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One-electron oxidation of paramagnetic chromium(II) alkyl complexes with alkyl halides: synthesis and structure of five-coordinate chromium(III) complexes

Michael D. Fryzuk,*[a] Daniel B. Leznoff,[a] (the late) Steven J. Rettig † and Victor G. Young, Jr.[b]

[a] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1*
[b] *X-ray Crystallographic Center, Department of Chemistry, 160 Kolthoff Hall, University of Minnesota, Minneapolis, Minnesota 55455, USA*

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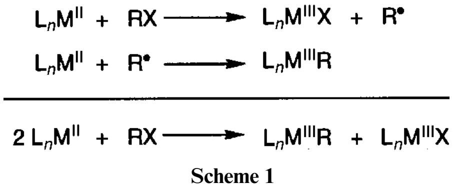
The reaction of square-planar, high-spin CrR[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (R = Me, CH$_2$SiMe$_3$) with alkyl halides (MeI, CF$_3$CH$_2$I, MeBr, PhCH$_2$Cl) generates one-electron oxidation products Cr(R)X[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], unusual examples of five-coordinate chromium(III) complexes. Cr(Me)Br[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] and Cr(CH$_2$SiMe$_3$)Cl[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] have been structurally characterized. Alkylation of the latter complex with LiCH$_2$SiMe$_3$ gave a five-coordinate Cr(III) dialkyl complex Cr(CH$_2$SiMe$_3$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], which was structurally characterized as well. Attempts to isolate sterically unencumbered Cr(III) dialkyl (*e.g.*, dimethyl) complexes resulted in decomposition. Addition of an excess of PhCH$_2$Cl to {[(Ph$_2$PCH$_2$SiMe$_2$)$_2$N]Cr}$_2$(μ-Cl)$_2$ resulted in halide-transfer to form CrCl$_2$(THF)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] in low yield. Reaction of the low-spin CrCp[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] complex with PhCH$_2$Cl, however, gave both Cr(Cp)(CH$_2$Ph)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] and Cr(Cp)Cl[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]. The five-coordinate Cr(III) alkyl halide complexes do not polymerize ethylene at 60 °C and 1 atm; the dialkyl complex Cr(CH$_2$SiMe$_3$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] does catalyze polyethylene formation but is quickly deactivated. A discussion comparing the structural distortions observed in these five-coordinate high-spin d^3 Cr(III) complexes with those observed in the analogous low-spin d^6 Ir(III) complexes is presented.

Introduction

Oxidative addition of a substrate to a metal complex is an important process in organometallic chemistry.[1,2] The most commonly examined oxidative addition reactions involve formal two-electron redox processes in which the oxidation state of the metal centre is increased by two. One-electron processes, on the other hand, have been less studied in an organometallic context.[1] For example, one very important group of substrates that undergoes oxidative addition reactions is alkyl halides. Studies on two-electron oxidative addition of substrates such as MeI to metal complexes L$_n$M^x to give L$_n$M^{x+2}(Me)(I) have been reported.[1,2] Chromium(II) complexes, however, are more likely to undergo one-electron oxidative addition, and this is indeed observed for reactions with alkyl halides. For example, the reactions of [Cr(H$_2$O)$_6$]$^{2+}$ with alkyl halides and other radical sources to generate aqueous organometallic Cr(III) cations have been well studied.[3–5] Although there are little structural data, mechanistic and kinetic data abound[6–9] and all support a radical-based atom abstraction mechanism,[10,11] shown in Scheme 1.



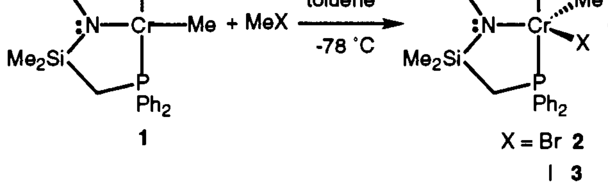
Scheme 1

More recently, 17-electron Cr(I) radical reactions with alkyl halides to give Cr(II) products have also been examined.[12–15] In this case, the chromium starting material, commonly a metal–metal bonded dimer such as [CpCr(CO)$_3$]$_2$, reacts cleanly only in cases where the metal-centred radicals are stable with respect to dimerization. Detailed mechanistic studies utilizing other stable 17-electron radicals such as that produced from flash photolysis of [CpM(CO)$_3$]$_2$ (M = Mo, W)[16] and Re(CO)$_4$L[17] have been reported. In every case studied, however, ML$_n$ has been a coordinatively saturated octahedral complex (n = 6), as have been the metal-containing products. There are also no examples of organometallic Cr^{II}L$_n$ reactants that undergo this reaction. A series of square-planar, high-spin chromium(II) alkyl complexes stabilized by a chelating amidodiphosphine ligand were previously prepared in our group;[18,19] in this study, we report their reactivity with alkyl halides to form unusual five-coordinate chromium(III) complexes.

Results and discussion

Reaction of CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] 1 with methyl-iodide and -bromide

A red-brown toluene solution of the Cr(II) methyl complex CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] **1**[18,19] reacts with MeX (X = Br, I) in a 2:1 stoichiometry to give a purple solution from which the chromium(III) alkyl halide complex Cr(Me)X[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (X = Br **2**, I **3**) was isolated in *ca.* 40% yield [eqn. (1)].



(1)

1

X = Br **2**
I **3**

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† Professional Officer: UBC Crystallographic Service.

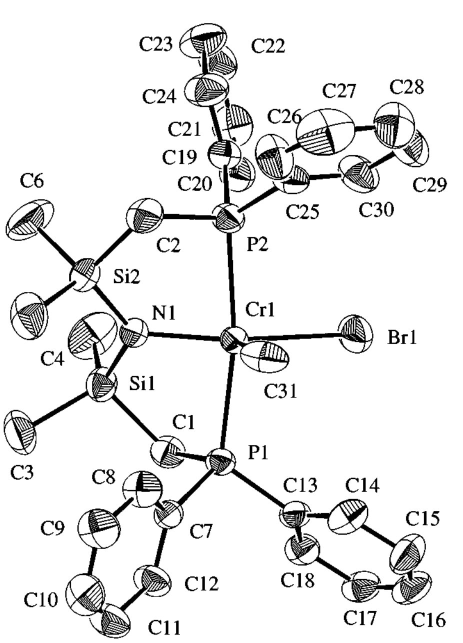


Fig. 1 Molecular structure (ORTEP)[69] and numbering scheme for $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2**, 33% ellipsoids.

These Cr(III) complexes are paramagnetic, with a solution magnetic moment of 3.8 μ_B (Evans' method),[20,21] consistent with a high-spin d^3 complex.[22] Note that this reactivity is different from that observed for the square-planar, high-spin Cr(II) mesityl complex $Cr(C_6H_2Me_3)_2(PMe_3)_2$; in this case reaction with methyl iodide does not give one-electron oxidation chromium(III) products but rather a substitution with the Cr–R fragment to give organic products ($C_6H_2Me_4$) and CrI_2.[23] The crystal structure of **2** is shown in Fig. 1, along with some pertinent bond lengths and angles in Tables 1 and 2.

