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Chromium bis(phosphoranimine) complexes; bridging chromium carbenes with no CO or Cp supporting ligands†

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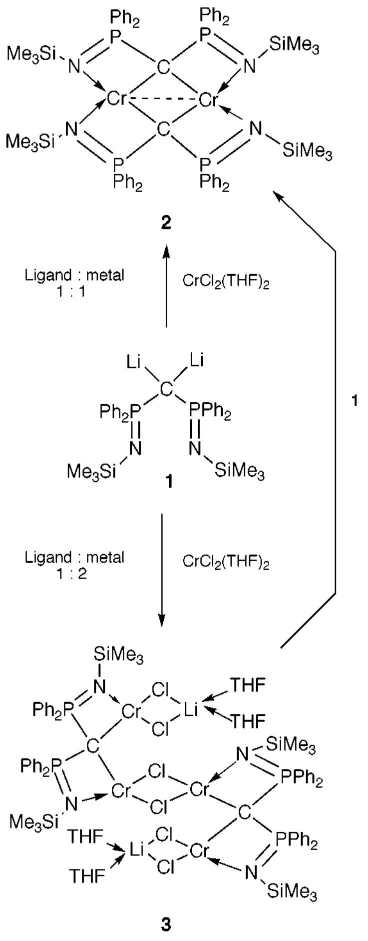
Novel dimeric and tetrametallic Cr(II) bridging carbene complexes supported by bis(phosphinimine) ligands are described.

Many carbene complexes have been synthesized since the first report by Fischer;[1] these extremely useful compounds have found widespread applications in organic synthesis and catalysis.[2–5] Chromium carbene chemistry is dominated by low-valent derivatives stabilized in general by carbonyl ligands.[6] High valent chromium carbene derivatives are rare[7–9] in contrast to the heavier group 6 metals, molybdenum and tungsten, which provide numerous examples of carbonyl-free carbene complexes.[3,4,10] Only three carbonyl-free chromium carbene complexes have been structurally characterized[11–13] although several attempts to make such chromium systems have been reported.[13–15] Here, we describe the synthesis and structure of a novel dimeric and tetrametallic carbene bridged chromium complexes obtained by a new route; the preliminary dilithiation of bis(iminophosphorano)methane[16,17] followed by the simple metathetical reaction of this salt with a metal halide. Using this and related routes we have recently prepared Ti and Zr carbene complexes.[18,19] The Cr complex described herein represents the first example of a bridging chromium carbene which is devoid of the usual carbonyl or cyclopentadienyl supporting ligands and it also represents the first example of a chromium carbene complex which contains two phosphorus substituents on the carbene carbon atom. In addition the partially substituted tetrachromium complex was also isolated and characterized.

Chromium dichloride (as the THF adduct) reacted with $Li_2\{C(Ph_2P{=}NSiMe_3)_2\}$ **1**[16,17] with elimination of 2 moles of LiCl to give $[Cr\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}]_2$ **2**‡ as a paramagnetic, red, air-sensitive crystalline solid (Scheme 1). A small quantity of a green complex was also isolated from the 1:1 reaction which proved to be the partially substituted tetranuclear complex $[Cr_2(\mu\text{-}Cl)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}(LiCl)(THF)_2]_2$ **3**. The latter was prepared in good yield by the reaction of 0.5 molar equivalent of the ligand with the metal precursor.§ The room temperature magnetic moments for **2** and **3**, respectively, were 2.76 μ_B (for the dimer) and 6.28 μ_B (for the tetrachromium unit). The magnetic moments of **2** and **3** are too low to account for the total number of unpaired electrons for Cr(II) which suggests interaction between the metals. The Cr–Cr bond distances in **2** and **3** however are not indicative of strong metal–metal interactions.[20]

