Professor J. D. Atwood for helpful discussions and Mr. Leigh Nevinger for the mass spectral determinations.

Registry No. $HRu_3(\mu\text{-COMe})(CO)_{10}$, 71737-42-3; $HRu_2Os(\mu\text{-COMe})(CO)_{10}(C_1$ isomer), 116079-24-4; $HRuOS_2(\mu\text{-COMe})(CO)_{10}$ (C_1 isomer), 116079-25-5; $HOs_3(\mu\text{-COMe})(CO)_{10}$, 69048-01-7; $H_3Ru3(\mu_3\text{-COMe})(CO)_9$, 71562-47-5; $H_3Ru_2O_5(\mu_3\text{-COMe})(CO)_9$, 116079-26-6; $H_3RuOs_2(\mu_3\text{-COMe})(CO)_9$, 116079-27-7; $H_3Ru_2Os(\mu_3\text{-COMe})(CO)_7(AsPh_3)_2$, 116079-28-8; $H_3RuOs_2(\mu_3\text{-COMe})(CO)_8(AsPh_3)$, 116079-29-9; $H_3Ru_2Os(\mu_3\text{-COMe})(CO)_8(AsPh_3)$, 116079-30-2; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_2Os(CO)_{12}$, 12389-47-8; $RuOs_2(CO)_{12}$, 12389-50-3; $So_3(CO)_{12}$, 15696-40-9; Os, 7440-04-2; Ru, 7440-18-8; $HRu_2Os(\mu\text{-COMe})(CO)_{10}(C_5$ isomer), 116079-31-3; $HRuOs_2(\mu\text{-CoMe})(CO)_{10}$ (C_5 isomer), 116102-37-5.

Twelve-Electron Organochromium Species: Synthesis and Characterization of High-Spin Square-Planar Chromium(II) Alkyls and Aryls

Ann R. Hermes, Robert J. Morris, and Gregory S. Girolami*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received April 28, 1988

Alkylation of the chromium phosphine complex $[CrCl_2(dippe)]_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane) with Grignard or dialkylmagnesium reagents gives the unusual 12-electron chromium(II) alkyls *cis*-$CrR_2(dippe)$ (R = CH_2CMe_3, CH_2SiMe_3, $C_6H_2Me_3$). The unidentate phosphine complex *trans*-$Cr(C_6H_2Me_3)_2(PMe_3)_2$ may be prepared similarly by treatment of $CrCl_2(THF)$ with dimesitylmagnesium in the presence of PMe_3. All of these four-coordinate alkyls possess magnetic moments characteristic of high-spin species, $\mu = 4.9\ \mu_B$, and exhibit broadened ^1H NMR resonances consistent with the paramagnetism. X-ray crystal structures of $Cr(CH_2CMe_3)_2(dippe)$ and $Cr(CH_2SiMe_3)_2(dippe)$ reveal tetrahedrally distorted square-planar structures, where the dihedral angle between the C–Cr–C and P–Cr–P planes is larger in the neopentyl complex, 28.4° vs 15.8°, due to steric effects. For similar reasons, the Cr–C and Cr–P distances in the neopentyl compound of 2.149 (8) and 2.556 (2) Å are slightly longer than those of 2.128 (4) and 2.517 (1) Å in the (trimethylsilyl)methyl derivative, and the C–Cr–C angle is also larger in the neopentyl complex at 101.9 (3)° vs 95.7 (2)°. In contrast to these results, the mesityl complex $Cr(C_6H_2Me_3)_2(PMe_3)_2$ is essentially flat: the ipso carbon atoms and the phosphorus atoms are +0.9° and −0.9° out of the mean CrC_2P_2 plane, respectively. The Cr–C and Cr–P distances in this molecule are 2.130 (6) and 2.462 (2) Å, while all the C–Cr–P angles fall between 89.3 (2)° and 90.8 (2)°. Crystal data: for $Cr(CH_2CMe_3)_2(dippe)$, space group $C2/c$, a = 15.867 (5) Å, b = 10.401 (4) Å, c = 18.154 (6) Å, β = 106.67 (3)°, V = 2870 (2) Å^3, Z = 4, R_F = 5.9%, R_{wF} = 7.7% on 126 variables and 1205 data; for $Cr(CH_2SiMe_3)_2(dippe)$, space group $C2/c$, a = 15.666 (4) Å, b = 10.983 (3) Å, c = 18.099 (6) Å, β = 102.43 (2)°, V = 3041 (1) Å^3, Z = 4, R_F = 4.1% R_{wF} = 4.6% on 128 variables and 1472 data; for $Cr(C_6H_2Me_3)_2(PMe_3)_2$, space group $P2_1/n$, a = 9.710 (2) Å, b = 14.121 (3) Å, c = 19.446 (3) Å, β = 98.36 (1)°, V = 2638.0 (9) Å^3, Z = 4, R_F = 5.1%, R_{wF} = 6.1% on 260 variables and 2199 data. The chromium alkyls are able to polymerize ethylene slowly at 25 °C and 10 atm.

Introduction

Square-planar d^8 complexes of the platinum metals constitute one of the largest and most useful classes of homogeneous catalysts.[1–4] Such species are active for the hydrogenation, hydroformylation, and hydrosilation of olefins and are consequently of great utility both in the laboratory and in industry. Even apart from their catalytic activity, square-planar d^8 complexes exhibit interesting stoichiometric reactivity; perhaps most notable is their ability to activate C–H bonds of saturated hydrocarbons under mild conditions.[5–7]

In part, the versatility of square-planar d^8 complexes as catalysts is due to the ease with which oxidative addition processes can occur. The relatively low coordination number facilitates oxidative addition since open coordination sites are already available. Furthermore, the products of oxidative addition are electronically favorable octahedral d^6 species, which can readily undergo reductive elimination to regenerate a d^8 complex if the electronic properties of the attendant ligands are properly chosen.

Apart from d^8 electronic configurations, square-planar geometries can also be adopted by d^7 and d^9 species. Among the former is the cobalt(II) aryl $Co(C_6H_2Me_3)_2(PEtPh_2)_2$,[8] while the latter class is represented by numerous copper(II) complexes such as the dithiocarbamate $Cu(S_2CNEt_2)_2$.[9] In these cases, the electronic preference for a square-planar geometry is not as great as for d^8 species, and this is reflected by the fact that four-coordinate cobalt(II) and copper(II) complexes are more commonly tetrahedral.

Of other electronic configurations, high-spin d^4 metal centers are expected to exhibit a preference for square-

---

(1) Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63–202.

(2) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; Chapter 30.

(4) Wilkinson, T.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 8.

(5) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725.

(6) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448–2450.

(7) Crabtree, R. H.; Demov, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994–7001.

(8) Falvello, L.; Gerloch, M. *Acta Crystallogr., Sect. B. Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2547–2550.

(9) Bonamico, M.; Dessy, G.; Mugnoli, A.; Vaciago, A.; Zambonelli, L. *Acta Crystallogr.* **1965**, *19*, 886–897.

