.1682128	-1.3832713
H	-0.9695079	-4.9042834	-1.2427472
H	-1.6450127	-4.2175987	-2.7218104
C	-1.2655818	2.7485540	-1.3861442
C	-0.5711003	3.9355613	-1.7251588
C	-1.2754552	5.1381484	-1.7917642
H	-0.7432697	6.0461736	-2.0448422
C	-2.6391734	5.1935763	-1.5676140
H	-3.1688796	6.1364433	-1.6298984
C	-3.3225378	4.0228311	-1.2875400
H	-4.3948987	4.0634320	-1.1420924
C	-2.6719640	2.7926701	-1.1931261
C	0.8998101	3.9529884	-2.1188156
H	1.3210812	2.9808236	-1.8730652
C	1.7167978	5.0134742	-1.3677592
H	1.4134460	6.0273318	-1.6394740
H	2.7755363	4.9132141	-1.6165547
H	1.6131391	4.9096901	-0.2876372
C	1.0540553	4.1268768	-3.6404438
H	0.5252119	3.3443126	-4.1869528
H	2.1087410	4.0794135	-3.9214098
H	0.6603420	5.0920880	-3.9693849
C	-3.5455661	1.5614660	-0.9514140
H	-2.8935402	0.6928753	-0.8705756
C	-4.3706556	1.6494286	0.3438838
H	-3.7453473	1.6506793	1.2339768
H	-5.0472735	0.7955594	0.4133931
H	-4.9861025	2.5507394	0.3660610
C	-4.5107882	1.3247780	-2.1300278
H	-5.2438817	2.1316002	-2.2012865
H	-5.0598964	0.3913967	-1.9872825
H	-3.9889438	1.2606077	-3.0829606



C	-0.0598711	-0.5675632	2.2626494
C	-0.4613103	-0.9853233	3.5607485
H	-0.6410419	-2.0337258	3.7391244
C	-0.5881454	-0.0699445	4.5671545
H	-0.8827599	-0.3890731	5.5596521
C	-0.3042141	1.2790817	4.3141268
H	-0.3695456	2.0204347	5.0977748
C	0.0791340	1.6702537	3.0511245
C	0.4253860	3.1185971	2.8495296
C	-0.5632907	4.0222043	2.4233641
C	-0.2481039	5.3746388	2.3044311
H	-1.0087469	6.0635901	1.9573671
C	1.0166039	5.8407255	2.6294666
H	1.2535714	6.8925637	2.5251685
C	1.9720828	4.9550640	3.1020672
H	2.9556540	5.3178457	3.3770044
C	1.6922406	3.5949692	3.2344997
C	-1.9721255	3.5647154	2.1765665
H	-2.5168437	4.2799067	1.5629694
H	-2.5106532	3.4496254	3.1226834
H	-1.9961271	2.6020531	1.6748339
C	2.7397786	2.7033241	3.8491977
H	2.6696713	2.7284357	4.9414436
H	3.7407324	3.0406276	3.5774987
H	2.6347231	1.6656850	3.5475529
C	-0.3589264	-2.7487096	1.3904218
C	-1.7575016	-2.9746823	1.3042129
C	-2.2453724	-4.2690459	1.4798406
H	-3.3123771	-4.4426852	1.4184638
C	-1.4042582	-5.3380967	1.7336802
H	-1.8067914	-6.3348511	1.8670816
C	-0.0426481	-5.1124654	1.8260486
H	0.6146787	-5.9435035	2.0461660
C	0.5012557	-3.8363940	1.6697724
C	-2.7844565	-1.8700910	1.0679500
H	-2.2493903	-0.9334079	0.9176002
C	-3.6352447	-2.1220290	-0.1884751
H	-3.0334099	-2.1171663	-1.0966327
H	-4.3946224	-1.3455763	-0.2890725
H	-4.1546968	-3.0808689	-0.1365171
C	-3.7068147	-1.6999096	2.2896987
H	-4.3123213	-2.5945811	2.4523397
H	-4.3894563	-0.8618447	2.1379452
H	-3.1392381	-1.5094578	3.2000213
C	1.9943094	-3.6635873	1.9028247
H	2.2701841	-2.6874269	1.5095442
C	2.8446384	-4.7210278	1.1841557
H	2.6771922	-5.7206605	1.5901298
H	3.9072553	-4.5022086	1.3133763
H	2.6314786	-4.7517256	0.1151647
C	2.3172164	-3.6628139	3.4083008
H	1.7753149	-2.8779149	3.9369246
H	3.3857972	-3.5032186	3.5722336
H	2.0489586	-4.6199462	3.8626568
C	3.7075758	-0.4285248	2.1351137
H	2.8675388	-0.5285362	2.8264744
H	4.1606543	-1.4147942	2.0271925
H	5.1240299	-1.6195979	-0.8827350
H	4.4439003	0.2208354	2.6128632
H	3.9494160	-2.5609875	0.0275400
H	3.7003743	-2.2705050	-1.6873816

