Effect of ligand modification on the reactivity of phosphinoamide-bridged heterobimetallic Zr/Co complexes

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SUPPORTING INFORMATION

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Table S1. Selected bond lengths and angles and N_2 stretching frequencies of **4** and $N_2Co(^iPr_2PNMes)_3ZrTHF$ (**1**)[1] as determined by X-ray crystallography (averages of two independent molecules in the asymmetric unit cell of each complex are reported).

Bond length (Å)	**1**	**4**	Angle (°)	**1**	**4**
Zr-Co	2.362(1)	2.382(5)	N4-Co-Zr	177.2(2)	177.9(3)
Co-N4	1.838(5)	1.840(5)	O-Zr-Co	173.3(7)	163.1(11)
Zr-O	2.452(5)	2.329(1)	N4-Co-P1	104.2(2)	104.7(2)
Co-P1	2.222(2)	2.228(8)	N4-Co-P2	107.8(2)	105.5(4)
Co-P2	2.230(2)	2.240(10)	N4-Co-P3	103.2(2)	106.7(10)
Co-P3	2.232(1)	2.232(5)	O-Zr-N1	98.7(2)	108.5(7)
Zr-N1	2.167(4)	2.080(2)	O-Zr-N2	90.2(2)	86.5(5)
Zr-N2	2.172(4)	2.141(2)	O-Zr-N3	88.6(1)	85.8(3)
Zr-N3	2.145(4)	2.155(10)	N5-N4-Co	177.8(10)	178.5(11)
N4-N5	1.132(7)	1.110(1)	**ν-N_2 (cm^{-1})**	**2026**	**2045**

Table S2. X-ray Diffraction Experimental Details for **4** and **5**

	4	**5**
chemical formula	$C_{46}H_{77}Co_1N_5P_3O_1Zr_1$	$C_{42}H_{69}Br_2Co_1N_3P_3Zr_1$
fw	959.22	1018.91
T (K)	120	120
λ (Å)	0.71073	0.71073
a (Å)	22.9948(17)	12.0391(3)
b (Å)	22.4923(17)	19.7151(5)
c (Å)	19.5321(14)	21.9331(6)
α (deg)	90	90
β (deg)	106.602(4)	97.6840(10)
γ (deg)	90	90
V (Å^3)	9681.0(13)	5159.1(2)
space group	$P2_1/c$	$P2_1/n$
Z, Z'	8, 2	4, 1
D_{calcd} (g/cm^3)	1.316	1.312
μ (cm^{-1})	0.696	2.194
R1, wR2[a] ($I > 2\sigma$)	0.0405, 0.1006	0.0291, 0.0713

[a] $R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Figure S1. Full cyclic voltammogram of ICo(^{i}Pr$_2$PNXyl)$_2$(μ-I)Zr(^{i}Pr$_2$PNXyl) (**3**) (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s).