0276-7333/88/2307-2372$01.50/0

Table I. Physical and Microanalytical Data for the CrR_2P_2 Complexes

			calcd		found	
compd	color	mp, °C	C	H	C	H
$Cr(CH_2CMe_3)_2$-(dippe)	red	130 dec	63.1	11.9	61.7	11.9
$Cr(CH_2SiMe_3)_2$-(dippe)	red	148 dec	54.1	11.1	53.4	11.3
$Cr(C_6H_2Me_3)_2$-(dippe)	orange-red	80 dec	69.5	9.85	69.5	9.62
$Cr(C_6H_2Me_3)_2$-$(PMe_3)_2$	orange	180 dec	65.1	9.04	65.2	9.30

planar geometries, since the four low-lying orbitals (d_{xz}, d_{yz}, d_{xy}, and d_{z^2}) would be half-filled. The only monomeric examples of such complexes occur for chromium(II). Inorganic species such as $Cr[N(SiMe_3)_2]_2(THF)_2$,[10] $Cr(O_2CCF_3)_2(lutidine)_2$,[11] $Cr[H_2B(pz)_2]_2$,[12] and others[13-18] are some of the few representatives known in this class. No studies of the reactivity of such species have been performed, and organometallic examples of square-planar chromium(II) are at best only poorly documented.[19,20]

We wish to report the synthesis and characterization of a new series of 12-electron chromium(II) alkyls that adopt square-planar coordination geometries. These high-spin organochromium complexes are obtained through the use of phosphine ligands that limit the coordination number and ensure coordinative unsaturation at the metal center. The complexes are of interest for two reasons: to explore the electronic analogy between d^8 and high-spin d^4 square-planar molecules and to examine the reactivity of coordinately unsaturated organochromium derivatives. Since coordinately unsaturated organochromium compounds, particularly in the +2 oxidation state, are thought to be active for the polymerization of olefins,[21-23] we have initiated an investigation of such compounds as homogeneous models of chromium-based Phillips' catalysts used in industry.

Results and Discussion

Synthesis of CrR_2(dippe) Complexes. We have described elsewhere the synthesis of the chromium(II) phosphine adduct $[CrCl_2(dippe)]_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane).[24] This molecule consists of square-planar Cr^{II} centers that are weakly dimerized via long axial Cr···Cl contacts. It serves as an excellent starting material for the synthesis of coordinately unsaturated chromium alkyls.

Table II. Crystal Data for $Cr(CH_2CMe_3)_2$(dippe) (1), $Cr(CH_2SiMe_3)_2$(dippe) (2), and $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4) at 25 °C

	1	2	4
space group	*C*2/*c*	*C*2/*c*	$P2_1/n$
a/Å	15.867 (5)	15.666 (4)	9.710 (2)
b/Å	10.401 (4)	10.983 (3)	14.121 (3)
c/Å	18.154 (6)	18.099 (6)	19.446 (3)
β/deg	106.67 (3)	102.43 (2)	98.36 (1)
$V/Å^3$	2870 (2)	3041 (1)	2638.0 (9)
Z	4	4	4
mol wt	456.64	488.79	442.53
$d_{calcd}/g\ cm^{-3}$	1.057	1.068	1.114
μ_{calcd}/cm^{-1}	5.05	5.54	5.48
size/mm	0.2 × 0.4 × 0.5	0.2 × 0.2 × 0.5	0.2 × 0.4 × 0.4
diffractometer		Syntex $P2_1$	
radiation		Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.710 73 Å	
monochromator		graphite crystal, $2\theta = 12°$	
scan range		$3.0 \leq 2\theta \leq 46°$	
scan speed, type		2–20° min^{-1}, $\omega/2\theta$	
rflctns, total	2296	2428	3832
rflctns, unique	2012	2131	3698
rflctns, $I > 2.58\sigma(I)$	1205	1472	2199
R_i/%	2.0	1.5	4.2
R_F/%	5.9	4.1	5.1
R_{wF}/%	7.7	4.6	6.1
variables	126	128	260
p factor	0.030	0.020	0.020

Table III. Final Atomic Coordinates for $Cr(CH_2CMe_3)_2$(dippe) (1) and $Cr(CH_2SiMe_3)_2$(dippe) (2)

	x/*a*	*y*/*b*	*z*/*c*
		1	
Cr	0.0	0.1616 (2)	0.25
P	0.1059 (1)	−0.0284 (2)	0.2873 (1)
C1	0.0481 (4)	−0.1804 (7)	0.2508 (5)
C2	0.1644 (5)	−0.0607 (8)	0.3901 (4)
C3	0.1015 (6)	−0.0932 (10)	0.4343 (5)
C4	0.2357 (6)	−0.1648 (9)	0.4050 (5)
C5	0.1950 (5)	−0.0257 (8)	0.2403 (5)
C6	0.1579 (7)	−0.015 (1)	0.1531 (6)
C7	0.2588 (6)	0.0820 (9)	0.2736 (6)
C8	0.0896 (5)	0.2917 (8)	0.3256 (5)
C9	0.0637 (5)	0.3611 (8)	0.3907 (5)
C10A	0.145 (2)	0.436 (3)	0.448 (2)
C11A	−0.007 (2)	0.477 (3)	0.352 (2)
C12A	0.017 (3)	0.272 (3)	0.436 (2)
C10B	0.141 (2)	0.376 (4)	0.468 (2)
C11B	−0.021 (2)	0.313 (4)	0.402 (2)
C12B	0.046 (3)	0.508 (3)	0.361 (2)
C10C	0.069 (3)	0.250 (3)	0.454 (2)
C11C	−0.030 (2)	0.422 (4)	0.367 (2)
C12C	0.127 (2)	0.476 (3)	0.422 (2)
		2	
Cr	0.0	0.34746 (7)	0.25
P	−0.10208 (7)	0.52299 (9)	0.20742 (7)
Si	0.05363 (8)	0.1375 (1)	0.38896 (7)
C1	0.0883 (3)	0.2174 (4)	0.3115 (2)
C2	−0.0514 (3)	0.1954 (6)	0.4083 (3)
C3	0.1361 (4)	0.1494 (7)	0.4800 (3)
C4	0.0345 (5)	−0.0278 (5)	0.3677 (4)
C5	−0.0425 (3)	0.6677 (4)	0.2257 (4)
C6	−0.1970 (3)	0.5413 (5)	0.2523 (3)
C7	−0.2600 (4)	0.4360 (6)	0.2324 (4)
C8	−0.1668 (4)	0.5561 (8)	0.3371 (3)
C9	−0.1517 (3)	0.5319 (5)	0.1053 (3)
C10	−0.2068 (4)	0.6452 (5)	0.0799 (3)
C11	−0.0835 (4)	0.5150 (7)	0.0585 (3)

Treatment of $[CrCl_2(dippe)]_2$ with Grignard or dialkylmagnesiusm reagents in diethyl ether gives the monomeric, 12-electron organochromium(II) complexes **1**–**3**. Physical properties of these new organometallic species are given in Table I. These hydrocarbon-soluble complexes are red to red-orange in color and are air- and moisture-sensitive. Magnetic susceptibility measurements in toluene

---

[10] Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567.

[11] Eremenko, I. L.; Pasynskii, A. A.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Y. T. *Inorg. Chim. Acta* **1981**, *54*, L85–L86.

[12] Dapporto, P.; Mani, F.; Mealli, C. *Inorg. Chem.* **1978**, *17*, 1323–1329.

[13] Ladd, M. F. C.; Larkworthy, L. F.; Lenoard, G. A.; Povey, D. C.; Tandon, S. S. *J. Chem. Soc., Dalton Trans.* **1984**, 2351–2352.

[14] Cotton, F. A.; Rice, C. E.; Rice, G. W. *Inorg. Chim. Acta* **1977**, *24*, 231–234.

[15] Cotton, F. A.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 1136–1139.

[16] Dorfman, J. R.; Rao, C. P.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 453–454.

[17] Larkworthy, L. F.; Povey, D. C.; Sandell, B. *Inorg. Chim. Acta* **1984**, *83*, L29–L32.

[18] Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1978**, *17*, 710–714.

[19] Seidel, W.; Stoll, G. *Z. Chem.* **1974**, *14*, 488–489.