Table S9. Cartesian coordinates of the optimized geometry of $[L_2Cr_2(MeCP)]$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	0.2762614	-1.0560023	0.8991334
N	-1.4390510	-0.1440283	1.5441201
N	-1.6854856	0.1154492	-0.7377340
C	-1.9504023	-0.1340835	2.8071178
C	-3.1405072	0.4981115	3.0979555
H	-3.5150622	0.4912854	4.1119174
C	-3.8644469	1.0998638	2.0587979
H	-4.8032880	1.5978740	2.2690045
C	-3.4089012	1.0143637	0.7684181
H	-3.9819499	1.4188002	-0.0518891

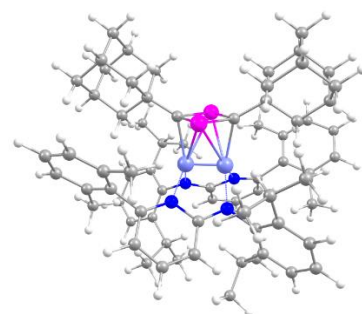


C	-2.1852074	0.3520440	0.4965009
C	-1.2454014	-0.9399958	3.8589401
C	-1.4860411	-2.3312035	3.8898040
C	-0.8582984	-3.1066233	4.8627674
H	-1.0354473	-4.1754165	4.8796863
C	-0.0338801	-2.5258996	5.8151883
H	0.4469443	-3.1404061	6.5664869
C	0.1534912	-1.1534433	5.8140122
H	0.7753223	-0.6931525	6.5726091
C	-0.4474534	-0.3409841	4.8504377
C	-2.4717356	-2.9843563	2.9545665
H	-3.4959413	-2.7126652	3.2262755
H	-2.3891571	-4.0698608	3.0070835
H	-2.3228157	-2.6836898	1.9192987
C	-0.2166004	1.1453908	4.9126001
H	0.5848412	1.4485269	4.2378378
H	0.0785257	1.4412025	5.9198456
H	-1.1064718	1.7104898	4.6386295
C	-2.3803366	0.6681098	-1.8666914
C	-2.2265603	2.0336960	-2.2081560
C	-2.8926018	2.5275869	-3.3301192
H	-2.7723370	3.5698557	-3.5983725
C	-3.7016770	1.7200984	-4.1107574
H	-4.2076878	2.1256701	-4.9783767
C	-3.8655945	0.3913077	-3.7602642
H	-4.5154022	-0.2364458	-4.3569779
C	-3.2270872	-0.1546586	-2.6464580
C	-1.3829191	3.0092551	-1.3969239
H	-0.9911632	2.4749108	-0.5330803
C	-0.1812988	3.5344173	-2.1988731
H	0.4939439	2.7277157	-2.4829957
H	0.3876353	4.2522355	-1.6056768
H	-0.5025216	4.0419443	-3.1114313
C	-2.2297182	4.1837870	-0.8769600
H	-1.6206439	4.8497116	-0.2628645
H	-3.0656049	3.8369671	-0.2680930
H	-2.6363499	4.7784275	-1.6977957
C	-3.5238563	-1.6008167	-2.2811832
H	-2.8333106	-1.8818059	-1.4893298
C	-4.9483421	-1.7471263	-1.7175823
H	-5.1015866	-1.1028601	-0.8504545
H	-5.1335488	-2.7793318	-1.4090059
H	-5.6986331	-1.4842091	-2.4675566
C	-3.3051559	-2.5666324	-3.4545462
H	-3.9980601	-2.3705706	-4.2757496
H	-3.4712814	-3.5967330	-3.1317072
H	-2.2911635	-2.4931706	-3.8509997
C	-0.5333265	-3.0382850	-0.2075709
P	1.0274410	-3.2383789	0.4028397
C	-1.5704935	-4.0663656	-0.5499841
Cr	-0.0856414	-1.1472022	-0.7578972
N	1.5336315	-0.1113488	-1.4915365
N	1.7499252	0.3234365	0.7668897
C	2.0510893	-0.1383621	-2.7521171
C	3.1851876	0.5713119	-3.0844133
H	3.5604946	0.5335406	-4.0974907
C	3.8588319	1.2890072	-2.0859205
H	4.7557235	1.8460833	-2.3283584
C	3.4083239	1.2439585	-0.7920041
H	3.9465822	1.7370240	0.0029870
C	2.2349009	0.5127393	-0.4804078
C	1.4273645	-1.0649202	-3.7545655
C	1.8318642	-2.4165885	-3.7421409
C	1.2792687	-3.2966337	-4.6725913
H	1.5815461	-4.3370878	-4.6565975
C	0.3753627	-2.8524480	-5.6256504
H	-0.0432261	-3.5465857	-6.3442839
C	0.0277677	-1.5110272	-5.6692613
H	-0.6566165	-1.1551923	-6.4300569
C	0.5472035	-0.5997232	-4.7487045
C	2.9122507	-2.9141229	-2.8154952
H	3.8942622	-2.5738583	-3.1571617
H	2.9274387	-4.0036350	-2.7916145
H	2.7859422	-2.5571706	-1.7944243
C	0.1656199	0.8519771	-4.8589211
H	-0.4760527	1.1608764	-4.0344523
H	-0.3808558	1.0336633	-5.7840901
H	1.0421167	1.5015254	-4.8479093