The structure reveals a distorted five-coordinate Cr(III) centre; the complex could be considered as a square-pyramid with the methyl C(31) in the apical position. The P(1)–Cr–P(2) angle of 170.88(7)° and the Br(1)–Cr–N(1) angle of 141.0(1)° define the distorted square base in this case. Alternatively, the phosphines can be considered the *trans*-axial ligands in a trigonal-bipyramid, with the Br(1)–Cr–N, Br(1)–Cr–C(31) and N(1)–Cr–C(31) angles of 141.0(1)°, 99.6(2)° and 119.4(2)° defining the equatorial plane. Five-coordinate complexes of chromium(III) are extremely rare. The few structurally characterized examples of five-coordinate chromium(III) complexes are trigonal-bipyramidal $CrCl_3(NMe_3)_2$,[24,25] distorted trigonal-bipyramidal $Na_2CrPh_5\cdot 3Et_2O\cdot THF$[26] and $Cr(Me)SPh[N(SiMe_2CH_2PPh_2)_2]$,[27] square-pyramidal Cr(tmtaa)Cl (H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine)[28] and two-legged piano-stool $[\eta^5\text{-}Me_4C_5SiMe_2\text{-}\eta^1\text{-}N^tBu]CrCH_2SiMe_3$.[29] The coordinative unsaturation of **2** and **3** can be compared with other complexes involving chromium(III) centres with alkyl and halide ligands; such complexes are invariably octahedral or dinuclear with bridging halides. Examples include $(\eta^3\text{-L})Cr(CH_2SiMe_3)_2Cl$ (L = 1,3,5-triazacyclohexane),[30] $Cr(^nBu)_2Cl[(Me_2PCH_2)_3CMe]$,[31] $CrMeCl_2(dippe)(THF)$ [dippe = 1,2-bis(diisopropylphosphino)ethane][32] and dinuclear $[Cp'CrR]_2(\mu\text{-}Cl)_2$ (Cp′ = Cp, R = Me;[33] Cp′ = Cp*, R = Me,[34] CH_2Ph[35]) complexes.

Table 1 Selected bond lengths (Å) for the complexes $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2**, $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** and $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6**

Complex **2**			
Cr(1)–P(1)	2.464(2)	Cr(1)–P(2)	2.452(2)
Cr(1)–N(1)	2.009(4)	Cr(1)–C(31)	2.181(7)
Cr(1)–Br(1)	2.602(1)	P(1)–C(1)	1.805(6)
P(1)–C(7)	1.827(6)	P(1)–C(13)	1.809(6)
P(2)–C(2)	1.803(6)	P(2)–C(19)	1.813(7)
P(2)–C(25)	1.816(7)	Si(1)–N(1)	1.712(5)
Si(1)–C(1)	1.884(6)	Si(1)–C(3)	1.892(7)
Si(1)–C(4)	1.848(8)	Si(2)–N(1)	1.725(4)
Si(2)–C(2)	1.890(7)	Si(2)–C(5)	1.865(7)
Si(2)–C(6)	1.837(9)		
Complex **5**			
Cr(1)–P(1)	2.525(2)	Cr(1)–P(2)	2.422(2)
Cr(1)–N(1)	2.022(4)	Cr(1)–C(31)	2.110(6)
Cr(1)–Cl(1)	2.315(2)	P(1)–C(1)	1.821(6)
P(1)–C(7)	1.832(5)	P(1)–C(13)	1.804(5)
P(2)–C(18)	1.805(5)	P(2)–C(19)	1.810(5)
P(2)–C(25)	1.711(6)	Si(1)–N(1)	1.731(4)
Si(1)–C(13)	1.895(6)	Si(1)–C(14)	1.867(6)
Si(1)–C(15)	1.881(5)	Si(2)–N(1)	1.715(5)
Si(2)–C(16)	1.876(6)	Si(2)–C(17)	1.867(6)
Si(2)–C(18)	1.894(5)		
Complex **6**			
Cr(1)–P(1)	2.563(2)	Cr(1)–P(2)	2.469(2)
Cr(1)–N(1)	2.071(4)	Cr(1)–C(31)	2.112(5)
Cr(1)–C(35)	2.090(5)	P(1)–C(1)	1.832(5)
P(1)–C(7)	1.831(5)	P(1)–C(13)	1.836(5)
P(2)–C(6)	1.808(5)	P(2)–C(19)	1.830(5)
P(2)–C(25)	1.817(5)	Si(1)–N(1)	1.714(4)
Si(1)–C(1)	1.892(5)	Si(1)–C(2)	1.868(5)
Si(1)–C(3)	1.875(5)	Si(2)–N(1)	1.722(4)
Si(2)–C(4)	1.868(5)	Si(2)–C(5)	1.868(5)
Si(2)–C(6)	1.887(5)		

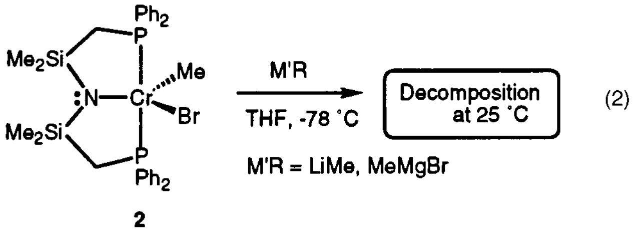
Table 2 Selected bond angles (°) for the complexes $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2**, $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** and $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6**

	2 X = Br(1)	**5** X = Cl(1)	**6** X = C(35)
P(1)–Cr(1)–P(2)	170.88(7)	148.95(6)	164.87(5)
X–Cr(1)–P(1)	92.60(5)	87.96(5)	99.4(2)
X–Cr(1)–P(2)	95.40(5)	92.10(6)	89.0(2)
X–Cr(1)–N(1)	141.0(1)	164.83(13)	105.0(2)
X–Cr(1)–C(31)	99.6(2)	93.5(2)	101.5(2)
P(1)–Cr(1)–N(1)	84.7(1)	86.63(13)	83.19(10)
P(2)–Cr(1)–N(1)	86.3(1)	85.32(13)	82.48(10)
P(1)–Cr(1)–C(31)	96.0(2)	119.9(2)	97.9(2)
P(2)–Cr(1)–C(31)	87.0(2)	91.1(2)	92.6(2)
N(1)–Cr(1)–C(31)	119.4(2)	101.5(2)	152.9(2)
Si(1)–N(1)–Si(2)	122.7(3)	118.4(2)	119.1(2)

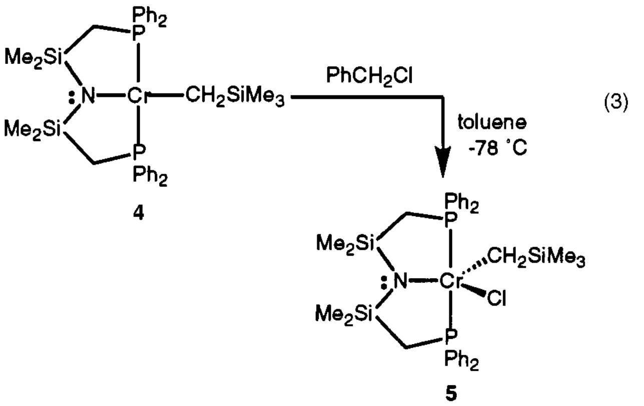
The Cr^{III}–P bond lengths of 2.464(2) and 2.452(2) Å in **2** are typical of high-spin Cr^{III}–P bonds. Other examples include Cr–P bonds ranging from 2.429(1) to 2.444(1) Å in $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$,[36] and 2.414(2) Å in $[CpCrCl_2]_2(dmpe)$[37] (dmpe = $Me_2PCH_2CH_2PMe_2$). The Cr–C bond length of 2.181(7) Å in **2** is slightly longer than some recently reported Cr^{III}–C bond lengths;[38] it can be compared to Cr^{III}–Me bond lengths of 2.09(2) and 2.14(2) Å in $CrMe_3[^tBuSi(CH_2PMe_2)_3]$,[39] 2.073(3) Å in $[CpCrMe]_2(\mu\text{-}Cl)_2$,[33] 2.087(2) Å in $[Cp^*CrMe]_2(\mu\text{-}Cl)_2$,[34] and is much longer than the 2.054(5) Å found in the related five-coordinate $Cr(Me)SPh[N(SiMe_2CH_2PPh_2)_2]$ complex.[27] The Cr–C bond length in **2** is also longer than the bond in the starting complex $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1** [2.151(3) Å].[19] On the other hand, the Cr–N bond length of 2.009(4) Å in **2** is significantly shorter than in **1** [2.117(3) Å]. This fact, coupled with the observed lengthening of the Si–N bonds in the product **2** [1.712(5), 1.725(4) Å *vs.* 1.697(3), 1.699(3) Å in **1**] implies that the amide lone pair is substantially more involved with stabilizing the Cr(III) metal centre than was the case for Cr(II). Other examples of Cr^{III}–N (amide) bond lengths include 1.996(2) and 2.017(2) Å in $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$[36] and a very short 1.87 Å in $Cr(N^iPr_2)_3$.[40] On the other hand, the Cr–Br bond length of 2.602(1) Å in **2** is long compared to other examples such as 2.478(2) Å in $[CpCrBr]_2(\mu\text{-}OCMe_3)_2$,[41] 2.496(1) Å in cationic $[CrBr_2(L)]Br$ (L = 1,4,8,11-tetraazacyclotetradecane)[42] and 2.518(1) Å (average) in anionic [4-BrC$_6$-