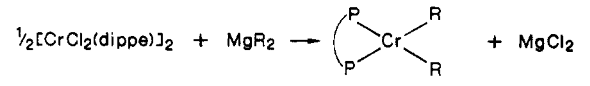
[20] Manzer, L. E.; Guggenberger, L. J. *J. Organomet. Chem.* **1977**, *139*, C34–C38.

[21] Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2621–2637.

[22] Krauss, H. L. *Catal., Proc. Int. Congr., 5th* **1973**, *1*, 207–218.

[23] Clark, A.; Hogan, J. P. *Polyethylene*, 2nd ed.; Renfew, A., Morgan, P., Eds.; Wiley: New York, 1960; p 29.

[24] Hermes, A. R.; Girolami, G. S. *Inorg.* **1988**, *27*, 1775–1781.



1, R=CH_2CMe_3
2, R=CH_2SiMe_3
3, R=$C_6H_2Me_3$

at room temperature by Evans' method[25] indicate that these organometallic species adopt high-spin d^4 electronic configurations; the magnetic moments of 4.7 μ_B are near the spin-only value of 4.9 μ_B for four unpaired electrons. All of the chromium(II) alkyls are EPR silent both in frozen toluene glasses at −196 °C and in solution at room temperature. The ^1H NMR spectra of complexes **1**–**3** show broad, overlapping resonances from which no structural information could be obtained. X-ray crystallography was therefore employed to determine the molecular structures of the CrR_2(dippe) species.

Structures of the CrR_2(dippe) Complexes. X-ray crystal structure determinations have been performed for both the neopentyl and (trimethylsilyl)methyl complexes **1** and **2**, respectively. Single crystals of both compounds were obtained by cooling saturated diethyl ether solutions to −20 °C. Crystal data are given in Table II, while final atomic coordinates and a list of significant bond lengths and angles are given in Tables III and IV.

The structural analysis shows that crystals of **1** and **2** are isomorphous and are composed of discrete CrR_2(dippe) monomers; perspective views of the molecules are shown in Figures 1 and 2. The molecules possess crystallographic C_2 symmetry, in which the 2-fold axis bisects the C–Cr–C and P–Cr–P angles and the chromium centers adopt coordination geometries that are best described in terms of tetrahedrally distorted square-planar environments. The distortion from planarity is gauged by the dihedral angle between the C–Cr–C and P–Cr–P planes: for an idealized square plane, this angle is 0°, whereas for a tetrahedron, the angle is 90°. In the neopentyl complex **1** and the (trimethylsilyl)methyl complex **2**, the dihedral angles are 28.4° and 15.8°, respectively. By comparison, the corresponding value for the tetrahedral complex $Fe(CH_2C_6H_4Me)_2$(dippe) is 83.3°.[26] The larger dihedral angle in **1** may be ascribed to the larger steric demand of the neopentyl group; this arises since the small quaternary carbon atom brings the pendant β-methyl groups closer to the metal center and increases the cone angle of CH_2CMe_3 relative to CH_2SiMe_3.

The higher degree of steric crowding in **1** is also reflected in other aspects of the structures. Thus, the C–Cr–C angle between the bulky neopentyl groups is relatively large at 101.9 (3)°, whereas the C–Cr–C angle of 95.7 (2)° between the smaller (trimethylsilyl)methyl ligands is nearer the 90° value expected for a square-planar geometry. In comparison, the P–Cr–P angles are less sensitive to the nature of the alkyl group, 78.75 (8)° in **1** vs 80.04 (4)° in **2**, since this parameter is affected most by the conformational constraints of the chelating dippe ligand. However, if the 1.3° smaller P–Cr–P angle in **1** is in fact chemically significant, the difference is most reasonably ascribed to steric compression of the phosphine ligand in the more crowded neopentyl complex.

The Cr–C and Cr–P bond lengths can be rationalized on similar grounds. Both distances are longer in the neopentyl complex, Cr–C by 0.021 Å and Cr–P by 0.039 Å, although the former is only of marginal significance statistically. Nevertheless, the increased bond distances

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Cr(CH_2CMe_3)_2$(dippe) (1) and $Cr(CH_2SiMe_3)_2$(dippe) (2)

1		2	
	Bond Distances		
Cr–C8	2.149 (8)	Cr–C1	2.128 (4)
Cr–P	2.556 (2)	Cr–P	2.517 (1)
C8–C9	1.54 (1)	C1–Si	1.833 (4)
C9–C10A	1.61 (3)	Si–C2	1.866 (5)
C9–C11A	1.66 (3)	Si–C3	1.866 (5)
C9–C12A	1.56 (3)	Si–C4	1.867 (5)
P–C1	1.853 (7)	P–C5	1.836 (5)
P–C2	1.861 (8)	P–C6	1.853 (5)
P–C5	1.850 (8)	P–C9	1.847 (5)
C1–C1′	1.518 (9)	C5–C5′	1.430 (7)
	Bond Angles		
C8–Cr–C8′	101.9 (3)	C1–Cr–C1′	95.7 (2)
P–Cr–P′	78.75 (8)	P–Cr–P′	80.04 (4)
C8–Cr–P	157.0 (2)	C1–Cr–P	166.6 (1)
C8–Cr–P′	93.1 (2)	C1–Cr–P′	93.2 (1)
Cr–C8–C9	120.8 (5)	Cr–C1–Si	117.1 (2)
Cr–P–C1	110.1 (2)	Cr–P–C5	110.0 (2)
Cr–P–C2	120.4 (3)	Cr–P–C6	117.8 (2)
Cr–P–C5	113.4 (3)	Cr–P–C9	116.7 (2)

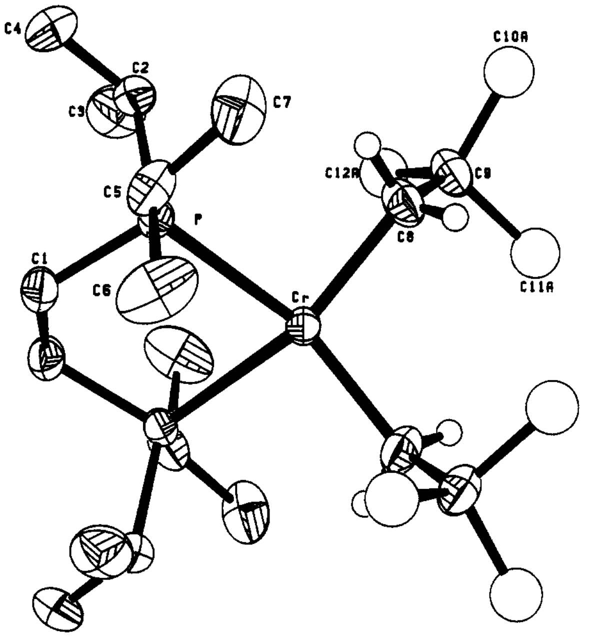


Figure 1. Molecular structure of $Cr(CH_2CMe_3)_2$(dippe) (1).