C	2.4518610	0.9114193	1.8730478
C	2.2346080	2.2632861	2.2295104
C	2.8871072	2.7770812	3.3505175
H	2.7186432	3.8089803	3.6330767
C	3.7447603	2.0006694	4.1117754
H	4.2352804	2.4191465	4.9822000
C	3.9839832	0.6906127	3.7341762
H	4.6770978	0.0910422	4.3113411
C	3.3670708	0.1280593	2.6161530
C	1.3467282	3.2027613	1.4234522
H	0.9770730	2.6507247	0.5608953
C	0.1257890	3.6794660	2.2251471
H	-0.5244914	2.8477526	2.4936410
H	-0.4620706	4.3873859	1.6385371
H	0.4254689	4.1843815	3.1464263
C	2.1435933	4.4101824	0.8993283
H	1.5081614	5.0455703	0.2788668
H	2.9962136	4.0967124	0.2954556
H	2.5212968	5.0266582	1.7179507
C	3.7518447	-1.2907258	2.2199237
H	3.1737574	-1.5564968	1.3374886
C	5.2370891	-1.3813230	1.8301008
H	5.4795807	-0.6837452	1.0263602
H	5.4752096	-2.3903046	1.4846108
H	5.8905103	-1.1574044	2.6767731
C	3.4132093	-2.3131257	3.3148491
H	3.9940040	-2.1348927	4.2231590
H	3.6367254	-3.3252955	2.9702862
H	2.3568701	-2.2765919	3.5859063
H	-1.3905021	-5.0249391	-0.0573774
H	-1.5717987	-4.2449205	-1.6296474
H	-2.5775788	-3.7312612	-0.2914558

Table S10. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,3-(AdCP)_2\}]$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	-0.0171404	-0.8778609	-0.0208500
Cr	-0.1264478	0.8474807	0.0314637
P	2.0647067	0.0288008	-1.2427953
P	1.9691958	0.2239157	1.4263740
N	-1.0755863	-1.2611096	-1.7917434
N	-1.4894926	1.0155794	-1.5155307
N	-1.3578755	1.0858956	1.7135860
N	-1.5029180	-1.2165980	1.3798174
C	2.0913263	-1.1008751	0.1728394
C	1.9364581	1.3493625	0.0202218
C	-1.7691448	-0.1295408	-2.1764598
C	-2.7088841	-0.1967966	-3.2415925
H	-3.2437860	0.6957767	-3.5177825
C	-2.9021807	-1.3639023	-3.9199229
H	-3.6275532	-1.4198286	-4.7225751
C	-2.1014927	-2.4650187	-3.6066336
H	-2.1482257	-3.3727053	-4.1912843
C	-1.1748187	-2.3754407	-2.5872055
C	-0.1870280	-3.5130453	-2.5701552
C	0.9168648	-3.3996620	-3.4447028
C	1.7314191	-4.5111117	-3.6550551
H	2.5769071	-4.4216613	-4.3268586
C	1.4625004	-5.7245677	-3.0399946
H	2.1007135	-6.5809085	-3.2204351
C	0.3702215	-5.8340236	-2.1962861
H	0.1499481	-6.7805584	-1.7170498
C	-0.4706088	-4.7454371	-1.9576348
C	1.1924749	-2.1401617	-4.2256521
H	0.4374572	-1.9924519	-5.0028100
H	2.1651671	-2.2000554	-4.7143175
H	1.1879664	-1.2511677	-3.5959124
C	-1.6826518	-4.9473764	-1.0930713
H	-1.8363201	-4.1247609	-0.4000565
H	-1.5919981	-5.8627670	-0.5086892
H	-2.5889182	-5.0317494	-1.6986491
C	-2.1247641	2.2147658	-2.0135376
C	-1.4306680	3.0402970	-2.9398891
C	-2.0284984	4.2304210	-3.3558765
H	-1.5022377	4.8747466	-4.0458348