$H_4NH_4]_3[CrBr_6]$.[43] This long bond length in the methyl bromide complex **2** implies that there is little or no π-donation from the bromide to the metal in this complex; short Cr–Br bond lengths of 2.393(4) and 2.375(5) Å in Cp^*CrOBr_2 were interpreted as being due to extensive bromide to metal π-donation.[44]

Although the formation of the isolated product $Cr(Me)X[N(SiMe_2CH_2PPh_2)_2]$ (X = Br **2**; X = I **3**) is consistent with the mechanism outlined in Scheme 1, where **2** and **3** are the products of halide atom-abstraction from RX, the product of alkyl radical addition to $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1**, namely $CrMe_2[N(SiMe_2CH_2PPh_2)_2]$ should also have been formed; however, this product was not detected. Instead, a substantial amount of brown material was extracted from the reaction mixture. GC-MS head-space analysis failed to detect either MeH or MeMe (radical solvent abstraction or coupling products) and therefore attempts were made to synthesize the Cr(III) dimethyl compound by another route in order to test its stability. Addition of one equivalent of MeLi or MeMgBr to $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2** gave only brown intractable material from which no viable compounds could be isolated; this suggests that the desired chromium(III) dimethyl complex is unstable [eqn. (2)].



Under the assumption that bulky alkyl groups might enhance the stability of chromium(III) dialkyl complexes, the chromium(II) alkyl complex, $Cr(CH_2SiMe_3)[N(SiMe_2CH_2PPh_2)_2]$ **4**[19] was utilized as a starting material for the chromium(III) dialkyl complex. The reaction of trimethylsilylmethyl **4** with several mole equivalents of benzyl chloride resulted in a colour change from purple to orange-brown. After workup, the chloride abstraction product, $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** was obtained in high yield [eqn. (3)]. Note that the use of



several equivalents of benzyl chloride in this case allows for the high-yield synthesis of the chromium(III) alkyl halide complex. This result does not seem to imply that the benzyl radical does not combine with any chromium(II) starting material, as it is known that the halide abstraction step is slow while the radical coupling is fast.[4,5,10] In particular, the lack of chromium(III) dialkyl or of decomposition products suggests that perhaps the reaction of the benzyl radical with **4** to form $Cr(CH_2SiMe_3)(CH_2Ph)[N(SiMe_2CH_2PPh_2)_2]$ is slow due to the very bulky nature of the Cr(II) centre in the starting complex. The isolated trimethylsilylmethyl–chloride complex **5** is similar to the methyl–bromide complex **2** in that it is also a high-spin, spin-only chromium(III) complex, with a solution magnetic moment of 3.8 μ_B.

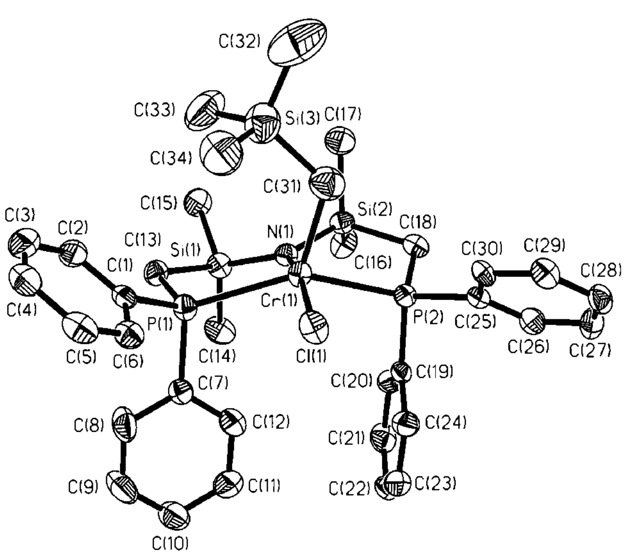
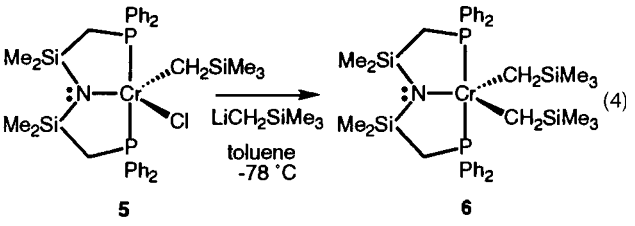


Fig. 2 Molecular structure (ORTEP) and numbering scheme for $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5**, 33% ellipsoids.

The crystal structure of **5**, shown in Fig. 2, reveals another distorted five-coordinate chromium(III) complex. Viewed as a distorted square pyramid, C(31) of the CH_2SiMe_3 unit is in the apical position and the *trans*-angles in the square base are 148.95(6)° and 164.83(13)° for P(1)–Cr–P(2) and N(1)–Cr–Cl(1) respectively (Table 2). Note that this orientation is the reverse of that observed in the methyl–bromide complex **2**, where the *trans*-phosphine angle was easily the largest. If the geometry is to be considered as a distorted trigonal-bipyramid the equatorial plane is defined in this case by the two phosphines and the CH_2SiMe_3 group, with the amide and chloride being *trans*-axially oriented. The equatorial angles are 148.95(6)°, 119.9(2)° and 91.1(2)° for P(1)–Cr–P(2), C(31)–Cr–P(1) and C(31)–Cr–P(2) respectively. The much greater distortions in this complex compared to the methyl–bromide complex **2** could be due to the increase in steric interactions with the introduction of a trimethylsilylmethyl group.

Distortions appear evident in the Cr–P bond lengths of 2.422(2) and 2.525(2) Å. Again, this is likely a reflection of increased steric congestion at the metal centre. The Cr–N bond length of 2.022(4) Å is also comparable to that observed in complex **2**. The Cr–Cl and Cr–C bond lengths of 2.315(2) Å and 2.110(6) Å are unremarkable.[38]

Reaction of trimethylsilylmethyl–chloride **5** with MeLi, MeMgBr or KCH_2Ph resulted in brown solutions from which no tractable products could be identified. However, metathesis with the bulky lithium reagent, $LiCH_2SiMe_3$, caused a change from orange-brown to dark green. Workup of the solution allowed for the isolation of a formally 13-electron, five-coordinate chromium(III) dialkyl complex, $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** in moderate yield [eqn. (4)].