The molecular structure of $[Cr\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}]_2$ **2**¶ (Fig. 1)[21] shows the complex to be a dimer with two independent molecules in the asymmetric unit. The basic framework of **2** consists a central square plane of two chromium atoms bridged by two carbene centers to form a planar Cr_2C_2 four membered, ring. The ligand backbone forms four fused, four-membered rings which are assembled from the bridging carbene carbon, the metal, the phosphorus and the imine nitrogen atoms. These four Cr, N, P, C rings arrange themselves above and below the central Cr_2C_2 plane to create a saddle-like structure in which the geometry around each Cr is approximately tetrahedral. Each of the iminophosphorane nitrogen units coordinate to the metal so that the ligand adopts a μ_2-κ^4 coordination. The two planar four-membered metallocyclic rings in **2** which are subtended around a specific carbene center [Cr(1), N(1), P(1), C(1) and Cr(2), N(2), P(2), C(1)] and [Cr(1), N(3), P(3), C(2) and N(4), P(4), C(2), Cr(2)] make respective dihedral angles of 46.8(1) and 44.8(2)°. The two different molecules in **2** have slightly different Cr–Cr distances averaging 2.573(2) Å.

The molecular structure of the tetranuclear chromium complex $[Cr_2(\mu\text{-}Cl)_2\{\mu_2\text{-}C(Ph_2P{=}SiMe_3)_2\text{-}\kappa^4C,C',N,N'\}\text{-}(LiCl)(THF)_2]_2$ **3** has been determined and substantiates the arrangement shown in Scheme 1 but is not illustrated here (see electronic supplementary information). This complex also contains carbene centers bridging two chromium atoms [Cr(1), Cr(2)] but in this case there are two types of Cr centers. One type forms a central Cr_2Cl_2 unit with a chlorine bridged Cr–Cr



Scheme 1

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† Electronic supplementary information (ESI) available: crystal structure of **3**, metrical parameters and crystal data. See http://www.rsc.org/suppdata/cc/1999/1993

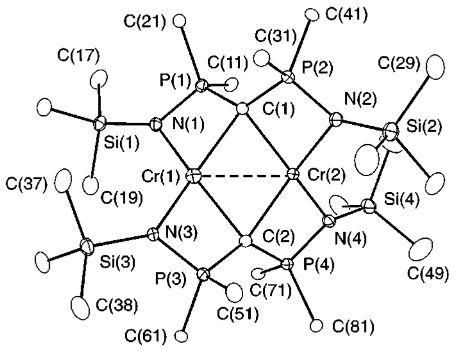

Fig. 1 An ORTEP[21] view of one of the crystallographically independent molecules of **2** showing the atom labelling scheme. The hydrogen atoms and phenyl carbon atoms except for *ipso*-C have been removed for clarity and the remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances (Å) and angles (°) for molecule A: Cr(1)–C(1) 2.148(5), Cr(2)–C(1) 2.137(5), Cr(1)–C(2) 2.150(5), Cr(2)–C(2) 2.128(5), Cr(1)–N(1) 2.103(5), Cr(1)–N(3) 2.093(5), Cr(2)–N(2) 2.091(4), Cr(2)–N(4) 2.081(4), Cr(1)–Cr(2) 2.569(1), N(1)–P(1) 1.605(5), P(1)–C(1) 1.702(6), P(2)–C(1) 1.724(6), P(2)–N(2) 1.603(5); Cr(1)–C(1)–Cr(2) 73.7(2), N(1)–Cr(1)–C(1) 76.2(2), N(2)–Cr(2)–C(1) 77.0(2), C(1)–Cr(1)–C(2) 105.7(2), P(1)–C(1)–P(2) 132.0(3), N(1)–P(1)–C(1) 105.0(3).