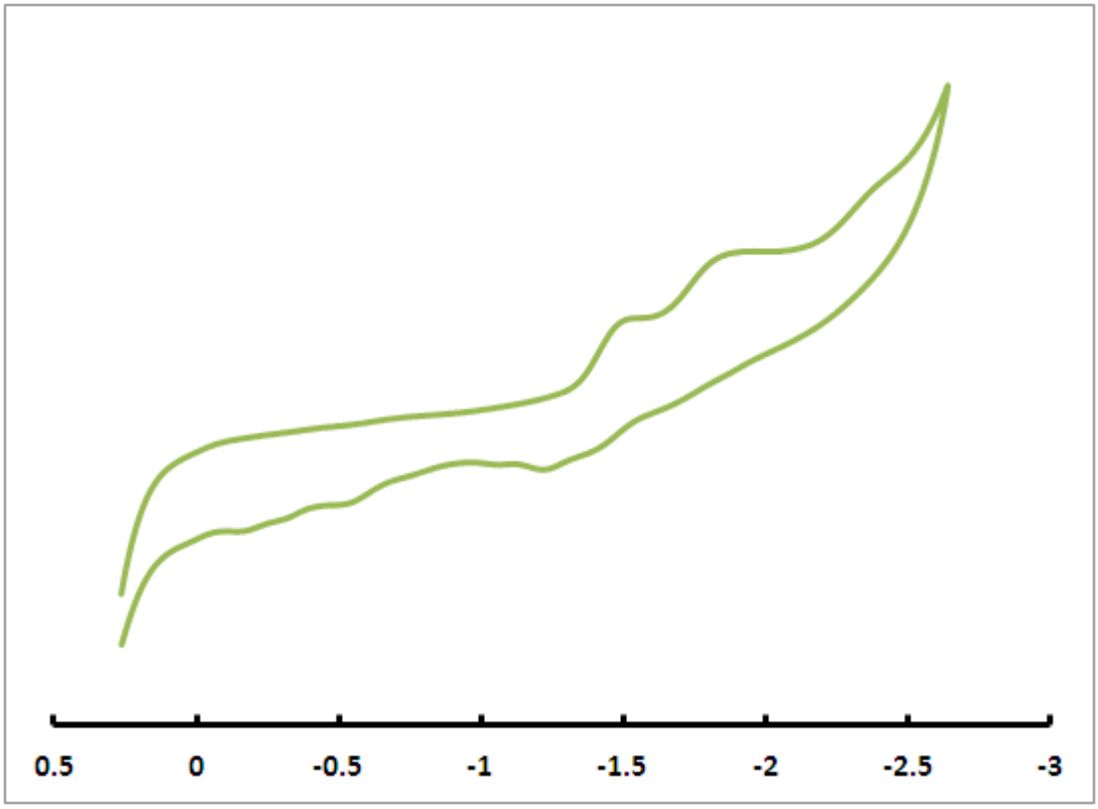


Figure S2. Cyclic voltammogram of ICo(^{i}Pr$_2$PNAr)$_2$(μ-I)Zr(^{i}Pr$_2$PNAr) (**3**) at different scan rates, showing the scan rate dependency of the reversibility of the two reductive processes (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s-1000mV/s).

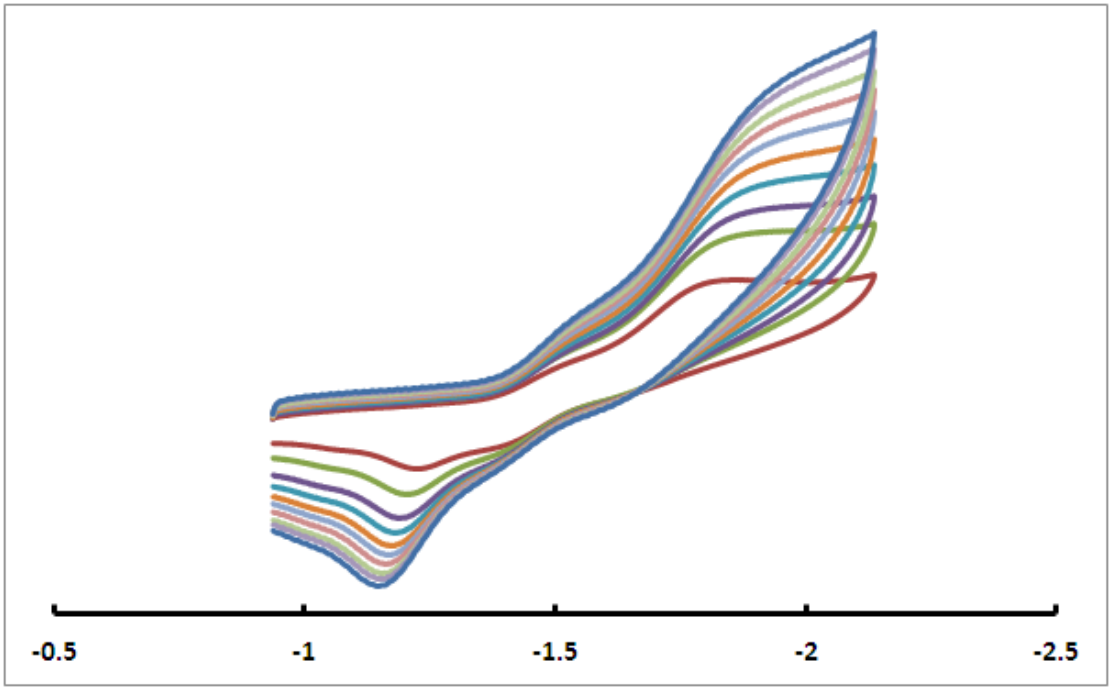


Figure S3. ^{1}H NMR spectrum of **3** (C_6D_6).