The dialkyl complex **6** is very soluble in alkane solvents. X-Ray quality crystals could be grown from the slow evaporation of a hexamethyldisiloxane solution; the structure of this five-coordinate Cr(III) complex is shown in Fig. 3. It is

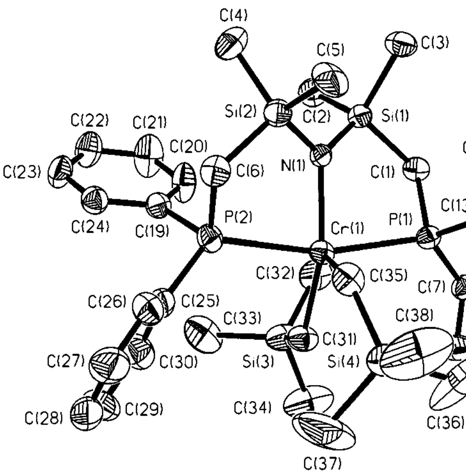


Fig. 3 Molecular structure (ORTEP) and numbering scheme for $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6**, 33% ellipsoids.

immediately apparent that there is a great deal of steric congestion around the metal and this manifests itself in the large distortions in this complex. The structure can be best described as a distorted square-based pyramid, with one trimethylsilylmethyl group [C(35)] in the apical position. The *trans* angles of the square base are defined by P(1)–Cr–P(2) [164.87(5)°] and N(1)–Cr–C(31) [152.9(2)°]. Alternatively, the complex could be considered as a very distorted trigonal-bipyramid, with the phosphines occupying the axial sites and the equatorial plane defined by the N(1)–Cr–C(31), N(1)–Cr–C(35) and C(31)–Cr–C(35) angles of 152.9(2)°, 105.0(2)° and 101.5(2)° respectively.

As in the trimethylsilylmethyl chloride complex **5**, severe distortions due to steric congestion are manifested in the different Cr–P bond lengths of 2.563(2) and 2.469(2) Å. Although one of the Cr–P bond lengths is particularly long when compared to other systems, the origin of the extreme asymmetry is not known. The Cr–N bond length of 2.071(4) Å is slightly longer than the 2.009(4) and 2.022(4) Å observed in the methyl–bromide complex **2** or the trimethylsilylmethyl–chloride **5** respectively; again, this could easily be due to the steric interactions at the metal centre. The Cr–C bond lengths in bis(trimethylsilylmethyl) **6** of 2.112(5) and 2.090(5) Å are fairly typical of high-spin chromium(III) systems.[38]

Chromium(III) dialkyl systems are relatively common; even β-hydrogen-containing *n*-butyl groups have been incorporated into a chromium(III) system. In almost every case, however, the alkyl complexes are octahedral. Structurally characterized examples of chromium(III) complexes containing more than one Cr–C σ-bond include $Cp^*Cr(py)(CH_2Ph)_2$ and $LiCp^*Cr(CH_2Ph)_3$,[45] $Cr(^nBu)_2Cl[(Me_2PCH_2)_3CMe]$,[31] $(\eta^3\text{-L})CrR_2Y$ (L = 1,3,5-triazacyclohexane; R = CH_2SiMe_3, Y = Cl;[30] R = Y = CH_2Ph),[46] $Cp^*CrMe_2(PMe_3)$,[47] $CrR_3[{}^tBuSi(CH_2PMe_2)_3]$ (R = Me, ^{n}Bu)[39] and anionic $Li_3CrMe_6{\cdot}3C_4H_8O_2$.[48] Hence, there is no inherent difficulty in preparing chromium(III) alkyl complexes; the restrictions with our system could be due to the ligand system present, or due to the coordinative unsaturation at the metal centre. The crystal structure of $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** illustrates the extreme steric protection around the metal centre which appears to be a factor in preparing dialkyl complexes stabilized by the amidodiphosphine ligand.

Survey of alkyl halide reactivity with $CrR[N(SiMe_2CH_2PPh_2)_2]$ complexes

The complex $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1** was shown to react with MeI and MeBr to yield the halide-transfer product $Cr(Me)X[N(SiMe_2CH_2PPh_2)_2]$. The generality of this reaction with respect to other alkyl halides and other chromium(II) systems was examined. Benzyl chloride was found to be a suitable substrate for the formation of the chloride-transfer product $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5**, as shown in the previous section. Similarly, the reaction of benzyl chloride with $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1** produced the purple chloride-transfer product $Cr(Me)Cl[N(SiMe_2CH_2PPh_2)_2]$ **7**. In both cases, the benzyl-transfer product was not detected. Note that benzyl chloride does not react with $[Cp^*Cr(CO)_3]$, a chromium(I) substrate that has been shown to undergo one-electron oxidation reactions.[15] The chromium(II) methyl complex **1** was also shown to react rapidly with CF_3CH_2I to form the purple iodide-transfer product **3**.

Attempts to isolate putative 13-electron Cr(III) dialkyl complexes that may have formed, prior to their decomposition, by conducting the redox reaction in the presence of suitable trapping agents such as PR_3 or pyridine are foiled by the fact that RX reacts preferentially with the trapping agents. However, incorporation of alkyl groups capable of donating more than two electrons to form more stable 15- or 17-electron dialkyl complexes was considered a viable option. Hence, the use of the 16-electron complex $Cr(\eta^5\text{-}C_5H_5)[N(SiMe_2CH_2PPh_2)_2]$ **8**[19] as a starting material allows for the formation of 15- or 17-electron chromium(III) products, although it should be noted that this is a low-spin complex and hence not directly comparable to the other reactions presented. Nevertheless, addition of 0.5 equivalent of benzyl chloride to a red solution of **8** gives a rapid colour change to green, from which pale green and dark green crystals (inseparable but distinctly observable) can be isolated. One set of crystals is likely $CrCp(CH_2Ph)[N(SiMe_2CH_2PPh_2)_2]$ **9**, tentatively identified by mass spectral peaks only and the other set is $Cr(Cp)Cl[N(SiMe_2CH_2PPh_2)_2]$ **10**, identified by mass spectrometry. Fifteen- and 17-electron complexes containing η^5-Cp and η^3-allyl fragments are quite common in chromium(III) chemistry[49–51] so this stabilization is not particularly surprising; such ligands are useful for probing the one-electron oxidation reactivity of our systems as both expected products become stable systems.

The reactivity of the dinuclear five-coordinate chromium(II) chloride compound $\{[(Ph_2PCH_2SiMe_2)_2N]Cr\}_2(\mu\text{-}Cl)_2$ **11**[18] with alkyl halides was also examined. Addition of benzyl chloride to **11** in THF resulted in the formation of the halide-transfer product $CrCl_2(THF)[N(SiMe_2CH_2PPh_2)_2]$ as an impure material; however, the corresponding alkyl-transfer product, $Cr(CH_2Ph)Cl[N(SiMe_2CH_2PPh_2)_2]$, could not be detected. Similar results were observed for 2-methylallyl chloride. Considering that in this situation the alkyl-transfer product should be stable, the fact that $Cr(CH_2Ph)Cl[N(SiMe_2CH_2PPh_2)_2]$ was not observed is not easily rationalized.

Reactivity of chromium(III) complexes with ethylene

Chromium(III) complexes have been shown to be active catalysts for the production of polyethylene. In particular, a coordinatively and electronically unsaturated molecule (usually a 13-electron system is considered the active catalyst) that also contains a chromium–carbon bond is necessary in order for catalysis to occur.[29,35,45,52] The charge on the system does not seem to be a vital component of the system.[53] The five-coordinate alkyl halide complexes $Cr(R)X[N(SiMe_2CH_2PPh_2)_2]$ (R = Me, X = Br **2**, I **3**; R = CH_2SiMe_3, X = Cl **5**) and the dialkyl complex $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** all formally satisfy these requirements; they contain an open site for reactivity and a Cr^{III}–C bond. However, addition of one atmosphere of ethylene at room temperature or 60 °C to a toluene solution of methyl–iodide complex **3** or the trimethylsilylmethyl–chloride complex **5** resulted in no production of polyethylene over one week. This lack of reactivity could be due to the fact that these complexes are not purely 13-electron systems but are closer to 15-electron systems by virtue of amide and/or halide π-donation. The added electron donation may effectively negate the catalytic ability of the complexes. In addition, although these are formally five-coordinate species, the steric congestion of the ligands around chromium may mitigate the ability of incoming olefins to interact with the metal centre. On the other hand, addition of ethylene to a solution of dialkyl **6** did result in the slow precipitation of a small amount of white solid, presumably polyethylene, but the solution turned brown over time and production quickly ceased. This catalyst deactivation is likely due to the same reaction that is responsible for the decomposition of sterically unencumbered chromium(III) dialkyl complexes; the colour of the final solution is reminiscent of such decompositions and may be due to some chromium(II) species. It appears then that simply the presence of an open site of reactivity on a chromium(III) centre is not sufficient to promote the polymerization of ethylene.