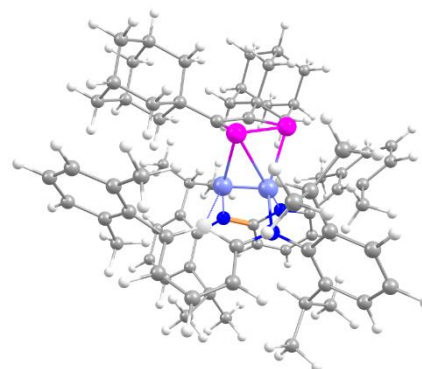


C	-3.2900957	4.6047287	-2.9240526
H	-3.7292771	5.5364970	-3.2591854
C	-3.9929471	3.7578480	-2.0894655
H	-4.9975702	4.0265810	-1.7880557
C	-3.4469360	2.5560493	-1.6344495
C	-0.0989664	2.6419709	-3.5738099
H	0.4665177	2.0691730	-2.8374692
C	0.7580943	3.8370918	-4.0163268
H	0.3590393	4.3026716	-4.9204476
H	1.7667925	3.4951049	-4.2549293
H	0.8332347	4.6078878	-3.2505315
C	-0.3017159	1.7301830	-4.7999189
H	-0.8090783	0.8021661	-4.5514623
H	0.6664503	1.4765917	-5.2383851
H	-0.8924019	2.2445057	-5.5628311
C	-4.3650047	1.6390300	-0.8314536
H	-3.7926963	0.7563333	-0.5540610
C	-4.8923206	2.2775470	0.4613867
H	-4.0884881	2.5412125	1.1427351
H	-5.5513464	1.5786269	0.9801859
H	-5.4712382	3.1802044	0.2527272
C	-5.5657047	1.1859356	-1.6857532
H	-6.1950881	2.0365621	-1.9563412
H	-6.1867395	0.4864808	-1.1232013
H	-5.2576598	0.6924396	-2.6063518
C	-1.9540596	-0.1212078	2.0298654
C	-2.9707454	-0.1760382	3.0227089
H	-3.4192149	-1.1269005	3.2545759
C	-3.3482112	0.9530349	3.6876978
H	-4.1341636	0.9160351	4.4323215
C	-2.6549780	2.1410454	3.4444394
H	-2.8487354	3.0282568	4.0300943
C	-1.6392815	2.1682725	2.5092522
C	-0.7808102	3.4049669	2.6110241
C	-1.1238965	4.6149623	1.9841145
C	-0.4765572	5.7903548	2.3693835
H	-0.7466794	6.7201949	1.8828265
C	0.4864398	5.7853626	3.3642866
H	0.9700067	6.7081678	3.6607379
C	0.8310158	4.5891266	3.9748953
H	1.5836492	4.5775164	4.7543184
C	0.2056590	3.3938569	3.6231748
C	-2.2099686	4.6996567	0.9489809
H	-2.1944023	3.8566558	0.2637432
H	-2.1098056	5.6103378	0.3583576
H	-3.1983257	4.7185922	1.4154661
C	0.5423694	2.1455688	4.3985598
H	-0.2709828	1.8784470	5.0788048
H	1.4396089	2.3008627	4.9980038
H	0.7174382	1.2890395	3.7485757
C	-2.0766794	-2.4797182	1.7828936
C	-3.3471674	-2.8970435	1.3127133
C	-3.8405591	-4.1414195	1.7094205
H	-4.8064365	-4.4649368	1.3426035
C	-3.1330711	-4.9660159	2.5620023
H	-3.5315148	-5.9309182	2.8510656
C	-1.9181450	-4.5312458	3.0643886
H	-1.3863622	-5.1646621	3.7598689
C	-1.3770848	-3.2942508	2.7124585
C	-4.2639196	-2.0369840	0.4486164
H	-3.7362213	-1.1135089	0.2197605
C	-4.6334820	-2.7057744	-0.8835253
H	-3.7554845	-2.9290542	-1.4832998
H	-5.2772058	-2.0453168	-1.4675967
H	-5.1801473	-3.6377473	-0.7220090
C	-5.5599966	-1.6781015	1.2013668
H	-6.1420941	-2.5745209	1.4258114
H	-6.1857334	-1.0287798	0.5863965
H	-5.3650600	-1.1616272	2.1399247
C	-0.1010764	-2.8350703	3.4124078
H	0.4623427	-2.2181103	2.7107067
C	0.8012686	-3.9909205	3.8622613
H	0.3767385	-4.5252250	4.7151817
H	1.7675454	-3.5997988	4.1841818
H	0.9754025	-4.7144197	3.0661254
C	-0.4120850	-1.9585914	4.6406877
H	-0.9728424	-1.0641109	4.3818343
H	0.5177576	-1.6447533	5.1211034