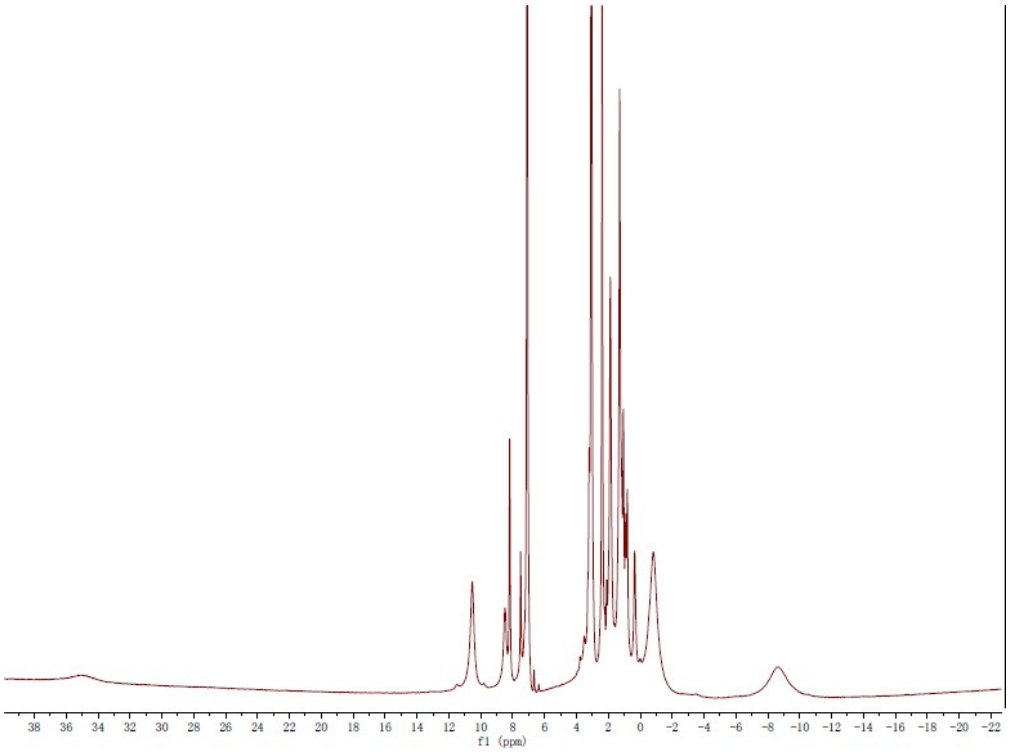


Figure S4. ^{1}H NMR spectrum of **5** (C_6D_6).