distance of 3.508(1) Å. Each of these Cr atoms is then also bound to a bridging carbene unit connecting it to another chromium and the distance between these carbon bridged Cr atoms is 2.9425(8) Å. The second type of Cr atom is connected to a solvated Li center *via* two chloride bridges. Imine nitrogens complete the roughly tetrahedral coordination about the Cr. There are two four-membered rings subtended from each carbene center and the dihedral angle between these two planar four-membered rings is 60.97(9)°. Both Cr–Cr distances in **3** are longer than those in **2**. The Cr–Cr distances in **2** fall in between the alkyl bridging distances in [{Cp*Cr(μMe)}$_2$(μ-CH$_2$)] [2.394(1) Å)][12] and [Cp*Cr(μ-CHSiMe$_3$)]$_2$ [2.687(4) Å].[11] The Cr–C distances in **2** [2.137(5) Å] and in **3** [2.170(3) Å] are slightly longer than those in the aforementioned Cr(III) alkylidene complexes, 2.042(8)[12] and 2.013(12) Å[11] respectively. As expected for neutral amine coordination, the Cr–N distances in **2** and **3** are longer than observed for Cr-amide complexes.[22]

The bond distances within the bicyclic framework of both **2** and **3** are also considerably altered relative to corresponding values in free bisiminophosphoranomethane ligands;[23,24] the P=N bond distances are slightly elongated and the endocyclic P–C bond distances are significantly shorter but the exocyclic P–C bond distances are not affected. These factors suggest that there is a delocalization of π-electron density within each of the two four membered rings. The P–C–P bond angles [av. 131.7(3)° in **2** and 131.4(2) in **3**)] are significantly expanded compared to the corresponding values in MeCH{Ph$_2$P=N(C$_6$H$_4$Me-*p*)}$_2$ [112.39(19)°][23] as well as in H$_2$C{Cy$_2$P=NSiMe$_3$}$_2$ [117.41(12)°].[24]

Thus we have prepared and structurally characterized a novel dimeric and tetranuclear chromium carbene complexes **2** and **3** wherein the bridging carbene is supported by phosphinimines. Access to such complexes is straightforward given the availability of the new dilithium salt. Reactivity studies of these new carbene complexes are presently being pursued.

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Notes and references

‡ *Preparation of* **2**: all experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. The dilithium salt Li$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ **1**,[16] (0.32 g, 0.56 mmol) was added to a stirred suspension of CrCl$_2$(THF)$_2$ (0.15 g, 0.56 mmol) in THF (10 ml) at room temp. The reaction mixture turned green and then red. The mixture was stirred at room temp. for 2 days. The solvent was then evaporated and the residue was extracted with 8 ml of diethyl ether and filtered to remove LiCl. The diethyl ether solution was reduced to one-half volume, and the red crystalline product, which deposited at room temp. over a period of two days, was filtered off and dried under vacuum. Yield: 0.19 g, 55.6%, μ_{eff} = 2.76 μ_{B}.

§ *Preparation of* **3**: anaerobic techniques were used. To a stirred suspension of CrCl$_2$(THF)$_2$ (0.20 g, 0.75 mmol) in THF (10 ml), the dilithium salt Li$_2$C(Ph$_2$P=NSiMe$_3$)$_2$ **1**,[16] (0.21 g, 0.37 mmol) was added at room temp. The reaction mixture turned green and was stirred at room temp. for 1 day. The solvent was then evaporated and the residue was extracted with 15 ml of diethyl ether and filtered to remove LiCl. The diethyl ether solution was reduced to one-half volume 1 ml of THF was added, and the solution cooled at −15 °C for 3 days to give a green crystalline product which was filtered off and dried under vacuum. Yield: 0.21 g, 61.1%. μ_{eff} = 6.28 μ_{B}.

¶ *Crystal data* for **2**: monoclinic, $P2_1/n$ (a non-standard setting of $P2_1/c$, no. 14), a = 22.1588(9), b = 26.7524(12), c = 23.2798(11) Å, β = 96.410(1)°, V = 13714.0(11) Å^3, Z = 4, μ = 0.522 mm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares procedures: R_1 = 0.0774 and 0.1512, (wR_2 = 0.2099 and 0.2480) for 12700 reflections with $F_o{}^2 \geqslant 2\sigma(F_o{}^2)$ and all data, respectively. CCDC 182/1397.

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