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Structural Isomers of the Chromium Bis(phosphoranimine)methanide Complex $[(HC(PPh_2NSiMe_3)_2)Cr(\mu\text{-}Cl)]_2$

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Summary: The species $[(HC(PPh_2NSiMe_3)_2Cr(\mu\text{-}Cl)_2]$ *was prepared and structurally characterized. It is shown to exist in two structural isomers: one in which the Cr center adopts a pseudo-square-planar coordination geometry and another where the metal coordination sphere is better described as trigonal bipyramidal. Preliminary assessment of the catalytic activity in ethylene polymerization is also reported.*

The longstanding efforts of Dehnicke and co-workers[1] have demonstrated the unique nature of phosphoranimine ligand complexes for a wide variety of elements. Recent studies have further increased interest in this class of ligands. For example, while others have alluded to the electronic analogy between phosphoranimide and cyclopentadienyl ligands,[1] we have exploited the steric analogy between these ligands[2] to develop active and, in some cases, remarkably active catalysts for ethylene polymerization.[3] Related systems have also been shown to prompt multiple C−H bond activations of $Ti-CH_3$ fragments[4] and the formation of unprecedented dizwitterions.[5] In a more fundamental vein, we[6] and Cavell and co-workers[7] have reported the synthesis of the dilithiomethane derivative $[Li_2C(PPh_2NSiMe_3)_2]_2$. Cavell et al. have developed the intriguing chemistry of this dilithio species, reporting the unique and extremely interesting carbene complexes of Ti and Zr,[8,9] Hf,[9] Sm,[10] and Cr.[11] Related studies of the monolithio derivative $LiCH(PPh_2NSiMe_3)_2$ have received much less attention but are of interest due to the structural analogy to β-diimine ligands. In this communication, the ligand bis(phosphoranimine)methanide is used to prepare the complex $[HC(PPh_2NSiMe_3)_2Cr(\mu\text{-}Cl)]_2$. This species is shown to exist in two isomeric forms, reflecting the conformational flexibility of this ligand.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and Innovative Technologies, Braun, or Vacuum Atmospheres inert-atmosphere gloveboxes. Solvents were purified employing Grubb-type column systems manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. ^{31}P NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H_3PO_4. Guelph Chemical Laboratories performed combustion analyses.

Synthesis of $[HC(PPh_2NSiMe_3)_2Cr(\mu\text{-}Cl)]_2$ (1). To a stirred solution of $(THF)_2CrCl_2$ (0.040 g, 0.325 mmol) in THF (5 mL) was added dropwise a solution of $LiCH(PPh_2NSiMe_3)_2$ (0.325 mmol) in THF (5 mL). The reaction turned dark green and was stirred overnight. The THF was removed in vacuo, the residue was extracted into benzene, and the extract was filtered through Celite. Removal of the solvent gave a green solid. Yield: 0.11 g, 55%. Green crystals of **1a**/**1b** were obtained from a slow evaporation of the benzene solution. Anal. Calcd (found) for $C_{31}H_{39}P_2N_2Si_2CrCl\cdot LiCl$: C, 54.15 (53.91); H, 5.71 (6.38); N, 4.07 (3.80). $^{31}P\{^1H\}$NMR (C_6H_6): δ −4.4. ^1H NMR (C_6D_6): δ 7.68 (8H, br), 7.03 (12H, br), 3.28 (1H, t), 0.26 (18H, s). $^{13}C\{^1H\}$ NMR (C_6D_6; partial): δ 143.8, 142.6, 131.0, 4.7. $\mu_{eff} = 4.25\ \mu_B$. Crystal data for **1a**/**1b** cocrystal: triclinic, $P\bar{1}$, $a = 11.895(8)$ Å, $b = 16.738(11)$ Å, $c = 18.430(12)$ Å, $\alpha = 106.427(11)°$, $\beta = 96.891(12)°$, $\gamma = 97.885(13)°$, $V = 3437(4)$ Å^3, $Z = 2$, $\mu = 0.596$ mm^{-1}, $R = 0.0361$, $R_w = 0.0815$, for 9800 reflections with $F_o^2 \geq 3\sigma(F_o^2)$.