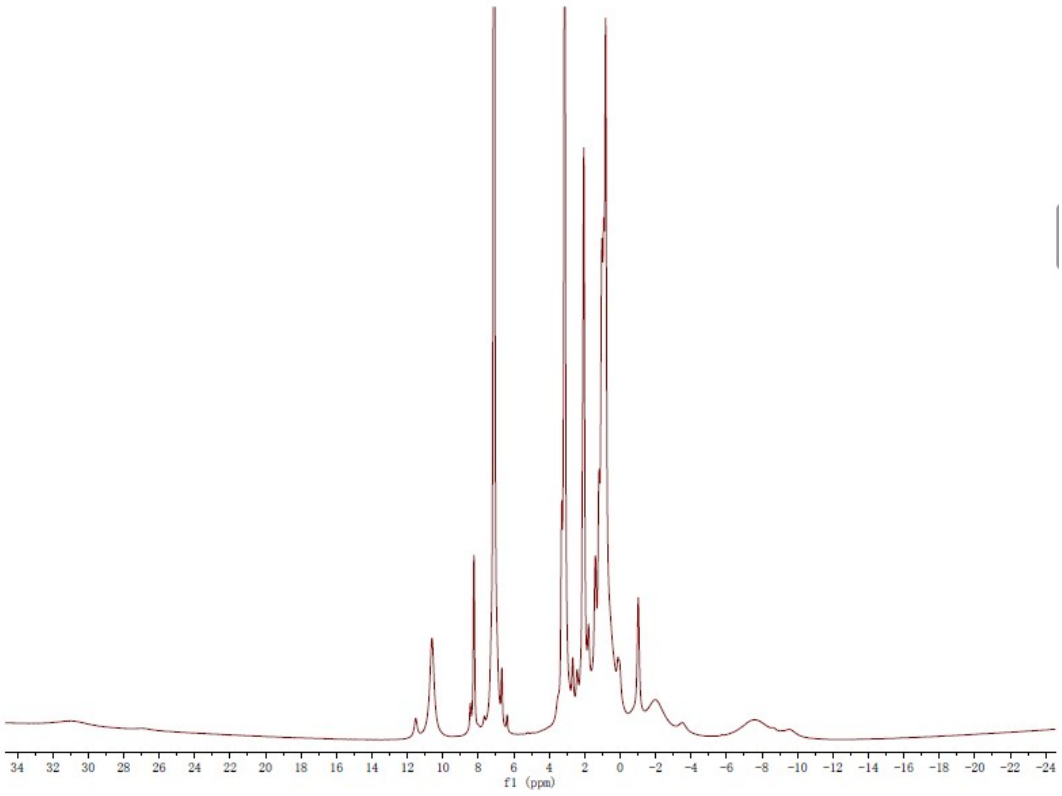


Figure S5. Comparison of selected region of the ^{1}H NMR spectrum (C_6D_6) of **3** (left) and the reaction of **4** with MeI (right). The extra peak at δ 0.80 corresponds to ethane.

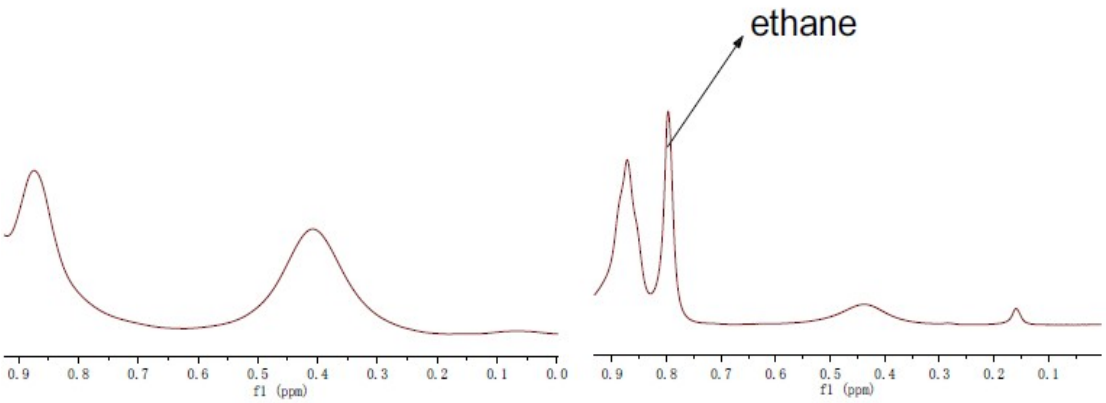
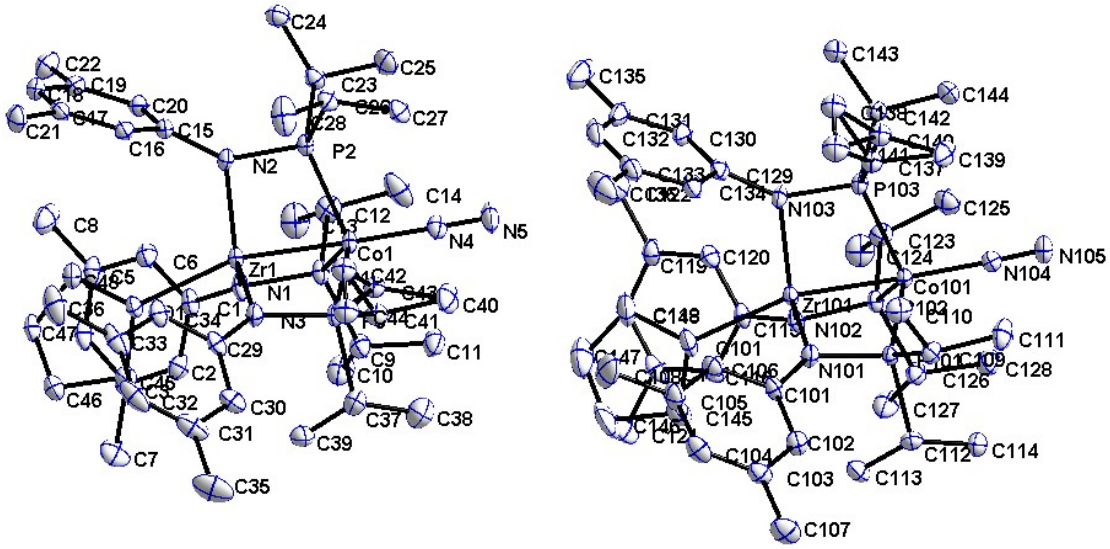


Figure S6. Fully-labelled displacement ellipsoid (50%) representation of **4**. All hydrogen atoms have been omitted for clarity.