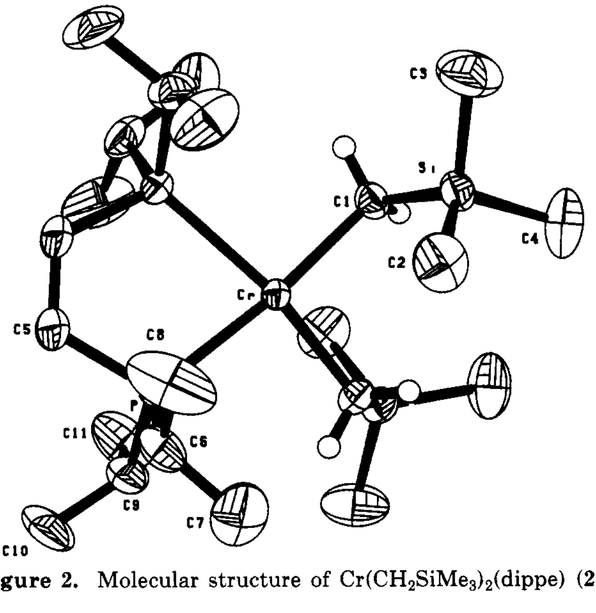
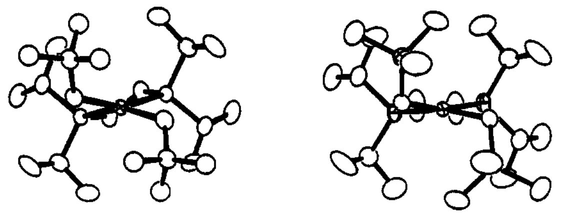


Figure 2. Molecular structure of $Cr(CH_2SiMe_3)_2$(dippe) (2).

---

[25] Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. *J. Chem. Soc. A* 1971, 1931–1934.

[26] Hermes, A. R.; Girolami, G. S. *Organometallics* 1987, *6*, 763–768.



1 2

Figure 3. Structures of $Cr(CH_2CMe_3)_2(dippe)$ (1) and $Cr(CH_2SiMe_3)_2(dippe)$ (2) viewed down C_2 axis, illustrating tetrahedral distortion from square-planar geometry; twist angles are 28.4° and 15.8° in 1 and 2, respectively.

in 1 are again consistent with a higher degree of steric congestion. In general, the chromium–carbon distances of 2.14 Å in 1 and 2 are similar to those of other chromium(II) alkyls in the literature: values of 2.131 (2) and 2.168 (4) Å have been determined[27,28] for the molecules $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ and $CrMe_2(dmpe)_2$, respectively. Slightly longer distances, 2.20–2.24 Å, have been noted for some quadruply bonded chromium(II) dimers including the anionic species $[Cr_2Me_8{}^{4-}]$,[29] $[Cr_2(C_4H_8)_4{}^{4-}]$,[30] and $[Cr_2(C_5H_{10})_4{}^{4-}]$[30] and the ylide $Cr_2[(CH_2)_2PMe_2]_4$.[31] The presence of C···Li interactions in the anionic species and residual ylide-like character in $Cr_2[(CH_2)_2PMe_2]_4$ are sufficient to explain the longer Cr–C bonds in these complexes.

The Cr–P bond lengths are much more sensitive to the electronic and steric nature of the metal center. Octahedral, low-spin Cr^{II} molecules such as $CrX_2(dmpe)_2$ (X = Cl, Me, or O_2CCF_3)[28,32–34] possess Cr–P distances of 2.345 (1)–2.387 (11) Å, and the diamagnetic Cr^{II} dimer $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ exhibits a Cr–P distance of 2.460 (1) Å.[27] All of these bond lengths are significantly shorter than the 2.556 (2) and 2.517 (1) Å distances in 1 and 2, respectively. The best comparison is with the analogous high-spin complex $[CrCl_2(dippe)]_2$, which is the synthetic precursor to 1 and 2: the Cr–P bond lengths in the chloro dimer are 2.481 (2) Å (trans to bridging Cl) and 2.512 (2) Å (trans to terminal Cl).[24] The Cr–P bond distances in 1 and 2 are the longest that have been observed, and this fact is a consequence of the high-spin nature of the chromium(II) centers (which inhibits π-bonding with the phosphine), the lengthening effect of the strongly labilizing trans alkyl groups, and the sterically congested nature of the molecules.

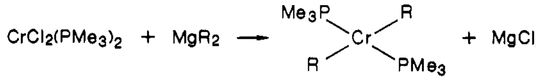
The alkyl groups have relatively normal $Cr–C_\alpha–C_\beta$ and $Cr–C_\alpha–Si$ angles at the α-carbon of 120.8 (5)° and 117.1 (2)°, respectively. By contrast, neopentyl and (trimethylsilyl)methyl ligands that are involved in agostic M···H–C interactions with the α-hydrogen atoms exhibit obtuse $M–C_\alpha–C_\beta$ and $M–C_\alpha–Si$ angles of 150–158°.[35,36]

Table V. Final Atomic Coordinates for $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4)

	x/a	*y/b*	*z/c*
Cr	0.4947 (1)	0.01167 (6)	0.73882 (5)
P1	0.3380 (2)	0.0553 (1)	0.82247 (9)
P2	0.6479 (2)	−0.0380 (1)	0.65507 (9)
C1	0.6288 (6)	−0.0551 (4)	0.8205 (3)
C2	0.7382 (7)	−0.0072 (5)	0.8613 (3)
C3	0.8197 (7)	−0.0496 (6)	0.9176 (3)
C4	0.7970 (8)	−0.1401 (6)	0.9366 (3)
C5	0.6892 (8)	−0.1892 (5)	0.8981 (4)
C6	0.6080 (7)	−0.1486 (5)	0.8409 (3)
C7	0.7680 (7)	0.0945 (5)	0.8449 (4)
C8	0.8852 (8)	−0.1885 (6)	0.9977 (4)
C9	0.4923 (7)	−0.2064 (5)	0.7999 (4)
C10	0.3602 (6)	0.0828 (4)	0.6584 (3)
C11	0.2456 (6)	0.0408 (5)	0.6160 (3)
C12	0.1630 (7)	0.0915 (6)	0.5643 (3)
C13	0.1856 (8)	0.1851 (6)	0.5517 (3)
C14	0.2990 (7)	0.2277 (5)	0.5913 (3)
C15	0.3832 (6)	0.1801 (4)	0.6438 (3)
C16	0.2131 (7)	−0.0633 (5)	0.6258 (4)
C17	0.0941 (8)	0.2418 (6)	0.4948 (4)
C18	0.5034 (7)	0.2327 (4)	0.6859 (4)
C19	0.3872 (9)	0.0199 (6)	0.9127 (3)
C20	0.1618 (8)	0.0120 (7)	0.8019 (5)
C21	0.3134 (10)	0.1820 (5)	0.8310 (4)
C22A	0.732 (2)	0.052 (1)	0.608 (1)
C23A	0.563 (2)	−0.120 (2)	0.584 (1)
C24A	0.803 (2)	−0.119 (2)	0.690 (1)
C22B	0.609 (4)	0.013 (3)	0.564 (2)
C23B	0.653 (4)	−0.167 (2)	0.647 (2)
C24B	0.839 (4)	−0.006 (3)	0.681 (2)
C22C	0.558 (6)	−0.066 (5)	0.567 (3)
C23C	0.753 (7)	−0.146 (4)	0.673 (3)
C24C	0.805 (6)	0.051 (4)	0.657 (3)
C22D	0.667 (3)	0.051 (2)	0.583 (1)
C23D	0.828 (3)	−0.072(2)	0.689 (1)
C24D	0.583 (3)	−0.148 (2)	0.607 (1)

Accordingly, the alkyl ligands in the square-planar $CrR_2(dippe)_2$ complexes are *not* agostic, despite the electron count of 12. This conclusion is consistent with the absence of low-energy ν_{CH} absorptions in the IR spectra.