In a similar fashion performance of the reaction in THF affords **1b** alone. $\mu_{eff} = 4.29\ \mu_B$. Crystal data for **1b**: triclinic, $P\bar{1}$, $a = 9.859(6)$ Å, $b = 11.918(7)$ Å, $c = 15.560(10)$ Å, $\alpha = 102.603(12)°$, $\beta = 93.100(10)°$, $\gamma = 104.091(12)°$, $V = 1719.4(18)$ Å^3, $Z = 2$, $\mu = 0.595$ mm^{-1}, $R = 0.0377$, $R_w = 0.0861$, for 4910 reflections with $F_o^2 \geq 3\sigma(F_o^2)$.

Ethylene Polymerization. A 1 L autoclave was dried under vacuum (10^{-2} mmHg) for several hours. Toluene (500 mL) was transferred into the vessel under a positive pressure of N_2 and was heated to 30 °C. The temperature was controlled (to ca. +2 °C) with an external heating/cooling bath and was monitored by a thermocouple that extended into the polymerization vessel. A solution of MAO (500 equiv) in toluene was injected, and the mixture was stirred for 3 min at 150 rpm. The precatalyst in a solution of toluene was then injected while the reaction mixture was stirred for 3 min further at the same rate. The rate of stirring was increased to 1000 rpm, and the vessel was vented of N_2 and pressurized with ethylene (33 psi).

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Any recorded exotherm was within the allowed temperature differential of the heating/cooling system. The solution was stirred for 1 h, after which time the reaction was quenched with 1 M HCl in MeOH. The precipitated polymer was subsequently washed with MeOH and dried at 100 °C for at least 24 h prior to weighing.

X-ray Data Collection and Reduction. The crystals of **1a**/**1b** and **1b** were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected for a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized above. The observed extinctions were consistent with the space groups in each case. A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy-atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The methine protons on the central carbon of the bis(phosphanimine)methanide ligands were located and refined in both structural studies. The remaining hydrogen atom contributions were calculated, but not refined. CIF files have been deposited as Supporting Information.

Results and Discussion

Reaction of $Li[(HC(PPh_2NSiMe_3)_2]$ with $(THF)_2CrCl_2$ in THF proceeds with a concurrent color change to dark green. Removal of the solvent and recrystallization of the residue from benzene affords dark green crystals of compound **1** in 55% yield. This compound exhibits a single $^{31}P\{^1H\}$ NMR resonance at −4.4 ppm. The corresponding ^1H and partial $^{13}C\{^1H\}$ NMR resonances suggest the presence of the ligand. The magnetic moment of 4.25 μ_B is consistent with that of a Cr(II) species. The spectroscopic and analytical data suggest the empirical formula $[HC(PPh_2NSiMe_3)_2CrCl]$, which was confirmed by a crystallographic study.

Compound **1** crystallizes in the space group $P\bar{1}$ with two units each having the empirical formulation $HC(PPh_2NSiMe_3)_2CrCl$ per asymmetric unit. Each of these units are half of centrosymmetric dimeric molecules in which two chlorine atoms bridge the pair of related Cr centers. In each case, the anionic nature of the bis(phosphoranimine) ligand was confirmed by both the formulation and the location and refinement of the lone protons on the central carbon of the ligands. However, these two dimers exhibit distinctly different coordination geometries about Cr. In one of the dimers, **1a** (Figure 1a), the central carbon of the bis(phosphoranimine) ligand is coordinated to Cr (Cr−C = 2.264(3) Å). This is significantly longer that the Cr−C distance of 2.148(5) Å found in $[(C(PPh_2NSiMe_3)_2Cr)_2]$.[11] This carbon atom is essentially trans to chloride, as the C−Cr−Cl angle is 172.65(8)°. The Cr−Cl distances are 2.4054(16) and 2.4365(14) Å, while the Cr···Cr separation is 3.504(1) Å. The Cr−N distances are 2.096(3) and 2.423(3) Å, as the N atoms occupy positions that are best described as part of the equatorial plane of a distorted trigonal bipyramid. The distorted geometry arises from the NC chelation, as evidenced by the N−Cr−C angles of 74.81(10) and 70.38(10)°. It is also noteworthy that two phenyl rings on the adjacent P atoms are approximately parallel, suggestive of π-stacking.