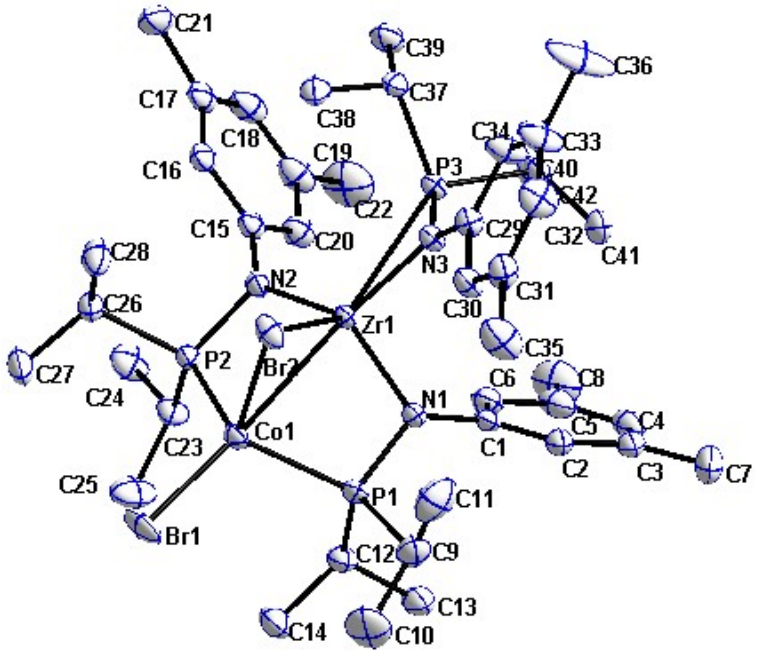


X-Ray data collection, solution, and refinement for 4. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKa radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[2] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.2%. A total of 2114 frames were collected. Final cell constants were obtained from the xyz centroids of 9917 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip*,[3] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[4] All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[5] Disorder of an isopropyl group on each of the molecules was observed. The disorder was modeled by using two components for each case. Occupancies of the major/minor components (molecule 1: (C(43)/C(44))/(C(41)/C(42)) and molecule 2: (C(137)/C(138))/ (C(140)/C(141)) were constrained to sum to 1.0; the major component occupancies for the two models refined to values of 0.514(8) and 0.861(8), respectively. Atoms involved in the disorder were refined using isotropic displacement parameters. An attempt to model the disordered isopropyl group containing atoms C(37), C(38), and C(39) led to unreasonable contacts and no improvement in R, and was therefore abandoned. The

final least-squares refinement converged to R_1 = 0.0405 ($I > 2s(I)$, 15829 data) and wR_2 = 0.1006 (F^2, 25761 data, 1025 parameters). The final CIF is available as supporting material.