Synthesis and Structure of $Cr(C_6H_2Me_3)_2(PMe_3)_2$. Despite the advantages afforded by chelating phosphines in the preparation of early first-row transition-metal complexes, unidentate phosphines in some instances serve as well. The chromous chloride solvate $CrCl_2(THF)$ reacts with trimethylphosphine to give a blue adduct in solution that cannot be obtained pure due to ready loss of phosphine.[37] However, diethyl ether solutions of $CrCl_2(PMe_3)_x$ may be treated in situ with the dimesitylmagnesium reagent $Mg(C_6H_2Me_3)_2(THF)_2$ to give a stable orange organometallic complex $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4). Unlike



$$CrCl_2(PMe_3)_2 + MgR_2 \longrightarrow trans\text{-}Cr(R)_2(PMe_3)_2 + MgCl_2$$

4, $R = C_6H_2Me_3$

the dippe complexes above, this high-spin, μ = 4.9 μ_B, chromium(II) complex possesses a well-resolved ^1H NMR spectrum (Figure 3) which contains shifted and broadened resonances for the PMe_3, para Me, and meta H groups at δ −26.2, −88.3, and 33.8, respectively. Integrations of the resonances are in agreement with these assignments; the lack of a resonance for the ortho Me substituents evidently means that these groups are too close to the paramagnetic center and that the resonance must be shifted and broadened significantly. The large chemical shift of the

---

(27) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1314–1318.

(28) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339–1348.

(29) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* **1970**, *21*, 159–168.

(30) Krausse, J.; Schödl, G. *J. Organomet. Chem.* **1971**, *27*, 59–67.

(31) Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713–2717.

(32) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685–692.

(33) Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1141–1154.

(34) Barron, A. R.; Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2947–2954.

(35) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56.

(36) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819–821.

(37) Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 56–57.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4)

Bond Distances			
Cr–C1	2.124 (6)	C2–C3	1.389 (9)
Cr–C10	2.137 (6)	C3–C4	1.36 (1)
Cr–P1	2.462 (2)	C4–C5	1.38 (1)
Cr–P2	2.463 (2)	C5–C6	1.39 (1)
P–C19	1.820 (7)	C6–C1	1.401 (9)
P1–C20	1.806 (8)	C10–C11	1.415 (8)
P1–C21	1.817 (7)	C11–C12	1.390 (9)
P2–C22A	1.82 (2)	C12–C13	1.37 (1)
P2–C23A	1.89 (2)	C13–C14	1.39 (1)
P2–C24A	1.93 (2)	C14–C15	1.386 (9)
C1–C2	1.404 (9)	C15–C10	1.426 (9)
Bond Angles			
C1–Cr–C10	178.3 (2)	Cr–C1–C6	122.2 (4)
P1–Cr–P2	177.86 (7)	Cr–C10–C11	125.0 (4)
C1–Cr–P1	89.3 (2)	Cr–C10–C15	120.1 (4)
C1–Cr–P2	90.3 (2)	C1–C2–C7	119.5 (6)
C10–Cr–P1	89.8 (2)	C1–C6–C9	118.9 (6)
C10–Cr–P2	90.8 (2)	C10–C11–C16	119.5 (5)
Cr–C1–C2	122.7 (5)	C10–C15–C18	119.6 (5)

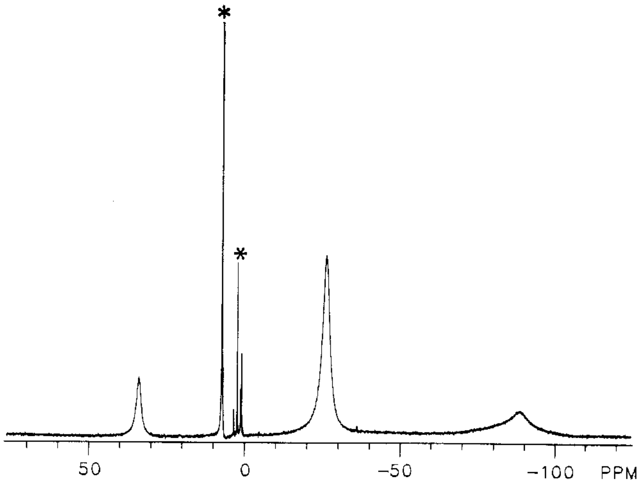


Figure 4. ^1H NMR spectrum of $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4) at 25 °C in C_6D_6. Asterisks indicate solvent and trace amounts of free PMe_3. A base-line-corrected spectrum is shown.

para Me group from its diamagnetic position (δ 2.0) implies that there is significant spin delocalization into the aromatic ring. A similarly large chemical shift has been noted for the para Me group in the five-coordinate d^4 Mn^{III} mesityl $Mn(C_6H_2Me_3)Br_2(PMe_3)_2$.[38]

Crystals of $Cr(C_6H_2Me_3)_2(PMe_3)_2$ were obtained by cooling saturated diethyl ether solutions and are composed of discrete chromium(II) monomers. Crystal data are given in Table II, while final atomic coordinates and significant bond lengths and angles are collected in Tables V and VI. A perspective view of 4 (Figure 4) reveals that the molecules adopt nearly ideal square-planar geometries. Although no crystallographic symmetry is imposed, the molecule possesses virtual D_{2h} symmetry. The aryl and phosphine ligands are arranged in a trans configuration, in contrast to the cis arrangement in the CrR_2(dippe) alkyls.

The C–Cr–P angles in the CrC_2P_2 unit are all within 0.8° of 90°, and all five atoms lie within 0.038 Å of the mean plane: the Cr–C and Cr–P vectors lie +0.9° and −0.9° out of the mean CrC_2P_2 plane, respectively. The trans C–Cr–C and P–Cr–P angles of 178.3° and 177.9° again emphasize the square-planar coordination geometry.

Based on the bond lengths in the CrR_2(dippe) alkyls, a short Cr–C distance in 4 of ca. 2.03 Å might be predicted

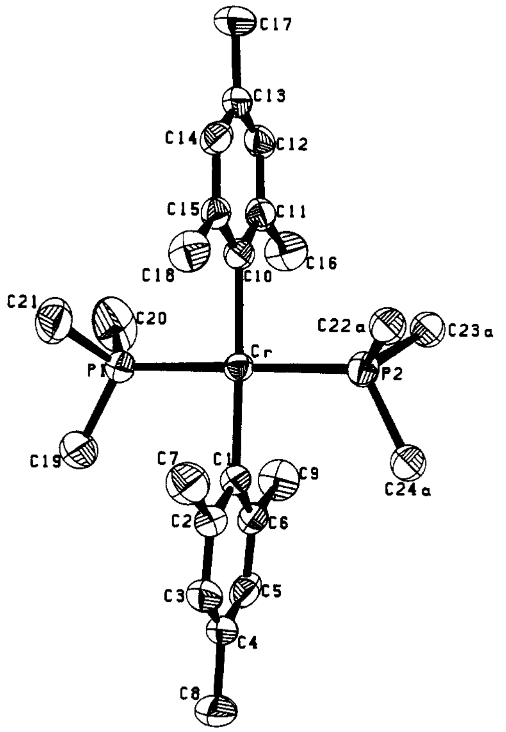


Figure 5. Molecular structure of $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4).

due to the 0.105 Å smaller covalent radius of sp^2 vs sp^3 carbon atoms.[39] Instead, the Cr–C distance of 2.130 (6) Å is much longer than expected and in fact is quite similar to the 2.149 (8) and 2.128 (4) Å Cr–C bond lengths in 1 and 2. In contrast, the Cr–P contact in $Cr(C_6H_2Me_3)_2(PMe_3)_2$ of 2.462 (2) Å is much shorter than the 2.54 Å distances in 1 and 2. Both of these anomalies are easily explained by a strong trans influence effect: in square-planar chromium(II) complexes, bonds to a ligand are approximately 0.10 Å longer when trans to an alkyl or aryl group than when they are trans to a phosphine group.