Comparison of five-coordinate Cr(III) and Ir(III) complexes

The crystal structures of the five-coordinate chromium(III) complexes presented here illustrate varying degrees of distortion from a regular trigonal-bipyramidal geometry. This distortion is electronic in origin; a perfect D_{3h} structure for a high-spin d^3 system is Jahn–Teller unstable due to the presence of one unpaired electron in the degenerate pair of orbitals $d_{x^2-y^2}$ and d_{xy}. Hence, trigonal-bipyramidal high-spin d^3 complexes will distort to remove this degeneracy. The nature of the distortion depends on the ligand set present. In the literature there are three other examples of trigonal-bipyramidal Cr(III) systems, and all show distortions from ideal D_{3h} symmetry. The distortions in the complex $CrCl_3(NMe_3)_2$ are very small; the *trans*-N–Cr–N angle is 178.8(5)° and the equatorial angles are 111.4(2)°, 124.3(1)° and 124.3(1)°.[25] Larger changes are observed in $Na_2CrPh_5\cdot 3Et_2O\cdot THF$; the *trans*-angle is 161° and the equatorial angles are 104°, 111° and 145°;[26] the angles observed here are reminiscent of those observed in our systems. The recently reported $Cr(Me)SPh[N(SiMe_2CH_2PPh_2)_2]$ complex has a *trans*-P–Cr–P angle of 166.30(6)° and equatorial angles of 150.0(1)°, 92.8(2)° and 117.2(2)°.[27] Steric effects are also important and must be taken into consideration. Of course, the incorporation of different ligands into a complex reduces the symmetry, resulting in the degeneracy of the two d-orbitals in question being removed to a certain extent.

A diamagnetic analogue of high-spin Cr(III) (d^3) would be low-spin Rh(III) and Ir(III) (d^6). Instead of three orbitals being half-filled, they are doubly occupied in the Rh(III) and Ir(III) systems. A substantial amount of work has been done using the amidodiphosphine ligand and these two diamagnetic metals.[54] In fact, complexes with the exact ligand set as chromium(III) have been prepared.[55–58] This provides an excellent opportunity to compare the geometries of two complexes which differ only in metal centre. The iridium(III) complexes $Ir(R)Y[N(SiMe_2CH_2PPh_2)_2]$ (R = alkyl; Y = alkyl or halide) all show substantial distortions from trigonal-bipyramidal geometry and the nature of the distortion has been explained theoretically.[59–62] Although the chromium(III) and iridium(III) crystal radii are different (0.755 *vs.* 0.82 Å for octahedral geometry),[63,64] it is not unreasonable to consider that the predictive theory for d^6 iridium(III) distortions would apply to d^3 chromium(III) systems as well.

When the structure of $Ir(Me)I[N(SiMe_2CH_2PPh_2)_2]$ is compared to $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2** it is clearly obvious the two structures are quite different. The iridium complex is almost perfectly square-pyramidal, with the methyl in the apical position.[55,57] The *trans*-angles in the square-base are 177.44(15)° and 170.02(6)°. All other angles are within six degrees of 90°. On the other hand, the chromium(III) complex could not be considered as a square-pyramid, with the two largest angles being 170.88(7)° and 141.0(1)°. In the case of the trimethylsilylmethyl–chloride complex **5** as well the difference is obvious [*trans*-angles are 164.83(13)° and 148.95(6)°] although perhaps a case for steric effects could be made here. Not so in the methyl–bromide complex. In fact, the iridium methyl–bromide complex is more sterically hindered; the Ir–P bond lengths of 2.327(2) and 2.335(2) Å are much shorter than those found in the high-spin chromium(III) complexes [2.452(2) and 2.464(2) Å in **2**] despite chromium(III) being a smaller metal centre. This implies that metal to phosphine electron-donation is increasingly more facile with diamagnetic iridium(III) than with paramagnetic chromium(III).

Dialkyl complexes of iridium(III) were also prepared and a comparison of the structures of $Ir(R)R'[N(SiMe_2CH_2PPh_2)_2]$ ($R = R' = CH_2Ph$;[58] $R = CH_2SiMe_3$, $R' = Me$[56]) with $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** reveals substantial differences. The iridium complexes were considered to be trigonal-bipyramidal in nature (the so-called Y-shape), with two large and one very small angle (opposite the amide) in the equatorial plane. As an example, the equatorial angles in the iridium dibenzyl complex are 141.6(1)°, 140.8(1)° and 77.6(1)°; the *trans*-phosphine angle is 170.2(5)°. In the chromium complex, the *trans*-phosphine angle is 164.87(5)° but the equatorial angles are 152.9(2)°, 105.0(2)° and 101.5(2)°, considerably different and in fact much more square-pyramidal in nature. However, the extreme steric congestion in the chromium dialkyl makes it difficult to ascribe the geometric differences purely to electronic effects.

The fact that complexes with exactly the same ligand sets yield different structures with chromium(III) and iridium(III) implies that the calculations which predict geometric distortions for low-spin d^6 iridium(III) complexes cannot be applied to high-spin d^3 chromium(III) complexes. One explanation for the lack of applicability of the d^6 iridium theoretical calculation to d^3 chromium could be the inherent difference between first and third row transition metals: the energy splitting of 3d orbitals is much smaller than that of 5d orbitals. Distortions are expected to be exacerbated in first-row metal systems and that is in fact observed; the chromium(III) complexes prepared all show greater distortions than the analogous iridium(III) systems and the Cr(III) distortions are not necessarily in the fashion predicted for Ir(III). Calculations done on a chromium(III) centre in a similar manner to that for iridium(III) would likely be able to model the observed distortions.

Conclusions

Coordinatively and electronically unsaturated chromium(II) complexes that contain a metal–carbon bond have been shown to undergo facile one-electron oxidation reactions to chromium(III) products with a variety of alkyl halides. However, unless the alkyl groups on chromium are very bulky, stable dialkyl complexes could not be prepared and hence in many cases the details of the reactivity and product formation could not be discerned. The structures that were solved were all unusual examples of five-coordinate chromium(III) complexes. None of the chromium(III) alkyl complexes prepared was an efficient ethylene polymerization catalyst despite the presence of an open coordination site.

Experimental

General procedures

Unless otherwise stated all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 workstation equipped with a MO-40-2H purification system and a −40 °C freezer. ^{1}H NMR spectroscopy was performed on a Bruker AC-200 instrument operating at 200 MHz and referenced to internal C_6D_5H (δ 7.15). Magnetic moments were measured by a modification of Evans Method[20,21] (C_6D_5H as a reference peak) on the NMR spectrometer listed above. Mass spectra were measured using a Kratos MS-50 EI instrument operating at 70 eV. Microanalyses (C, H, N) were performed by Mr. P. Borda of this department.

Materials

The preparation of the lithium salt $LiN(SiMe_2CH_2PPh_2)_2$[65] and the chromium complexes $\{[(Ph_2PCH_2SiMe_2)_2N]Cr\}_2(\mu\text{-}Cl)_2$[18] and $CrR[N(SiMe_2CH_2PPh_2)_2]$[18,19] have been previously described. NaCp·DME was prepared by the reaction of Na with CpH in dry DME. KCH_2Ph and $LiCH_2SiMe_3$ were prepared by literature procedures.[66] Alkyl halides were either distilled under N_2 or passed through a column of activated neutral alumina, and then degassed by 3 freeze–pump–thaw cycles. All other reagents were obtained from commercial sources and used as received.