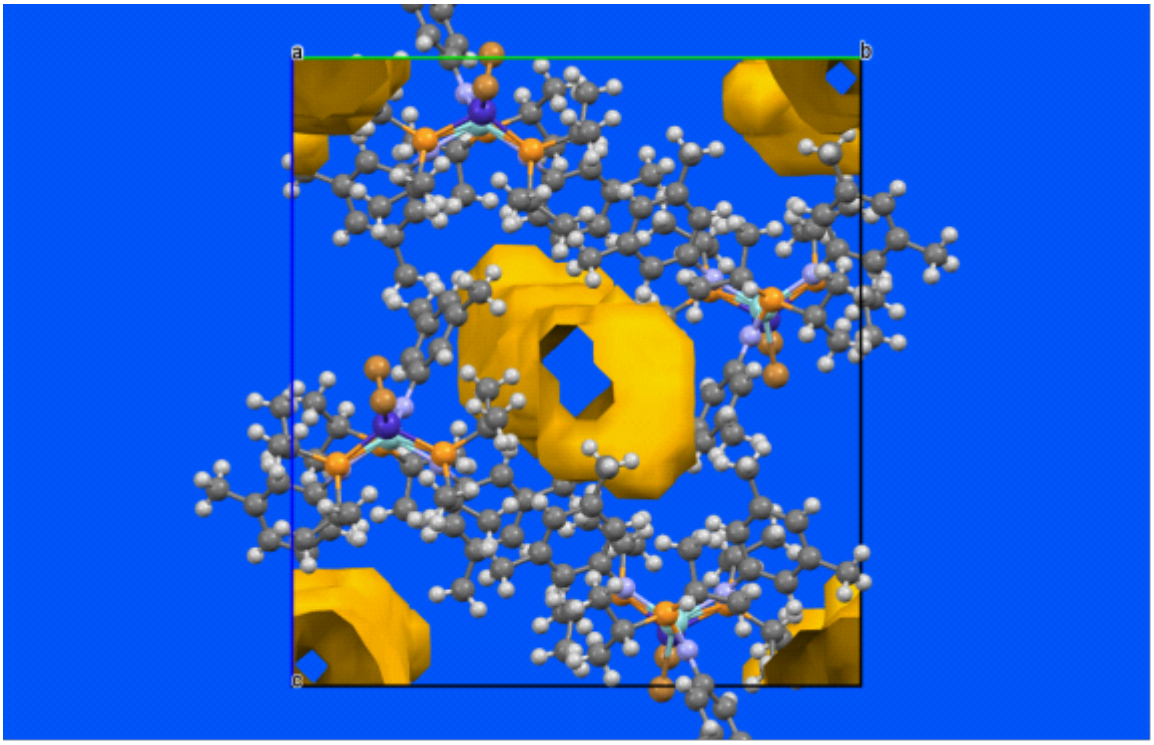
Figure S7. Fully-labelled displacement ellipsoid (50%) representation of **5**. All hydrogen atoms have been omitted for clarity.



X-Ray data collection, solution, and refinement for 5. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKa radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software. Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 135K, using a frame time of 40 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of two phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 99.9%. A total of 1988 frames were collected. Final cell constants were obtained from the xyz centroids of 9875 reflections after integration.

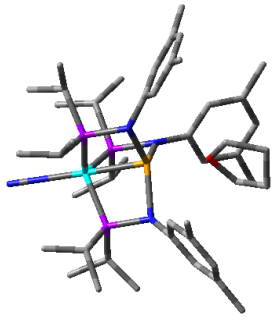
From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/n$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,[6] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program. The asymmetric unit contains one molecule of the complex, and *ca.* one molecule of pentane, which required modeling by the SQUEEZE procedure (for the complex, Z = 4; Z' = 1), as modeled using the SQUEEZE procedure (see below). All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. During the structure solution, electron density difference maps revealed that there were disordered solvent molecule(s) which could not be

successfully modeled. The pentane solvate was highly disordered in a volume PLATON SQUEEZE reported to be 704.8 Å^3 per unit cell (13.6%). It appeared that the cavity area contained *ca.* four pentane molecules, located near the centers of symmetry at (0, 0, 0) and (0, ½, ½) as shown in the *bc* projection below.[7]



Modeling with or without restraints was unsuccessful, as was step by step acquisition of peaks using successive electron density difference maps. Thus, the structure factors were modified using the PLATON SQUEEZE[8] technique, in order to produce a "solvate-free" structure factor set. PLATON reported a total electron density of 158 e$^-$ per unit cell, likely representing four pentane molecules, consistent with our earlier observations. Use of the SQUEEZE technique resulted in a decrease of *ca.* 1.3 % in *R*. The final least-squares refinement converged to R_1 = 0.0291 ($I >$ 2s(I), 9631 data) and wR_2 = 0.0713 (F^2, 12445 data, 469 parameters). The final CIF is available as supporting material.

Table S8. XYZ coordinates of the DFT-optimized geometry of **4**.