H	-0.9961487	-2.5228899	5.3727706
C	2.9807506	-2.3603158	0.3277912
C	2.2425158	-3.7122380	0.2158602
H	1.4597779	-3.7698839	0.9769955
H	1.7487050	-3.7766031	-0.7519370
C	3.2159714	-4.8994216	0.3760751
H	2.6502016	-5.8318505	0.2873916
C	3.9065833	-4.8386171	1.7469046
H	4.5971334	-5.6818296	1.8562648
H	3.1731406	-4.9247526	2.5510597
C	4.6720220	-3.5122853	1.8661108
H	5.1460000	-3.4463770	2.8508785
C	3.7010604	-2.3301265	1.7040399
H	4.2535222	-1.3917112	1.8036023
H	2.9618450	-2.3424853	2.5094317
C	4.0880440	-2.3428867	-0.7636606
H	4.6349955	-1.3972815	-0.7048997
H	3.6243470	-2.3777064	-1.7532958
C	5.0634588	-3.5206912	-0.6042621
H	5.8187146	-3.4635496	-1.3948906
C	4.2913633	-4.8430837	-0.7204324
H	3.8295028	-4.9214461	-1.7065553
H	4.9767852	-5.6912544	-0.6164347
C	5.7456983	-3.4410331	0.7696382
H	6.4603982	-4.2625410	0.8858749
H	6.3133696	-2.5086509	0.8569275
C	2.6227077	2.7316735	-0.0650886
C	3.7157366	2.6760332	-1.1711380
H	4.4010157	1.8505790	-0.9568830
H	3.2508401	2.4525104	-2.1356214
C	4.4999893	3.9936682	-1.2675156
H	5.2525590	3.9005253	-2.0572807
C	5.1901210	4.2772003	0.0751625
H	5.7699795	5.2042300	0.0147766
H	5.8952957	3.4739609	0.3134695
C	4.1208121	4.3901076	1.1719915
H	4.6007338	4.5870565	2.1361188
C	3.3411245	3.0662549	1.2687714
H	2.6081273	3.1265238	2.0765950
H	4.0287897	2.2545398	1.5224123
C	1.6814796	3.9117996	-0.3929418
H	0.9270980	4.0023970	0.3901974
H	1.1524449	3.7109424	-1.3245144
C	2.4640592	5.2373351	-0.5059964
H	1.7621474	6.0429338	-0.7446221
C	3.5323378	5.1373349	-1.6065908
H	3.0691616	4.9586911	-2.5799332
H	4.0777992	6.0839354	-1.6832013
C	3.1602403	5.5388862	0.8297002
H	3.7127976	6.4823715	0.7599523
H	2.4198474	5.6571582	1.6213606

Table S11. Cartesian coordinates of the optimized geometry of $[L_2Cr_2\{1,2-(AdCP)_2\}]$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	-0.1408198	-0.2403884	-0.5762540
Cr	-0.2332659	1.3986212	-0.1556759
P	1.7095911	0.8464817	-1.9550030
P	2.0236853	2.1064368	-0.1519662
C	2.4431318	0.4301831	0.4429990
N	-1.4569543	-0.2415366	-2.2609924
N	-1.6623601	1.9491275	-1.4892900
N	-1.1732723	1.3396447	1.6997502
N	-1.5013558	-0.8446307	0.9502242
C	2.2585110	-0.3945278	-0.7138839
C	-2.0678541	0.9951677	-2.3557143
C	-3.0601288	1.2467934	-3.3422978
H	-3.5062761	2.2255228	-3.3913279
C	-3.4381313	0.2614221	-4.2043763
H	-4.2171562	0.4354799	-4.9367025
C	-2.7586499	-0.9561613	-4.1621016
H	-2.9574692	-1.7270609	-4.8927010
C	-1.7458978	-1.1594740	-3.2431218
C	-0.9174242	-2.3751230	-3.5852469
C	-0.0182985	-2.2203962	-4.6669767