The ortho methyl substituents of the mesityl ligands partially occupy the axial positions above and below the square plane, and this arrangement undoubtedly enhances the preference for this geometry. In this respect, the structure of the mesityl complex resembles that of the amido species $Cr[N(SiMe_3)_2]_2(THF)_2$,[10] the trifluoroacetate $Cr(O_2CCF_3)_2$(lutidine)$_2$,[11] and the cobalt analogue $Co(C_6H_2Me_3)_2(PEt_2Ph)_2$,[8] all of which possess nonbonded groups that sterically occlude the axial sites. The Cr···C distances to the ortho methyl groups along the axial direction are 3.292 (6), 3.302 (7), 3.328 (7), and 3.417 (7) Å for C18, C9, C7, and C16, respectively. These distances are somewhat longer than the 3.2 Å sum of the van der Waals radius of a methyl group (2.0 Å) and the metallic radius of chromium (1.2 Å).[39] The Cr···H contacts with the ortho methyl hydrogens are calculated to be approximately 2.63–2.78 Å; all of these distances are longer than expected for strong agostic M···C–H interactions.

Electronic Structure and Reactivity of $CrR_2(PR_3)_2$ Species. Although the CrR_2(dippe) complexes in some cases show tetrahedral distortions due to steric effects, there is no doubt that chromium(II), when four-coordinate, has an electronic preference for square-planar coordination environments. Whereas in square-planar Rh^I, Ir^I, Pd^{II}, and Pt^{II} complexes the four low-lying d orbitals are filled, in high-spin Cr^{II} complexes they are half-filled. Only the $d_{x^2-y^2}$

---

[38] Morris, R. J.; Girolami, G. S. *Organometallics* **1987**, *6*, 1815–1816.

[39] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 260.

orbital is empty, and the absence of agostic interactions in the CrR_2(dippe) species can be understood since this orbital is of σ and not π symmetry with respect to the ligands. The absence of M···H–C interactions in these 12-electron four-coordinate complexes reemphasizes that the electronic configuration and the presence or absence of empty orbitals of suitable energy and symmetry are more reliable guides to molecular structure and reactivity than the traditional gauges, electron count and coordination number.[40]

Since square-planar d^8 metals are often excellent catalysts for organic transformations such as olefin hydrogenations, hydroformylations, and hydrosilylations,[1-4] we have investigated the reactions of the square-planar chromium(II) alkyls with a selection of small molecules.

$$4 \xrightarrow{H_2} NR$$

$$4 \xrightarrow{CO} (C_6H_2Me_3)_2CO + Cr(CO)_x(PR_3)_{6-x}$$

$$4 \xrightarrow{MeI} C_6H_2Me_4 + CrI_2$$

The mesityl complex $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4) was investigated in greatest detail: hydrogen does not react, carbon monoxide gives 2,2′,4,4′,6,6′-hexamethylbenzophenone and chromium(0) carbonyls, while methyl iodide gives 1,2,3,5-tetramethylbenzene (isodurene) and CrI_2. Thus, treatment of the $CrR_2(PR_3)_2$ complexes with CO and CH_3I leads to the formation of organic derivatives of the alkyl or aryl group; if oxidative addition or Lewis base association processes are occurring, they are quickly followed by irreversible, stoichiometric reactions with the Cr–R groups.

Coordinately unsaturated transition-metal alkyls are of fundamental importance as catalysts for the polymerization of olefins.[41,42] Although the majority of the polyethylene and polypropylene produced is made by titanium-based Ziegler–Natta catalysts, more than 60% of the world's current production of high-density polyethylene is made with related chromium-based catalysts.[23] These Phillips' catalysts were discovered in the 1950s and are typically prepared by impregnating a silica or silica–alumina support with aqueous solutions of chromium trioxide. Silica-supported organochromium species such as Cp_2Cr[43] and $Cr(C_3H_5)_3$[44-46] are also active olefin polymerization catalysts. Mass spectra of the low polymer–Cr products are indicative of the presence of Cr–C σ-bonds in the functioning catalysts, since stable $[Cr(CH_2)_n{}^+]$ fragments are observed.[22] Valence states from Cr^{II} to Cr^{VI} have been proposed to be present in the catalyst,[23] but infrared studies of the catalysts under carbon monoxide suggest that the active sites are coordinately unsaturated chromium(II) centers.[22]

Treatment of toluene solutions of the CrR_2(dippe) complexes with ethylene (10 atm) at room temperature results in the formation of only small amounts of polyethylene. The solutions retain their deep red color throughout the reaction, and apart from the precipitated polyethylene, no suspended solids are evident. The polyethylene produced was insoluble in a wide variety of solvents including hydrocarbons, aromatics, chlorinated hydrocarbons, chlorinated aromatics, dimethyl sulfoxide, and ethereal solvents. When heated, the polyethylene remained unchanged in appearance until 200 °C, at which point partial melting occurred. These observations suggest that the polyethylene produced is high-density, is crystalline, and may be highly cross-linked. Although it has been proposed that organochromium(II) complexes are the active catalytic sites in Phillips' catalysts, our isolated chromium(II) alkyls at best polymerize ethylene very slowly at 25 °C and 10 atm.

Summary

We have prepared a series of highly reactive four-coordinate chromium(II) alkyls of stoichiometry $CrR_2(PR_3)_2$. X-ray crystallographic studies of these high-spin, 12-electron organometallic molecules reveal square-planar geometries that in some cases are tetrahedrally distorted due to steric effects. No agostic interactions are present in these electronically and coordinately unsaturated species since the only empty d orbital is of σ-symmetry with respect to the ligands. The chromium(II) alkyls polymerize ethylene only slowly, and this result suggests that low-valent Cr^{II} centers are probably not the active sites in Phillips' catalysts, despite previous claims.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium (toluene) or sodium–benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. 1,2-Bis(diisopropylphosphino)ethane[47] and trimethylphosphine[48] were prepared via literature routes. Dialkylmagnesium[49] and diarylmagnesium[50] reagents were prepared from the alkyl halides and used as stock solutions in diethyl ether or tetrahydrofuran. The halide complexes $CrCl_2$(THF) and $[CrCl_2(dippe)]_2$ were prepared as described elsewhere.[24]

Microanalyses were performed by Mr. Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B as Nujol mulls, and ^1H NMR spectra were obtained on a General Electric QE-300 instrument at 300 MHz. Magnetic moments were determined by a modification of Evans' method[25] on a Varian EM 390 instrument at 90 MHz. Melting points were determined on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

1. **Dineopentyl[1,2-bis(diisopropylphosphino)ethane]chromium(II).** To a cold (–78 °C) suspension of $[CrCl_2(dippe)]_2$ (0.11 g, 0.14 mmol) in diethyl ether (30 mL) was added dineopentylmagnesium (2.0 mL of a 0.22 M solution in diethyl ether, 0.44 mmol). No color change occurred at –78 °C, but upon warming to room temperature the solution turned red as the blue solid disappeared. After being stirred for 12 h, the solution was filtered and concentrated to ca. 25 mL. Cooling to –20 °C resulted in the formation of dark red crystals: yield 0.10 g (76%); IR (cm^{-1}) 2718 w, 1405 w, 1402 w, 1360 s, 1341 s, 1292 w, 1253 w, 1238 w, 1228 s, 1217 s, 1194 m, 1150 w, 1089 m, 1041 w, 1022 s, 917 w, 875 s, 848 w, 774 w, 729 m, 715 w, 676 s, 649 s, 599 m, 520 m, 451 w, 444 w.

2. **Bis[(trimethylsilyl)methyl][1,2-bis(diisopropylphosphino)ethane]chromium(II).** To a cold (–78 °C) suspension of $[CrCl_2(dippe)]_2$ (0.19 g, 0.25 mmol) in diethyl ether (30 mL) was added bis[(trimethylsilyl)methyl]magnesium (3.0 mL of a 0.44 M solution in diethyl ether, 1.3 mmol). Upon warming to room temperature, the solution turned red. After

---

(40) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2631–2637.