Symbol	X	Y	Z
Zr	0.022522	0.095877	0.170779
Co	-0.49218	-1.67282	-1.41622
P	-0.28606	0.215833	-2.60476
P	-2.22579	-1.59594	0.001123
P	1.428336	-2.28382	-0.41857
O	0.429424	1.698854	1.909748
N	0.092989	1.482478	-1.45388
N	-1.86041	-0.31467	1.125553
N	1.769341	-1.01819	0.715978
N	-0.86637	-2.97622	-2.61397
N	-1.10145	-3.79539	-3.37447
C	0.916791	2.633535	-1.62957
C	2.336937	2.524252	-1.51872
C	3.181724	3.655531	-1.63193
C	2.592606	4.931881	-1.83353
C	1.184234	5.081112	-1.92804
C	0.362544	3.930883	-1.81767
C	-1.90596	0.73238	-3.47427
C	-2.13826	2.241156	-3.73232
C	-2.16127	-0.11301	-4.75307
C	1.101192	0.318316	-3.91035
C	1.106437	1.566625	-4.83317
C	1.207025	-0.98051	-4.75416
C	-2.73711	0.630192	1.73347
C	-3.24345	0.457873	3.053797
C	-4.05739	1.440785	3.672345
C	-4.36264	2.630286	2.959731
C	-3.87154	2.840813	1.644219
C	-3.05661	1.844982	1.052107
C	-2.44969	-3.1985	1.019638
C	-3.09109	-3.07602	2.423266
C	-3.12203	-4.31407	0.173299
C	-3.93686	-1.13408	-0.70343
C	-5.14936	-1.22997	0.260635

C	-4.24135	-1.86607	-2.03886
C	2.633706	-0.89426	1.837302
C	3.593783	0.160688	1.863375
C	4.4147	0.393384	2.993146
C	4.26903	-0.44467	4.130898
C	3.31929	-1.49936	4.144147
C	2.50275	-1.70462	3.003403
C	2.944835	-2.32805	-1.57312
C	2.908694	-3.55155	-2.5288
C	4.339752	-2.16479	-0.91544
C	1.411771	-3.94238	0.531266
C	0.668333	-5.0533	-0.26111
C	2.769839	-4.48234	1.056422
C	0.422755	3.191298	1.788021
C	0.619544	3.711886	3.22301
C	-0.06789	2.614886	4.081255
C	0.341364	1.321054	3.357684
H	-2.64983	0.415118	-2.71703
H	-1.39097	2.677494	-4.41689
H	-2.11099	2.806328	-2.78555
H	-3.14076	2.386883	-4.18512
H	-3.22214	-0.01631	-5.05826
H	-1.95289	-1.18582	-4.59323
H	-1.54219	0.236912	-5.60001
H	2.003863	0.374182	-3.26562
H	2.043663	1.577323	-5.42617
H	0.266071	1.53934	-5.55099
H	1.055016	2.5117	-4.26753
H	2.156593	-0.97623	-5.32691
H	1.18445	-1.88082	-4.1197
H	0.379752	-1.06081	-5.48113
H	-1.3931	-3.49708	1.17384
H	-2.49827	-2.40141	3.06463
H	-4.12721	-2.69841	2.385237
H	-3.11038	-4.07363	2.908977
H	-2.70378	-4.36871	-0.84762
H	-2.96415	-5.2984	0.657117
H	-4.21361	-4.15811	0.092573
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H	-6.04372	-0.80039	-0.23536
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H	-4.53172	-2.91805	-1.86773
H	-5.08637	-1.36711	-2.55535

H	-3.36787	-1.86521	-2.71145
H	2.758321	-1.41953	-2.18223
H	1.90691	-3.7091	-2.96668
H	3.624714	-3.40033	-3.36092
H	3.205856	-4.47843	-2.00348
H	5.102548	-2.00842	-1.70607
H	4.370159	-1.29784	-0.2353
H	4.636107	-3.05921	-0.34093
H	0.780125	-3.68181	1.409
H	-0.29817	-4.69735	-0.65242
H	1.265871	-5.40821	-1.12007
H	0.485019	-5.92409	0.400705
H	3.364329	-3.71358	1.576578
H	2.583618	-5.31111	1.770136
H	3.377821	-4.89718	0.231408
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H	1.225075	3.46674	1.08489
H	1.694813	3.780796	3.471291
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H	5.175034	4.390072	-1.10916
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H	1.733587	-2.48628	3.024299
H	3.678478	0.807545	0.980128
C	5.454934	1.507342	2.977043
H	5.142393	2.342262	2.323559
H	5.633273	1.911031	3.990729
H	6.427465	1.13648	2.596137
C	3.178028	-2.40449	5.362254
H	3.554997	-1.9145	6.27828
H	2.123687	-2.69035	5.534125
H	3.753241	-3.34236	5.228389

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