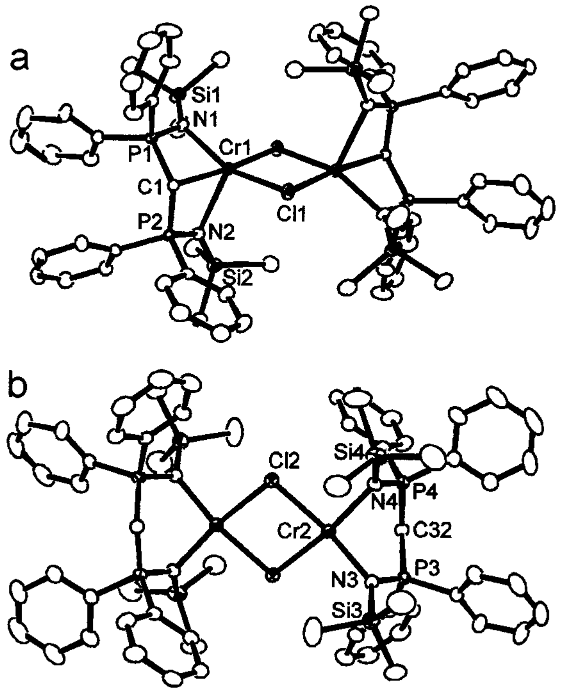

Figure 1. ORTEP drawings of the two conformations of $[(HC(PPh_2NSiMe_3)_2CrCl)_2]$ (**1**; 30% thermal ellipsoids are shown). Hydrogen atoms have been omitted for clarity. Bond distances (Å) and angles (deg) for the two conformations are as follows: (a) Cr(1)−N(1) = 2.096(3), Cr(1)−C(1) = 2.264(3), Cr(1)−Cl(1) = 2.4054(16), Cr(1)−N(2) = 2.423(3), Cr(1)−Cl(1) = 2.4365(14), Cr(1)−P(1) = 2.7310(16), N(1)−Cr(1)−C(1) = 74.81(10), N(1)−Cr(1)−Cl(1) = 98.51(7), C(1)−Cr(1)−Cl(1) = 172.65(8), N(1)−Cr(1)−N(2) = 103.54(9), C(1)−Cr(1)−N(2) = 70.38(10), Cl(1)−Cr(1)−N(2) = 108.88(7), N(1)−Cr(1)−Cl(1) = 149.91(7), C(1)−Cr(1)−Cl(1) = 100.03(8), Cl(1)−Cr(1)−Cl(1) = 87.30(5), N(2)−Cr(1)−Cl(1) = 102.35(7), Cr(1)−Cl(1)−Cr(1) = 92.70(5), P(1)−N(1)−Si(1) = 134.67(15), P(1)−N(1)−Cr(1) = 94.48(11), Si(1)−N(1)−Cr(1) = 130.42(13), P(2)−N(2)−Si(2) = 139.37(16), P(2)−N(2)−Cr(1) = 89.70(11), Si(2)−N(2)−Cr(1) = 128.98(12), P(1)−C(1)−P(2) = 126.46(18); (b) Cr(2)−N(4) = 2.112(3), Cr(2)−N(3) = 2.121(3), Cr(2)−Cl(2)′ = 2.4275(15), Cr(2)−Cl(2) = 2.4468(15), N(4)−Cr(2)−N(3) = 94.29(11), N(4)−Cr(2)−Cl(2)′ = 169.46(7), N(3)−Cr(2)−Cl(2)′ = 93.92(9), N(4)−Cr(2)−Cl(2) = 92.04(8), N(3)−Cr(2)−Cl(2) = 167.47(7), Cl(2)−Cr(2)−Cl(2)′ = 81.19(6), Cr(2)−Cl(2)−Cr(2)′ = 98.81(6), P(3)−N(3)−Si(3) = 127.88(15), P(3)−N(3)−Cr(2) = 106.80(12), Si(3)−N(3)−Cr(2) = 125.31(13), P(4)−N(4)−Si(4) = 134.05(16), P(4)−N(4)−Cr(2) = 106.24(13), Si(4)−N(4)−Cr(2) = 119.69(13), P(4)−C(32)−P(3) = 127.93(19).