(41) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic: New York, 1979.

(42) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapters 22–5.

(43) Hogan, J. P. *Applied Industrial Catalysis*; Academic: San Diego, 1983; Vol. 1, pp 149–176.

(44) Wilke, G. U.S. Patent 3 379 706, 1968.

(45) Herwig, W.; Gumbolt, A. G. M.; Weissermel, K. U.S. Patent 3 501 415, 1970.

(46) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263–325.

(47) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185–191.

(48) Luetkens, M. L.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718–1726.

(49) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262–264.

(50) Seidel, W.; Burger, I. *Z. Anorg. Allg. Chem.* **1978**, *447*, 195–198.

being stirred for 12 h, the solution was filtered and concentrated to ca. 20 mL. Cooling to −20 °C resulted in the formation of dark red crystals: yield 0.11 g (45%); IR (cm^{-1}) 2712 w, 1417 w, 1410 w, 1364 s, 1332 w, 1287 w, 1263 w, 1242 s, 1232 s, 1155 w, 1111 w, 1094 w, 1073 w, 1027 m, 900 s, 882 s, 840 vs, 814 s, 742 m, 722 s, 671 s, 640 m, 615 w, 520 w, 484 m, 452 m.

3. Dimesityl[1,2-bis(diisopropylphosphino)ethane]chromium(II). To a cold (−78 °C) suspension of [CrCl$_2$(dippe)]$_2$ (0.17 g, 0.22 mmol) in tetrahydrofuran (30 mL) was added dimesitylmagnesium (3 mL of a 0.30 M solution in tetrahydrofuran, 0.9 mmol). Upon warming to room temperature, the solution turned bright orange-red. After being stirred for 2 h, the solution was filtered and concentrated to ca. 20 mL. Cooling to −20 °C resulted in formation of orange-red crystals: yield 0.12 g (49%); IR (cm^{-1}) 2713 w, 1713 w, 1570 w, 1392 s, 1345 s, 1278 m, 1257 w, 1227 m, 1219 m, 1193 m, 1144 m, 1083 m, 1055 s, 1017 s, 1000 m, 942 w, 915 w, 895 w, 867 s, 827 vs, 778 w, 705 w, 693 w, 687 w, 669 s, 636 s, 593 w, 564 m, 527 s, 457 w.

4. Dimesitylbis(trimethylphosphine)chromium(II). To a suspension of CrCl$_2$(THF) (0.85 g, 4.36 mmol) in diethyl ether (70 mL) at 25 °C was added trimethylphosphine (0.68 g, 9.0 mmol). The solution turned deep blue as the solid dissolved. After the solution was stirred for 10 min, dimesitylmagnesium (0.64 g, 4.48 mmol, 0.14 M in THF) was added to give a dark orange solution. The solution was stirred for 1 h, whereupon the solvent was removed under vacuum. The residue was extracted with diethyl ether (2 × 30 mL), and the filtered extracts were combined and concentrated to ca. 50 mL. Cooling to −20 °C resulted in the formation of large orange prisms. Additional crops were obtained from the supernatant: yield 0.97 g (50%); magnetic moment (toluene, 25 °C) 4.7 μ_B; IR (cm^{-1}) 2718 w, 2686 w, 1710 w, 1583 m, 1530 w, 1457 s, 1428 s, 1413 s, 1362 m, 1352 m, 1298 s, 1250 m, 1205 w, 1030 w, 1010 w, 940 s, 871 w, 841 s, 797 w, 739 s, 707 w, 682 w, 662 w, 572 w, 545 w, 537 m, 476 w; ^{1}H NMR δ 33.8 (s, fwhm = 500 Hz, meta *H*), −26.2 (s, fwhm = 700 Hz, P*Me*$_3$), −88.3 (s, fwhm = 2000 Hz, para *Me*).

5. Reactions of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$. A. With Dihydrogen. A stirred solution of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$ (0.30 g, 0.68 mmol) in diethyl ether (30 mL) was pressurized with hydrogen (6 atm) in a Fischer-Porter bottle. No color change was observed over 24 h, and only starting material was recovered. Repeating the reaction at 50 °C quickly led to decomposition of the orange solution to give black, insoluble products.

B. With Carbon Monoxide. A solution of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$ (1.59 g, 3.6 mmole) in pentane (150 mL) was stirred under an ambient pressure of carbon monoxide for 30 min to give a dark purple solution and a very small amount of precipitate. After being filtered, the solution was cooled to −20 °C to give colorless prisms of 2,2′,4,4′,6,6′-hexamethylbenzophenone: mp 138 °C; IR (cm^{-1}) 1632 s (ν_{CO}); ^{1}H NMR (CDCl$_3$, 25 °C) δ 2.11 (s, 12 H, ortho *CH*$_3$), 2.28 (s, 6 H, para *CH*$_3$), 6.84 (s, 4 H, meta *H*). Anal. Calcd: C, 85.7; H, 8.3. Found: C, 85.7; H, 8.7. The chromium-containing products were identified by ^{31}P{^{1}H} NMR[51] as *mer*-Cr(CO)$_3$(PMe$_3$)$_3$ (A$_2$B pattern, δ_A 22.7, δ_B 12.4, J_{AB} = 25 Hz), *cis*-Cr(CO)$_2$(PMe$_3$)$_4$ (A$_2$B$_2$ pattern, δ_A 18.5, δ_B 7.5, J_{AB} = 28 Hz), *trans*-Cr(CO)$_4$(PMe$_3$)$_2$ (δ 22.0), and *cis*-Cr(CO)$_4$(PMe$_3$)$_2$ (δ 8.6) in an approximate molar ratio of 50:20:15:15, respectively.

C. With Methyl Iodide. To a stirred room-temperature solution of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$ (0.37 g, 0.84 mmol) in diethyl ether (80 mL) was added a solution of methyl iodide (0.12 g, 0.84 mmol) in toluene (5 mL). After being stirred for 3 h, a large amount of white precipitate was produced, which was identified as a mixture of tetramethylphosphonium iodide and chromium(II) iodide. IR (cm^{-1}): 1290 m, 1280 m, 981 w, 968 s. Anal. Found: Cr, 5.1. After hydrolysis, the organic product was identified by GC/MS as 1,2,3,5-tetramethylbenzene [*m/e* 135.1 (M$^+$, 6%)].

D. With Ethylene. A yellow solution of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$ (0.20 g, 0.44 mmol) in toluene (30 mL) was transferred to a Fisher-Porter bottle and pressurized with ethylene (150 psi) at 25 °C. After 12 h, some dark solid had formed and the solution had turned dark brown. The solid was isolated by filtration and washed repeatedly with 2 M HCl and ethanol, yielding 0.3 g of off-white polyethylene. Similar amounts of polyethylene were obtained from solutions of the CrR$_2$(dippe) complexes.