Hexanes, toluene and THF were heated to reflux over CaH_2 prior to a final distillation from either sodium metal or sodium benzophenone under an Ar atmosphere. Deuteriated solvents were dried by distillation from sodium benzophenone under nitrogen; oxygen was removed by trap-to-trap distillation and 3 freeze–pump–thaw cycles.

Synthesis and reactivity of complexes

Synthesis of $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ 2. A 10 mL purple toluene solution of $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1** (0.12 g, 0.19 mmol) in a bomb was frozen in liquid nitrogen. To this was added one-half equivalent of MeBr by quantitative vacuum transfer. Upon removal of the liquid nitrogen bath and melting of the toluene, a rapid reaction resulted in a dark purple solution. After being warmed to room temperature and being stirred for one hour, the solvent was removed *in vacuo*, the residue extracted with toluene, filtered through Celite and reduced to a minimum volume. Layering with hexanes (5 mL) yielded purple crystals of $Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ **2** which were used for X-ray analysis. Yield: 0.050 g (39%) (Calc. for $C_{31}H_{39}BrCrNP_2Si_2\cdot0.5C_7H_8$: C, 57.41; H, 6.00; N, 1.94. Found: C, 57.57; H, 6.20; N, 2.05%). ^1H NMR (C_6D_6): δ 11.2 (v br), 10.4 (br), 7.0 (br, sh), 6.2 (v br, overlap), 5.8 (v br, overlap), 4.2 (v br) and resonances for C_7H_8. MS: *m*/*z* 661 ($M^+ - Me$), 580 ($M^+ - Me - Br$). $\mu_{eff} = 3.8\ \mu_B$.

Synthesis of $Cr(Me)I[N(SiMe_2CH_2PPh_2)_2]$ 3. The reaction was performed as for **2**, substituting one-half equivalent of MeI for MeBr. After workup, $Cr(Me)I[N(SiMe_2CH_2PPh_2)_2]$ **3** was isolated as purple crystals. Yield: 0.060 g (43%) (Calc. for $C_{37}H_{44}CrINP_2Si_2\cdot0.5C_7H_8$: C, 53.90; H, 5.64; N, 1.82; I, 16.51. Found: C, 54.17; H, 5.66; N, 1.60; I, 16.30%). ^1H NMR (C_6D_6): δ 11.2 (v br), 10.4 (br), 6.3 (v br, overlap), 5.9 (v br, overlap), 4.1 (v br) and resonances for C_7H_8. MS: *m*/*z* 722 (M^+), 707 ($M^+ - Me$). $\mu_{eff} = 3.8\ \mu_B$.

Synthesis of $CrCl_2(THF)[N(SiMe_2CH_2PPh_2)_2]$. $\{[(Ph_2PCH_2SiMe_2)_2N]Cr\}_2(\mu\text{-}Cl)_2$ **11** (0.10 g, 0.08 mmol) was dissolved in 10 mL THF and cooled to −78 °C to give a blue solution. To this was added two drops of neat $PhCH_2Cl$, causing an immediate change to dark brown. After being stirred overnight at room temperature, the solvent was then removed *in vacuo*, the residue extracted with minimum toluene (2 mL), filtered through Celite and hexanes added (2 mL). Purple crystals of $CrCl_2(THF)[N(SiMe_2CH_2PPh_2)_2]$ precipitated from the solution overnight. Repeated elemental analysis had varying amounts of ligated THF remaining; extended drying *in vacuo* failed to remove all THF (Calc. for $C_{30}H_{36}Cl_2CrNP_2Si_2\cdot C_4H_8O$: C, 56.42; H, 6.13; N, 1.94. Calc. for $C_{30}H_{36}Cl_2CrNP_2Si_2\cdot0.5THF$: C, 55.89; H, 5.86; N, 2.04. Calc. for $C_{30}H_{36}Cl_2CrNP_2Si_2$: C, 55.30; H, 5.57; N, 2.15. Found: C, 55.80; H, 6.15; N, 2.05%). ^1H NMR (C_6D_6): δ 12.5 (v br, 4 H), 3.5 (v br, 12 H) and resonances for THF. MS: *m*/*z* 650 (M^+), 615 ($M^+ - Cl$). $\mu_{eff} = 3.8\ \mu_B$.

Synthesis of $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ 5. To a 10 mL purple toluene solution of $Cr(CH_2SiMe_3)[N(SiMe_2CH_2PPh_2)_2]$ **4** (approximately 0.10 g, 0.15 mmol) was added 2 drops of neat benzyl chloride at −78 °C. No immediate reaction occurred but upon being warmed to room temperature the solution changed to golden orange-brown. After being stirred overnight, the solvent was removed *in vacuo*, the residue extracted with a minimum of toluene, filtered through Celite and hexanes added (1 : 1). Overnight, from the solution, dark orange crystals of $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** suitable for X-ray analysis were deposited. Yield: 0.095 g (90%) (Calc. for $C_{34}H_{47}ClCrNP_2Si_3$: C, 58.06; H, 6.73; N, 1.99. Found: C, 58.43; H, 6.79; N, 1.92%). MS: *m*/*z* 701 ($M^+ - H$), 615 ($M^+ - CH_2SiMe_3$). $\mu_{eff} = 3.8\ \mu_B$.

Synthesis of $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ 6. Crystals of $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** (0.13 g, 0.18 mmol) were dissolved in 10 mL THF to give a dark orange solution, which was cooled to −78 °C. To this was added dropwise a 10 mL toluene solution of $LiCH_2SiMe_3$ (0.017 g, 0.18 mmol), which resulted in an instant colour change to dark green. Upon being warmed the solution turned a darker green and after 30 minutes of being stirred at room temperature the THF was removed *in vacuo*, the residue was extracted with 2 mL hexanes, filtered through Celite and then pumped to dryness again. This residue was dissolved in a minimum amount of hexamethyldisiloxane (1.5 mL) (and placed in a −40 °C freezer and allowed to slowly evaporate). Overnight, long green bars of $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** suitable for X-ray analysis were isolated. Yield: 0.070 (51%) (Calc. for $C_{38}H_{58}CrNP_2Si_4\cdot0.5(Me_3Si)_2O$: C, 58.88; H, 8.07; N, 1.67. Found: C, 59.20; H, 7.61; N, 1.70%). MS: *m*/*z* 580 [$M^+ - (CH_2SiMe_3)_2$].

Reaction of $CrMe[N(SiMe_2CH_2PPh_2)_2]$ 1 with $PhCH_2Cl$ and CF_3CH_2I. Addition of two drops of neat $PhCH_2Cl$ or CF_3CH_2I to a toluene solution of $CrMe[N(SiMe_2CH_2PPh_2)_2]$ **1** (0.05 g, 0.08 mmol) at room temperature resulted in a rapid colour change to dark purple. After being stirred for one hour, the solvent was removed *in vacuo*, the residue extracted with toluene, filtered through Celite and the solvent removed again. A mass spectrum of the crude products indicated the formation of $Cr(Me)Cl[N(SiMe_2CH_2PPh_2)_2]$ **7** [*m*/*z* 630 (M^+), 615 ($M^+ - Me$)] from the benzyl chloride reaction and $Cr(Me)I[N(SiMe_2CH_2PPh_2)_2]$ **3** [*m*/*z* 707 ($M^+ - Me$)] from the CF_3CH_2I reaction.