The second fragment **1b** in the asymmetric units (Figure 1b) also constitutes half of a centrosymmetric

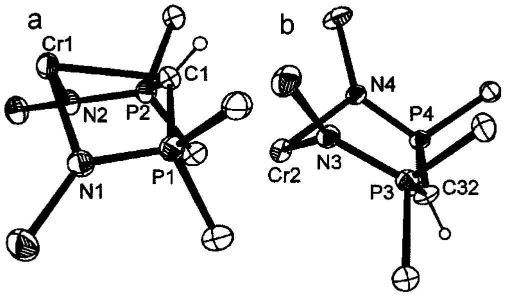

Figure 2. ORTEP drawings of the chelate ring geometry for the structural isomers **1a** and **1b**.

chloro-bridged dimer. The coordination sphere about Cr is comprised of the two chlorine atoms as well as two nitrogen atoms in a distorted-square-planar geometry. This is demonstrated by the pseudo-trans N−Cr−Cl angles of 169.46(7) and 167.47(7)°. The bite angle of the chelate ligand, i.e. N−Cr−N, is 94.29(11)°. The Cr−N distances are similar, averaging 2.116(4) Å, similar to that seen in the donor−acceptor species $(Me_3SiNPMe_3)_2$-$CrCl_2$ (2.117(2) Å).[12] These are similar to the shorter of the two Cr−N distances in **1a**. The Cr−Cl distances of 2.4275(15) and 2.4468(15) Å differ slightly and are similar to those seen in isomer **1a**. Another notable difference from **1a** is the significantly longer Cr−C distance of 2.921(3) Å in **1b**. The Cr···Cr separation in **1b** is 3.704(3) Å, longer than in **1a**, and these are consistent with the differing ligand binding geometries. In the pseudo-trigonal-bipyramidal case **1a**, due to steric demands, the nitrogen-bound $SiMe_3$ substituents are pulled away from the Cr center, whereas in the pseudo-square-planar case **1b**, these groups tend to crowd the Cr coordination sphere.

The metric parameters of the ligand backbones are also distinct in these two isomers. The P−N distances range from 1.575(3) to 1.608(3) Å, with the shortest P−N distance corresponding to the weaker Cr−N bond in **1a**. The P−C distances average 1.763(3) Å in **1a** and 1.722(3) Å in **1b**. The longer P−C distances in **1a** are consistent with both the presence of a formal Cr−C bond and strained four-membered rings formed by chelation. The P−C−P angles also differ slightly, being 126.46(18)° in **1a** and 127.93(19)° in **1b**.

The best description of the difference between the two isomers is based an examination of the geometry of the chelate ring. In **1a** CrN_2P_2C adopts a pseudo-boat conformation resulting from the proximity of the Cr and the transannular C atom. Presumably, the interaction of Cr with C results in ligand adjustments and the observed pseudo-trigonal-bipyramidal coordination sphere about Cr (Figure 2a). In the second isomer **1b** the chelate ring adopts a more pseudo-chairlike conformation (Figure 2b). This increases the Cr−C distance and gives rise to the observed pseudo-square-planar Cr coordination sphere. This geometry is similar to that seen in Zn and alkali-metal bis(phosphoranimine)methanide complexes.[13,14] The observation of both structural isomers in a single cocrystal suggests that the energy barrier between these two forms is low and that packing forces dictate the cocrystallization from solution.

This notion was further supported by the repetition of the reaction in THF. In this case, isolation of the product and the subsequent crystallographic study revealed the formation of **1b** alone. The metric parameters of **1b** found in this case were indistinguishable from those found in the initial crystallographic determination.

Preliminary screening shows **1** in the presence of 500 equiv of MAO catalyzes ethylene polymerization, generating 135 g of PE/(mmol h). GPC data for the resulting polymer reveal an M_w value of 344 000. However, the molecular weight distributions are very broad (PDI = 47), suggesting multisite catalysis. While the accessibility of different structural isomers may be only part of the rationale for this observation, it may account for the reactive nature of bis(phosphoranimine)methanide complexes in general.[13,14]

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Supporting Information Available: Tables giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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