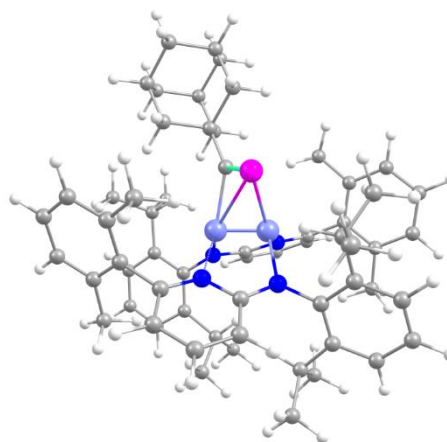


C	0.5494695	-3.3527893	-5.2460049
H	1.2321909	-3.2297252	-6.0783132
C	0.2479472	-4.6247726	-4.7815863
H	0.6954790	-5.4952966	-5.2454854
C	-0.6261010	-4.7712769	-3.7191444
H	-0.8715475	-5.7610995	-3.3521242
C	-1.2301277	-3.6621895	-3.1208389
C	0.3101920	-0.8678826	-5.2479088
H	-0.5331762	-0.4629504	-5.8127508
H	1.1598245	-0.9432793	-5.9268047
H	0.5598536	-0.1396863	-4.4756437
C	-2.2687689	-3.8985087	-2.0638312
H	-2.2899957	-3.1099882	-1.3197041
H	-2.0932704	-4.8424307	-1.5482226
H	-3.2674704	-3.9501350	-2.5073196
C	-2.1499765	3.2855483	-1.7456933
C	-1.4030067	4.1421434	-2.5905320
C	-1.8622141	5.4405592	-2.8137472
H	-1.2888118	6.0991544	-3.4540117
C	-3.0390591	5.9010328	-2.2502825
H	-3.3788171	6.9124784	-2.4371555
C	-3.7862429	5.0456933	-1.4593552
H	-4.7193384	5.3982112	-1.0382602
C	-3.3732586	3.7389924	-1.1966308
C	-0.1408558	3.7019819	-3.3202823
H	0.1149482	2.7025941	-2.9752270
C	1.0630350	4.6114630	-3.0300641
H	0.9083940	5.6221026	-3.4152118
H	1.9591077	4.2097711	-3.5076216
H	1.2640864	4.6879002	-1.9606097
C	-0.3813994	3.6032235	-4.8370250
H	-1.2082112	2.9295162	-5.0664822
H	0.5130408	3.2233120	-5.3363810
H	-0.6150160	4.5805139	-5.2668921
C	-4.3037151	2.8599242	-0.3687562
H	-3.7921081	1.9162885	-0.1833120
C	-4.6549568	3.4800739	0.9932730
H	-3.7680762	3.7190907	1.5773116
H	-5.2565927	2.7807671	1.5778014
H	-5.2386717	4.3957218	0.8762010
C	-5.6060399	2.5593699	-1.1345491
H	-6.1491580	3.4813978	-1.3542223
H	-6.2628731	1.9268078	-0.5342226
H	-5.4184652	2.0480815	-2.0780340
C	-1.8214697	0.1234165	1.8322971
C	-2.7809655	-0.0527931	2.8719449
H	-3.2537966	-1.0129787	2.9881513
C	-3.1094413	0.9898094	3.6851393
H	-3.8802922	0.8757713	4.4380314
C	-2.3781080	2.1799601	3.5969574
H	-2.5363146	2.9764649	4.3085285
C	-1.3522431	2.2931833	2.6850820
C	-0.3574905	3.3908641	2.9829592
C	-0.1216841	4.4993840	2.1564254
C	0.7642437	5.4986223	2.5648101
H	0.9292350	6.3472657	1.9112454
C	1.4109106	5.4270070	3.7836507
H	2.0947586	6.2089401	4.0905136
C	1.1630806	4.3461849	4.6165570
H	1.6584918	4.2861482	5.5784043
C	0.2859053	3.3285732	4.2478877
C	-0.8116686	4.6714368	0.8411948
H	-0.1536235	4.3846875	0.0190736
H	-1.0916380	5.7127520	0.6758325
H	-1.7116891	4.0720503	0.7726774
C	0.0721581	2.2145212	5.2494860
H	-0.8298394	2.3748106	5.8437045
H	0.9097324	2.1751342	5.9455779
H	-0.0268524	1.2360037	4.7825981
C	-2.1994106	-2.0977533	1.1068041
C	-3.5559765	-2.2500288	0.7171317
C	-4.1704345	-3.4924653	0.8821238
H	-5.2036693	-3.6109024	0.5809177
C	-3.4997014	-4.5751278	1.4185259
H	-3.9970409	-5.5311047	1.5284937
C	-2.1890010	-4.4139661	1.8330033
H	-1.6753462	-5.2524261	2.2826537
C	-1.5278603	-3.1919291	1.7083776

C	-4.4263158	-1.1245961	0.1634996
H	-3.8116518	-0.2295526	0.0850097
C	-4.9730560	-1.4394257	-1.2374400
H	-4.1774005	-1.6258361	-1.9534752
H	-5.5652658	-0.5997091	-1.6056625
H	-5.6236982	-2.3168827	-1.2203516
C	-5.6122956	-0.8164140	1.0979413
H	-6.2886634	-1.6713127	1.1652181
H	-6.1888700	0.0251034	0.7093374
H	-5.2915107	-0.5625884	2.1064793
C	-0.1444329	-3.0491386	2.3280031
H	0.3873446	-2.2755743	1.7732149
C	0.6939064	-4.3329226	2.2753103
H	0.3093067	-5.0964401	2.9547653
H	1.7184445	-4.1215080	2.5867704
H	0.7270075	-4.7597333	1.2724159
C	-0.2580736	-2.5753437	3.7895876
H	-0.7705789	-1.6172878	3.8679070
H	0.7330427	-2.4680626	4.2369872
H	-0.8156722	-3.3036953	4.3841143
C	3.2015688	0.3041492	1.7773644
C	3.3129979	-1.1097608	2.3888576
H	2.3101044	-1.4974239	2.5803001
H	3.7956680	-1.7958353	1.6992506
C	4.1237706	-1.0977774	3.6983835
H	4.1830214	-2.1219598	4.0805404
C	3.4350054	-0.1968198	4.7308362
H	3.9979264	-0.1949957	5.6702874
H	2.4350395	-0.5790477	4.9588355
C	3.3428010	1.2245528	4.1596960
H	2.8360166	1.8774317	4.8716361
C	2.5355915	1.2029614	2.8493908
H	2.4351546	2.2215865	2.4691224
H	1.5247731	0.8362873	3.0379775
C	4.6437678	0.8785230	1.5639031
H	4.5601661	1.9033858	1.1953815
H	5.1737189	0.3165590	0.7973209
C	5.4507670	0.8629465	2.8721551
H	6.4566649	1.2417326	2.6647201
C	5.5402921	-0.5705286	3.4186679
H	6.0499917	-1.2192969	2.6986216
H	6.1364304	-0.5870930	4.3369787
C	4.7567775	1.7633435	3.9013146
H	5.3268830	1.7865160	4.8361554
H	4.7070984	2.7915395	3.5299528
C	2.9672499	-1.7061269	-1.1503424
C	2.7547260	-1.9594320	-2.6622690
H	1.6906402	-2.0665381	-2.8658351
H	3.1064307	-1.0963706	-3.2340014
C	3.4959863	-3.2202000	-3.1463998
H	3.2959583	-3.3517119	-4.2130549
C	3.0031124	-4.4526653	-2.3743032
H	3.5375297	-5.3470679	-2.7132279
H	1.9423823	-4.6203112	-2.5678051
C	3.2372642	-4.2280615	-0.8757665
H	2.8732111	-5.0918591	-0.3105712
C	2.4624386	-2.9754881	-0.4232599
H	2.5442668	-2.8642315	0.6537326
H	1.3982420	-3.1091640	-0.6447188
C	4.5032351	-1.5749161	-0.9545550
H	4.7423009	-1.4065971	0.0899472
H	4.8559351	-0.6981344	-1.5068714
C	5.2510248	-2.8335047	-1.4216039
H	6.3213920	-2.6947659	-1.2376629
C	5.0042799	-3.0535198	-2.9187170
H	5.3845135	-2.2007976	-3.4906813
H	5.5415750	-3.9407015	-3.2702317
C	4.7420326	-4.0434323	-0.6208079
H	5.2839309	-4.9479846	-0.9159853
H	4.9339677	-3.8952755	0.4472637