Reaction of $Cr(\eta^5\text{-}C_5H_5)[N(SiMe_2CH_2PPh_2)_2]$ 8 with $PhCH_2Cl$. To a deep red solution of $Cr(\eta^5\text{-}C_5H_5)[N(SiMe_2CH_2PPh_2)_2]$ **8** (0.09 g, 0.14 mmol) in 10 mL toluene at −78 °C was added $PhCH_2Cl$ (toluene stock solution, 0.07 mmol). No immediate reaction occurred but as the solution was warmed to room temperature, the solution turned dark green. After being stirred overnight, the dark green solution was reduced to a minimum (1 mL), hexanes added (2 mL). Dark green and light green crystals were deposited from the solution overnight. The two products were tentatively identified as $Cr(Cp)Cl[N(SiMe_2CH_2PPh_2)_2]$ **10** (MS as reported below) and $CrCp(CH_2Ph)[N(SiMe_2CH_2PPh_2)_2]$ **9** [*m*/*z* 735 ($M^+ - H$), 670 ($M^+ - Cp - H$)]. The solids could not be separated sufficiently to obtain elemental analysis.

Conditions of attempted reaction of $Cr(R)X[N(SiMe_2CH_2PPh_2)_2]$ with ethylene. Addition of one atmosphere of ethylene to a bomb containing a 10 mL toluene solution of $Cr(Me)I[N(SiMe_2CH_2PPh_2)_2]$ **3** (0.05 g, 0.07 mmol) or $Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ **5** (0.05 g, 0.07 mmol) resulted in no apparent reaction over one week. No polyethylene was produced and no colour change occurred. Mild heating to 60 °C for three days also had no effect.

Reaction of $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ 6 with ethylene. Addition of one atmosphere of ethylene to a bomb containing a 10 mL toluene solution of $Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ **6** (0.05 g, 0.07 mmol) caused no immediate colour change but over twelve hours a small amount of white solid, presumably polyethylene, had been produced. After 24 hours, the solution had changed from green to dark brown-red and no further polymer formation was observed.

X-Ray crystallographic analysis

$Cr(Me)Br[N(SiMe_2CH_2PPh_2)_2]$ 2. *Crystal data.* $C_{31}H_{39}BrCrNP_2Si_2$, $M = 675.67$, triclinic, $a = 10.217(3)$, $b = 19.705(5)$, $c = 9.353(3)$ Å, $\alpha = 101.94(2)$, $\beta = 109.69(2)$, $\gamma = 95.21(2)°$, $U = 1707(1)$ Å^3 (by least-squares refinement on the setting angles for 25 reflections with $12° < 2\theta < 18°$, $\lambda = 0.710\,69$ Å, $T = 21$ °C), space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.314$ g cm^{-3}, $F(000) = 698$. Brown irregular crystals. Crystal dimensions: $0.20 \times 0.30 \times 0.35$ mm, μ(Mo-Kα) = 16.92 cm^{-1}.

Data collection and processing.[67] Rigaku AFC6S diffractometer, ω–2θ scan mode, ω scan width $1.37 + 0.35 \tan\theta$, ω scan speed 16 min^{-1} (up to 8 rescans), graphite-monochromated Mo-Kα radiation; 7846 unique reflections measured ($1 \le \theta \le 27.5°$, $h, \pm k, \pm l$), 4106 having $I \geqslant 3\sigma(I)$. Absorption correction: azimuthal scans (relative transmission factors 0.88–1.00). The intensities of three standard reflections, measured each 200 reflections, decayed linearly by 6.9% (correction applied).

Structure analysis and refinement. Direct methods followed by Fourier synthesis. Full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions [C–H = 0.99 Å, $B_{iso} = 1.2B$(parent atom)]. Statistical weights $= 4F_o/\sigma^2(F^2)$.[67] Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.067$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.030$ for 4106 reflections with $I \geqslant 3\sigma(I)$. Computer programs and source of scattering factors are given in ref. 67. Selected bond lengths and bond angles appear in Tables 2 and 3.

$Cr(CH_2SiMe_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ 5. *Crystal data.* $C_{34}H_{47}ClCrNP_2Si_3$, $M = 703.39$, triclinic, $a = 11.0802(3)$, $b = 11.2193(3)$, $c = 17.9349(1)$ Å, $\alpha = 95.385(1)$, $\beta = 100.353(1)$, $\gamma = 118.882(1)°$, $U = 1877.71(7)$ Å^3, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.244$ g cm^{-3}, $F(000) = 742$. Brown wedge crystals. Crystal dimensions: $0.35 \times 0.20 \times 0.12$ mm, μ(Mo-Kα) = 5.80 cm^{-1}.

Data collection and processing. Siemens SMART CCD diffractometer, ω–2θ scan mode. Graphite-monochromated Mo-Kα radiation; 6320 unique reflections measured ($1 \le \theta \le 25°$, $h, \pm k, \pm l$), 6318 having $I \geqslant 2\sigma(I)$. Absorption correction: SADABS.[68] A crystal of **5**, sealed in a glass capillary, was mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from 80 reflections. Final cell constants are calculated from a set of 3459 strong reflections from the actual data collection. Final cell constants reported in this manner usually are about one order of magnitude better in precision than reported from four-circle diffractometers.

The data technique used for this specimen is generally known as a hemisphere collection. Here, a randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames are collected with 0.30° steps in ω. This collection strategy provides a high degree of redundancy. The redundant data provide good ψ input in the event an empirical absorption correction is applied.

Structure analysis and refinement. The space group was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. Function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0010F_o^{\,2}$, $R = \Sigma|F_o - |F_c|/\Sigma|F_o|$ and $R_w = \Sigma|(w^{\frac{1}{2}}(F_o - F_c)|/\Sigma|(w)^{\frac{1}{2}}F_o|$. Final $R = 0.072$, $R_w = 0.166$ for 6318 reflections with $I \geqslant 2\sigma(I)$. The crystal was twinned; the twin was a minor component randomly oriented with respect to the major component. No integration of the minor component was necessary. Selected bond lengths and angles appear in Tables 2 and 3.

$Cr(CH_2SiMe_3)_2[N(SiMe_2CH_2PPh_2)_2]$ 6. *Crystal data.* $C_{38}H_{58}CrNP_2Si_4$, $M = 755.15$, monoclinic, $a = 12.9279(6)$, $b = 19.5790(9)$, $c = 17.1414(8)$ Å, $\beta = 95.295(1)°$, $U = 4320.2(3)$ Å^3, space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 1.161$ g cm^{-3}, $F(000) = 1612$. Black needle crystals. Crystal dimensions: $0.48 \times 0.16 \times 0.10$ mm, μ(Mo-Kα) = 4.75 cm^{-1}.

Data collection and processing. Siemens SMART CCD diffractometer, ω–2θ scan mode. Graphite-monochromated Mo-Kα radiation; 7471 unique reflections measured ($1 \le \theta \le 25$, $h, \pm k, \pm l$), 7469 having $I \geqslant 2\sigma(I)$. Absorption correction: SADABS.[68] The data collection for **6** is analogous to that for **5** (above). Orientation matrices for initial cell constant calculations were determined from 24 reflections. Final cell constants were calculated from a set of 6991 strong reflections from the actual data collection. The sample diffracted poorly and was collected with 45 second frames.

Structure analysis and refinement. The structure analysis and refinement for **6** is analogous to that for **5** (above). Function minimized $\Sigma(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0010F_o^{\,2}$, $R = \Sigma|F_o - |F_c|/\Sigma|F_o|$ and $R_w = \Sigma|(w^{\frac{1}{2}}(F_o - F_c)|/\Sigma|(w)^{\frac{1}{2}}F_o|$. Final $R = 0.073$, $R_w = 0.127$ for 7469 reflections with $I \geqslant 2\sigma(I)$. Selected bond lengths and angles appear in Tables 2 and 3.