Crystallographic Studies.[52] Single crystals of Cr(CH$_2$CMe$_3$)$_2$(dippe), grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. [Single crystals of Cr(CH$_2$SiMe$_3$)$_2$(dippe) were also grown from diethyl ether. This compound was crystallographically isomorphous to the neopentyl derivative, and subsequent comments in brackets will refer to the (trimethylsilyl)methyl species.] Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 15 reflections yielded the cell dimensions given in Table II.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) by using measurement parameters listed in Table II. Systematic absences for hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$ were consistent with space groups $C2/c$ and Cc. The average values of the normalized structure factors suggested the centric choice $C2/c$, which was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change, and absorption corrections were applied, the maximum and minimum transmissison factors being 0.932 and 0.854 [0.914 and 0.879], respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by using direct methods (SHELXS); correct positions for all the non-hydrogen atoms were deduced from an E map. Subsequent difference Fourier calculations revealed the positions of the hydrogen atoms, but instability in the matrix prevented refinement. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.84/(\sigma(F_o)^2 + (pF_o)^2)$. [$w = 2.28/\sigma(F_o)^2 + (pF_o)^2$.] The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. Methyl carbon atoms C10, C11, and C12 were disordered over three sites; the relative site occupancies for groups "A" and "B" were 0.40 (1) and 0.27 (1); these atoms were refined isotropically while all other non-hydrogen atoms were refined with anisotropic thermal parameters. [The (trimethylsilyl)methyl compound showed no such disorder.] A group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in "idealized" positions (for methyl hydrogens, staggered with respect to the substituents on the attached sp^3 atom) with C–H = 0.95 Å. [For the (trimethylsilyl)methyl compound, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in "idealized" positions. A group isotropic parameter was varied for the methyl hydrogen atoms, while the remaining hydrogen atoms were refined with independent isotropic thermal coefficients.] Successful convergence was indicated by the maximum shift/error of 0.013 [0.013] in the last cycle. Final refinement parameters are given in Table II. The final difference Fourier map had no significant features, and there were no apparent systematic errors among the final observed and calculated structure factors.

Single crystals of Cr(C$_6$H$_2$Me$_3$)$_2$(PMe$_3$)$_2$, grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. Cell dimensions were obtained as above.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) by using measurement parameters listed in Table II. Systematic absences for $0k0$, $k \neq 2n$, and $h0l$, $h + l \neq 2n$, uniquely defined the space group $P2_1/n$. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change, and absorption corrections were applied, the maximum and minimum transmission factors being 0.903 and 0.836, respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with

---

(51) Mathieu, R.; Lenzi, M.; Poilblanc, R. I. *Inorg. Chem.* **1970**, *9*, 2030–2034.

(52) For details of the data collection and refinement procedure, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977–4982.

$I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by using direct methods (MULTAN) and weighted difference Fourier methods. The positions of 20 non-hydrogen atoms were deduced from an *E* map. Subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.73/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. Methyl carbon atoms C22–C24 were disordered over four sites, A–D, with occupancy factors of 0.38 (1), 0.20 (1), 0.12 (1), and 0.31 (1), respectively. In the final cycle of least-squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients; for C22–C24, the 12 disordered positions were refined with separate isotropic thermal parameters. A group isotropic thermal parameter was varied for the methyl hydrogen atoms, which were fixed in "idealized" positions with C–H = 0.95 Å, while the remaining hydrogen atoms were refined with independent isotropic thermal coefficients (hydrogen atoms attached to C22–C24 were excluded from the calculations; hydrogen atoms on the methyl groups of the mesityl ring were placed in arbitrary rotational conformations about the C–CH_3 bonds). An empirical extinction coefficient was also varied to give a value of 1.7 (2) × 10^{-7}. Successful convergence was indicated by the maximum shift/error of 0.23 in the last cycle. Final refinement parameters are given in Table II. The final difference Fourier map had no significant features, and there were no apparent systematic errors among the final observed and calculated structure factors.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program for support of this research and Exxon (A.R.H.) and Lubrizol (R.J.M.) for fellowships. G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990). We particularly thank Dr. Scott Wilson and Charlotte Stern of the University of Illinois X-Ray Crystallographic Laboratory for performing the X-ray crystal structure determinations.

Registry No. 1, 116026-51-8; 2, 116026-52-9; 3, 116026-53-0; 4, 55272-61-2; *mer*-$Cr(CO)_3(PMe_3)_3$, 30476-93-8; *cis*-$Cr(CO)_2(PMe_3)_4$, 69364-17-6; *trans*-$Cr(CO)_4(PMe_3)_2$, 17548-29-7; *cis*-$Cr(CO)_4(PMe_3)_2$, 16027-42-2; $[CrCl_2(dippe)]_2$, 114059-91-5; $CrCl_2(THF)$, 36463-97-5; 2,2′,4,4′,6,6′-hexamethylbenzophenone, 5623-45-0; 1,2,3,5-tetramethylbenzene, 527-53-7.

Supplementary Material Available: Tables of hydrogen atom positions and anisotropic thermal parameters for $Cr(CH_2CMe_3)_2(dippe)$ (1), $Cr(CH_2SiMe_3)_2(dippe)$ (2), and $Cr(C_6H_2Me_3)_2(PMe_3)_2$ (4) (5 pages); listings of final observed and calculated structure factors for 1, 2, and 4 (23 pages). Ordering information is given on any current masthead page.

Intermolecular Activation of C–D Bonds in Benzene-d_6 by *trans*-Neopentyl(trifluoromethanesulfonato)bis(trimethylphosphine)platinum(II)[1]

Robert L. Brainard,[2] W. Rodger Nutt,[2] T. Randall Lee, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received May 12, 1988

trans-$(Me_3P)_2Pt(CH_2C(CH_3)_3)(SO_3CF_3)$ ($L_2PtNpTf$, 1) reacts with benzene-d_6 at 133 °C and gives *trans*-$(Me_3P)_2Pt(C_6D_5)(SO_3CF_3)$ (2) and neopentane-d_1 as the major products. When this reaction is carried out in concentrated solutions ($[1]_0 \geq 0.04$ M), small quantities of neopentane-d_0 (8–17%) and 1,1-dimethylcyclopropane (1–3%) are also detected; larger quantities of neopentane-d_0 are produced (32–45%) when the initial concentration of 1 is low ($[1]_0 = 0.01$–0.03 M). The rate of reaction is decreased by the addition of $Bu_4N^+Tf^-$ and increased by the addition of $Bu_4N^+BF_4^-$. A competitive kinetic isotope effect was estimated by allowing 1 to react with C_6D_5H and comparing the relative yields of neopentane-d_0 and neopentane-d_1: k_H/k_D is large, but its quantitative value is uncertain because of experimental ambiguities. The mechanism for this reaction seems to involve generation of L_2PtNp^+ as an essential intermediate. This intermediate appears to react with benzene by direct oxidative addition of a C–H bond, but electrophilic attack on the benzene ring cannot be rigorously excluded.

Introduction

Although intermolecular activation of C–H bonds by homogeneous organometallic compounds is an area of intensive research,[3-12] examples based on soluble organoplatinum species have only recently been reported.[13] Clean platinum surfaces cleave C–H bonds under mild

---

(1) Supported by the National Science Foundation, Grant CHE-85-08702.

(2) Present address of R.L.B.: Polaroid Corp., Waltham, MA. W.R.N. was on sabbatical leave from Davidson College.

(3) Parshall, G. W. *Catal. (London)* **1977**, *1*, 335. Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Boston, 1984.

(4) Garnett, J. L.; Hodges, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 4546–47. Garnett, J. L.; West, J. C. *Aust. J. Chem.* **1974**, *27*, 129–42 and references therein.

(5) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1969**, *43*, 1222–3.

(6) Shul'pin, G. B.; Shilov, A. E.; Kitagorodskii, A. N. *J. Organomet. Chem.* **1980**, *201*, 319–325. Shilov, A. E. *Organomet. Chem.* **1981**, *212*, 267–274. Shul'pin, G. B.; Nizova, G. V.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.*, **1983**, 671–672. *J. Organomet. Chem.* **1981**, *220*, 271–276. Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729–733.

(7) For example: Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742–51. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–42. Gomez, M.; Robinson, D. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 825–6. Fisher, B. J.; Eisenberg, R.; *Organometallics* **1983**, *2*, 764–67. Morris, R. H.; Shiralian, M. *J. Organomet. Chem.* **1984**, *260*, C47–C51. Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305–306.

0276-7333/88/2307-2379$01.50/0