Table S2. Cartesian coordinates of the optimized geometry of [L₂Cr₂(AdCP)] (**4**) at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Cr	0.5515976	-0.2146151	1.0366685
N	-1.2257950	0.6289094	1.6461780
N	-1.4628196	0.8305302	-0.6550351
C	-1.7326496	0.6881126	2.9105701
C	-2.9945849	1.1824448	3.1626528
H	-3.3592021	1.2194569	4.1794805
C	-3.7835086	1.6189398	2.0902132
H	-4.7819422	1.9995498	2.2691440
C	-3.2991083	1.5411824	0.8105905
H	-3.9022924	1.8459916	-0.0308274
C	-2.0023971	1.0197519	0.5743466
C	-0.9005790	0.1730309	4.0498758
C	-0.9033767	-1.2078269	4.3386357
C	-0.1609324	-1.6778911	5.4193072
H	-0.1581721	-2.7398757	5.6344342
C	0.5590826	-0.8056931	6.2241567
H	1.1385446	-1.1863479	7.0563663
C	0.5216996	0.5533203	5.9648919
H	1.0686531	1.2406400	6.5994768
C	-0.2140245	1.0634760	4.8929348
C	-1.7520157	-2.1677898	3.5503629
H	-2.8147715	-1.9996689	3.7472113
H	-1.5203697	-3.1987723	3.8174203
H	-1.6040803	-2.0535582	2.4785269
C	-0.2893940	2.5564699	4.7187528
H	-0.6082927	2.8364190	3.7196466
H	0.6779133	3.0192573	4.9133231
H	-1.0101890	2.9865076	5.4213411
C	-2.0970324	1.5008005	-1.7615805
C	-1.9735047	2.9066769	-1.9083759
C	-2.5943612	3.5357558	-2.9875218
H	-2.5008365	4.6089776	-3.0952656
C	-3.3267207	2.8285748	-3.9229599
H	-3.8008307	3.3389620	-4.7524549
C	-3.4509415	1.4595574	-3.7753139
H	-4.0379013	0.9043688	-4.4948787
C	-2.8577497	0.7783843	-2.7114961
C	-1.2172038	3.8031666	-0.9350985
H	-0.7740096	3.1757278	-0.1631265
C	-0.0737624	4.5587181	-1.6323851
H	0.6794478	3.8751154	-2.0250728
H	0.4194992	5.2336433	-0.9324008
H	-0.4416632	5.1638393	-2.4631829
C	-2.1697791	4.7997440	-0.2491836
H	-1.6336825	5.3974344	0.4893540
H	-2.9841347	4.2866394	0.2624075
H	-2.6101680	5.4876891	-0.9743692
C	-3.1372967	-0.7091194	-2.5829381
H	-2.4079502	-1.1169324	-1.8843259
C	-4.5381839	-0.9418994	-1.9881247
H	-4.6364494	-0.4845114	-1.0026144
H	-4.7460641	-2.0094520	-1.8863287
H	-5.3069737	-0.5130117	-2.6357672
C	-2.9871773	-1.4647424	-3.9101944
H	-3.7496978	-1.1722300	-4.6349635
H	-3.1000551	-2.5376473	-3.7487969
H	-2.0099588	-1.2916112	-4.3607142
C	-0.0895945	-2.3477488	-0.0223960
P	1.5043036	-2.3045394	0.5382597
C	-0.9056311	-3.6011960	-0.3083062
C	-0.4034181	-4.8120696	0.5262309
H	0.6589357	-4.9711804	0.3254685
H	-0.4893411	-4.5763404	1.5912826
C	-1.1924976	-6.0892323	0.1994249
H	-0.8075571	-6.9124829	0.8097268
C	-1.0146373	-6.4246161	-1.2904763
H	-1.5560388	-7.3430973	-1.5400802
H	0.0422900	-6.6069537	-1.5103975
C	-1.5398293	-5.2555386	-2.1391042
H	-1.4109023	-5.4839756	-3.2019173
C	-0.7486381	-3.9762531	-1.8084385
H	-1.0867398	-3.1496450	-2.4367545
H	0.3120310	-4.1261424	-2.0285545
C	-2.4138681	-3.4224340	-0.0074480