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References

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
2 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, New York, 1994.
3 J. K. Kochi and J. W. Powers, *J. Am. Chem. Soc.*, 1970, **92**, 137.
4 J. H. Espenson, *Prog. Inorg. Chem.*, 1983, **30**, 189.
5 J. H. Espenson, *Acc. Chem. Res.*, 1992, **25**, 222.
6 W. C. Kupferschmidt and R. B. Jordan, *J. Am. Chem. Soc.*, 1984, **106**, 991.
7 M. J. Sisley and R. B. Jordan, *Inorg. Chem.*, 1988, **27**, 1963.
8 Z. Zhang and R. B. Jordan, *Inorg. Chem.*, 1993, **32**, 5472.
9 A. Bakac, V. Butkovic, J. H. Espenson and M. Orhanovic, *Inorg. Chem.*, 1993, **32**, 5886.
10 M. C. Baird, *Chem. Rev.*, 1988, **88**, 1217.
11 D. R. Tyler, *Prog. Inorg. Chem.*, 1988, **36**, 125.
12 T. A. Huber, D. H. Macartney and M. C. Baird, *Organometallics*, 1993, **12**, 4715.
13 T. A. Huber, D. H. Macartney and M. C. Baird, *Organometallics*, 1995, **14**, 592.
14 C. A. Goulin, T. A. Huber, J. M. Nelson, D. H. Macartney and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 1991, 798.
15 C. A. MacConnachie, J. M. Nelson and M. C. Baird, *Organometallics*, 1992, **11**, 2521.
16 S. L. Scott, J. H. Espenson and Z. Zhu, *J. Am. Chem. Soc.*, 1993, **115**, 1789.

17 K.-W. Lee and T. L. Brown, *J. Am. Chem. Soc.*, 1987, **109**, 3269.
18 M. D. Fryzuk, D. B. Leznoff, S. J. Rettig and R. C. Thompson, *Inorg. Chem.*, 1994, **33**, 5528.
19 M. D. Fryzuk, D. B. Leznoff and S. J. Rettig, *Organometallics*, 1995, **14**, 5193.
20 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
21 S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169.
22 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin, 1986.
23 A. R. Hermes, R. J. Morris and G. S. Girolami, *Organometallics*, 1988, **7**, 2372.
24 G. W. A. Fowles and P. T. Greene, *Chem. Commun.*, 1966, 784.
25 P. T. Greene, B. J. Russ and J. S. Wood, *J. Chem. Soc. A*, 1971, 3636.
26 E. Müller, J. Krause and K. Schmiedeknecht, *J. Organomet. Chem.*, 1972, **44**, 127.
27 M. D. Fryzuk, D. B. Leznoff and S. J. Rettig, *Organometallics*, 1997, **16**, 5116.
28 F. A. Cotton, J. Czuchajowska, L. R. Falvello and X. Feng, *Inorg. Chim. Acta*, 1990, **172**, 135.
29 Y. Liang, G. P. A. Yap, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1996, **15**, 5284.
30 R. D. Köhn and G. Kocoik-Köhn, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1877.
31 E. G. Thaler, K. Folting, J. C. Huffman and K. G. Caulton, *J. Organomet. Chem.*, 1989, **376**, 343.
32 A. R. Hermes and G. S. Girolami, *Inorg. Chem.*, 1990, **29**, 313.
33 D. S. Richeson, S.-W. Hsu, N. H. Fredd, G. v. duyne and K. H. Theopold, *J. Am. Chem. Soc.*, 1986, **108**, 8273.
34 W. A. Herrmann, W. R. Thiel and E. Herdtweck, *J. Organomet. Chem.*, 1988, **353**, 323.
35 G. Bhandari, Y. Kim, J. M. McFarland, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1995, **14**, 738.
36 A. R. H. Al-Soudani, A. S. Batsanov, P. G. Edwards and J. A. K. Howard, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 987.
37 J. C. Fettinger, S. P. Mattamana, R. Poli and R. D. Rogers, *Organometallics*, 1996, **15**, 4211.
38 K. H. Theopold, *Acc. Chem. Res.*, 1990, **23**, 263.
39 T. G. Gardner and G. S. Girolami, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1758.
40 D. C. Bradley, M. B. Hursthouse and C. W. Newing, *Chem. Commun.*, 1971, 411.
41 S. E. Nefedov, A. A. Pasynskii, I. L. Eremenko, B. Orazsakhatov, O. G. Ellert, V. M. Novotortsev, S. B. Katser, A. S. Antsyshkina and M. A. Porai-Koshits, *J. Organomet. Chem.*, 1988, **345**, 97.
42 J. N. Lisgarten, R. A. Palmer, A. M. Hemmings and D. M. Gazi, *Acta Crystallogr.*, *Sect. C*, 1990, **46**, 396.
43 D. M. Halepoto, L. F. Larkworthy, D. C. Povey, R. A. Siddiqui and G. W. Smith, *Inorg. Chim. Acta*, 1994, **227**, 167.
44 D. B. Morse, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1988, **110**, 8234.
45 G. Bhandari, A. L. Rheingold and K. H. Theopold, *Chem. Eur. J.*, 1995, **1**, 199.
46 R. D. Köhn, G. Kociok-Köhn and M. Haufe, *J. Organomet. Chem.*, 1995, **501**, 303.
47 A. Grohmann, F. H. Köhler, G. Müller and H. Zeh, *Chem. Ber.*, 1989, **122**, 897.
48 J. Krausse and G. Marx, *J. Organomet. Chem.*, 1974, **65**, 215.
49 P. W. Jolly, *Acc. Chem. Res.*, 1996, **29**, 544.
50 R. Poli, *Chem. Rev.*, 1996, **96**, 2135.
51 R. P. A. Sneeden, *Organochromium Compounds*, Academic Press, New York, London, 1975.
52 B. J. Thomas, S. K. Noh, G. K. Schulte, S. C. Sendlinger and K. H. Theopold, *J. Am. Chem. Soc.*, 1991, **113**, 893.
53 K. H. Theopold, R. A. Heintz, S. K. Noh and B. J. Thomas, in *Homogeneous Chromium Catalysts for Olefin Polymerization*, ed. W. R. Moser and D. W. Slocum, American Chemical Society, Washington, DC, 1992.
54 M. D. Fryzuk, *Can. J. Chem.*, 1992, **70**, 2839.
55 M. D. Fryzuk, P. A. MacNeil and S. J. Rettig, *J. Am. Chem. Soc.*, 1985, **107**, 6708.
56 M. D. Fryzuk, P. A. MacNeil and R. G. Ball, *J. Am. Chem. Soc.*, 1986, **108**, 6414.
57 M. D. Fryzuk, P. A. MacNeil and S. J. Rettig, *Organometallics*, 1986, **5**, 2469.
58 M. D. Fryzuk, P. A. MacNeil, R. L. Massey and R. G. Ball, *J. Organomet. Chem.*, 1989, **368**, 231.
59 D. L. Thorn and R. Hoffmann, *New J. Chem.*, 1979, **3**, 39.
60 Y. Jean and O. Eisenstein, *Polyhedron*, 1988, **7**, 405.
61 I. E.-I. Rachidi, O. Eisenstein and Y. Jean, *New J. Chem.*, 1990, **14**, 671.
62 J. F. Riehl, Y. Jean, O. Eisenstein and M. Pelissier, *Organometallics*, 1992, **11**, 729.
63 R. D. Shannon and C. T. Prewit, *Acta Crystallogr.*, *Sect. B*, 1969, **25**, 925.
64 R. D. Shannon, *Acta Crystallogr.*, *Sect. B*, 1976, **32**, 751.
65 M. D. Fryzuk, P. A. MacNeil, S. J. Rettig, A. S. Secco and J. Trotter, *Organometallics*, 1982, **1**, 918.
66 M. Schlosser and V. Ladenberger, *J. Organomet. Chem.*, 1967, **8**, 193.
67 M. D. Fryzuk, G. Giesbrecht and S. J. Rettig, *Organometallics*, 1996, **15**, 3329.
68 G. M. Sheldrick, SADABS, University of Göttingen, 1997.
69 C. K. Johnson, ORTEP, report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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