H	-2.8071728	-2.5775497	-0.5701118
H	-2.5500373	-3.1842026	1.0485904
C	-3.2032331	-4.7010799	-0.3448094
H	-4.2623334	-4.5306590	-0.1268383
C	-2.6819088	-5.8693323	0.5061517
H	-2.8189054	-5.6520904	1.5705238
H	-3.2526989	-6.7786106	0.2902386
C	-3.0312591	-5.0435726	-1.8327894
H	-3.5962113	-5.9489471	-2.0783105
H	-3.4368600	-4.2412053	-2.4543581
Cr	0.1975595	-0.3812785	-0.6141562
N	1.8240280	0.6890613	-1.3481589
N	2.0460740	1.1387261	0.9136834
C	2.3396185	0.6768045	-2.6104993
C	3.5246897	1.3098437	-2.9233890
H	3.8868862	1.2826381	-3.9415265
C	4.2602235	1.9317365	-1.9078735
H	5.2061232	2.4096734	-2.1322516
C	3.7941468	1.8959917	-0.6204452
H	4.3662771	2.3171878	0.1913137
C	2.5562414	1.2718423	-0.3322926
C	1.6605174	-0.1211132	-3.6841924
C	2.0074629	-1.4784468	-3.8355320
C	1.4462289	-2.2057070	-4.8857446
H	1.7037378	-3.2522856	-4.9980320
C	0.5904206	-1.6025625	-5.7944338
H	0.1666407	-2.1790441	-6.6078229
C	0.2896898	-0.2547135	-5.6656745
H	-0.3646442	0.2241414	-6.3842892
C	0.8187992	0.5042527	-4.6219206
C	3.0385585	-2.1378736	-2.9553235
H	4.0457194	-1.8231637	-3.2440862
H	2.9907944	-3.2226990	-3.0511072
H	2.9149401	-1.8867193	-1.9027970
C	0.5207469	1.9776473	-4.5521986
H	0.1763859	2.2736723	-3.5636538
H	-0.2538287	2.2493372	-5.2682197
H	1.4113787	2.5709484	-4.7757597
C	2.7561497	1.7272051	2.0213718
C	2.6304139	3.1074713	2.3191824
C	3.2443384	3.6076535	3.4678265
H	3.1457656	4.6605004	3.7013795
C	3.9896803	2.7998508	4.3093221
H	4.4484361	3.2104781	5.2006400
C	4.1732717	1.4711544	3.9722626
H	4.7979620	0.8466358	4.5987579
C	3.5937277	0.9193150	2.8294385
C	1.9420218	4.1099748	1.3993431
H	1.4821757	3.5563148	0.5826155
C	0.8389434	4.9174354	2.0987242
H	0.0037525	4.2871969	2.3974622
H	0.4539081	5.6877141	1.4284027
H	1.2127921	5.4241545	2.9904156
C	2.9731417	5.0822949	0.7929782
H	2.4925202	5.7473863	0.0722385
H	3.7746833	4.5557758	0.2764479
H	3.4258177	5.7053364	1.5677753
C	3.9649430	-0.5125151	2.4713360
H	3.4416805	-0.7706097	1.5548130
C	5.4696826	-0.6403776	2.1757810
H	5.7795922	0.0479559	1.3873740
H	5.7025278	-1.6561668	1.8470615
H	6.0750279	-0.4302973	3.0607773
C	3.5376322	-1.5197089	3.5478690
H	4.0657135	-1.3474681	4.4889223
H	3.7596591	-2.5386850	3.2229471
H	2.4685243	-1.4577479	3.7551374

5. References

- [1] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch., Teil B* **1981**, 36B, 16.
- [2] J.-C. Guillemin, T. Janati, J.-M. Denis, *J. Org. Chem.* **2001**, 7864.
- [3] T. Allspach, M. Regitz, G. Becker, W. Becker, *Synthesis* **1986**, 31.
- [4] a) A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem. Int. Ed.* **2008**, 47, 7246; b) A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, 120, 7356.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339.
- [6] G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3.
- [7] G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3.
- [8] a) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* **2014**, 4, 91; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, 162, 165; c) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, 102, 346
- [9] TURBOMOLE V6.4, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, <http://www.turbomole.com>
- [10] a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, 242, 652; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, 97, 119.
- [11] a) P. A. M. Dirac, *Proc. Royal Soc. A* **1929**, 714; b) J. C. Slater, *Phys. Rev.* **1951**, 385; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 1200; d) A. D. Becke, *Phys. Rev. A* **1988**, 3098; e) A. D. Becke, *J. Chem. Phys.* **1993**, 5648; f) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 785.
- [12] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Letters* **1998**, 294, 143; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297.
- [13] M. Sierka, A. Hogeckamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, 118, 9136.