1712 *Organometallics* **2003,** *22,* 1712−1717

Cationic and Neutral Phosphido-Bridged Pentamethylcyclopentadienyl−Chromium Dimers

Pingrong Wei and Douglas W. Stephan*

School of Physical Sciences, Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Received December 4, 2002

The species $[(Cp^*Cr)_2(\mu\text{-}Cl)_3]X$ (X = $[AlCl_4]$ (**3**), $[GaCl_4]$ (**4**), $[B(C_6F_5)_4]$ (**5**)) were generated from $(Cp^*CrCl(\mu\text{-}Cl))_2$ (**1**) via reaction with a chloride abstraction reagent. Using a similar synthetic route, the reaction of **1**, generated in situ, with MeLi and the borane $B(C_6F_5)_3$ gave crystals of the salt $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][MeB(C_6F_5)_3]$ (**6**), while the complex $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][Me_2B(C_6F_5)_2]$ (**7**) was obtained, albeit in low yield, from the reaction of $[Cp^*CrMe(\mu\text{-}Cl)]_2$ with $HB(C_6F_5)_2$. Monoalkylation of **5** with MeLi gave $[(Cp^*Cr(\mu\text{-}Cl))_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**8**), while the related mono(phosphide)-bridged cationic species $[(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2][B(C_6F_5)_4]$ (**9**) was derived from **5** via reaction with Ph_2PLi. The bis(phosphide)-bridged species $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Cl)][AlMe_3Cl]$ (**10**) was derived from reaction mixtures of **1**, Ph_2PLi, and $AlMe_3$, while monoalkylation of **1** with MeLi followed by treatment with Ph_2PLi and $AlMe_3$ yielded $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Me)][(Me_3Al)_2(\mu\text{-}Cl)]$ (**11**). The neutral phosphide-bridged species $(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}CH_2)$ (**12**) and $(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(\mu\text{-}CH_2)$ (**13**) were obtained from reactions of **1**, MeLi, and Ph_2PLi. X-ray structural data are reported from compounds **5**−**13**. The synthetic routes and the structural data are discussed.

Introduction

The chemistry of Cr(III) is particularly difficult to study, as a result of its paramagnetic nature. Nonetheless, the research groups of Theopold,[1−4] and more recently Poli[5−7] and others,[8−11] have made extensive progress in developing an understanding of the structure, magnetic properties,[12−14] and reactivity of Cr(III). While much of this work has been focused on the organometallic chemistry of Cr alkyls with olefin polymerization catalysis as the principal motivation,[2,3,11,13,15−22] other work has focused on the fundamental structural and reactivity questions around Cr oxo and sulfido complexes.[23−29] In exploring alternative ligand sets for Cr, amido derivatives have garnered recent attention.[9,18,30,31] While constrained-geometry[18] and diimine[30] Cr complexes have been shown to offer new polymerization catalysts, the variety of structural types of Cp^*Cr^{III} amides has been explored and shown to depend on the nature of the amido substituents.[9] In seeking development of Cr(III) chemistry employing phosphido ligands, we report herein a series of diphenylphosphido-bridged dinuclear Cr(III) salts. The nature of these species is described, and the implications of this chemistry are considered.

---

(1) Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263−270.
(2) Theopold, K. H. *CHEMTECH* **1997**, *27*, 26−32.
(3) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15−24.
(4) Pariya, C.; Theopold, K. H. *Curr. Sci.* **2000**, *78*, 1345−1351.
(5) Mattamana, S. P.; Poli, R. *Organometallics* **1997**, *16*, 2427−2433.
(6) Fettinger, J. C.; Mattamana, S. P.; Poli, R.; Rogers, R. D. *Organometallics* **1996**, *15*, 4211−4222.
(7) Bender-Gresse, M.; Collange, E.; Poli, R.; Mattamana, S. *Polyhedron* **1998**, *17*, 1115−1119.
(8) Bazan, G. C.; Rogers, J. S.; Fang, C. C. *Organometallics* **2001**, *20*, 2059−2064.
(9) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 271−281.
(10) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *353*, 323−336.
(11) Peucker, U.; Heitz, W. *Macromolecular Rapid Communications* **1998**, *19*, 159−162.
(12) Janiak, C.; Silvestre, J.; Theopold, K. H. *Chem. Ber.* **1993**, *126*, 631−643.
(13) Bhandari, G.; Rheingold, A. L.; Theopold, K. H. *Chem. Eur. J.* **1995**, *1*, 199−203.
(14) Bluemel, J.; Herker, M.; Hiller, W.; Koehler, F. H. *Organometallics* **1996**, *15*, 3474−3476.
(15) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902−5903.
(16) Dawkins, G. M. (BP Chemicals Ltd.) Eur. Pat. Appl. Ep, 1991; p 8ff.
(17) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738−745.
(18) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284−5286.
(19) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473−5475.
(20) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543.
(21) Tani, K.; Mashima, K.; Oshiki, T.; Urata, T. (Mitsubishi Chemical Industries Ltd., Japan) Jpn. Kokai Tokkyo Koho, 1998; p 15ff.
(22) Andell, O.; Maaranen, J.; Hoikka, J.; Vanne, T.; Rautio, S. (Borealis Technology Oy, Finland; Campbell, Neil) PCT Int. Appl., 2002, p 55ff.
(23) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333−2335.
(24) Hess, A.; Horz, M. R.; Liable-Sands, L. M.; Lindner, D. C.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 166−168.
(25) Noh, S. K.; Heintz, R. A.; Haggerty, B. S.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 1892−1893.
(26) Hubbard, J. L.; McVicar, W. K. *Inorg. Chem.* **1992**, *31*, 910−913.
(27) Hess, J. S.; Leelasubcharoen, S.; Rheingold, A. L.; Doren, D. J.; Theopold, K. H. *J. Am. Chem. Soc.* **2002**, *124*, 2454−2455.
(28) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 8234−8235.
(29) Brunner, H.; Kauermann, H.; Pfauntsch, J.; Wachter, J.; Enemark, J. H.; Young, C. G. *J. Organomet. Chem.* **1987**, *331*, 45−52.
(30) Theopold, K. H.; Kim, W.-K.; Power, J. M.; Mora, J. M.; Masino, A. P. (University of Delaware, Chevron Chemical Co.) PCT Int. Appl, 2001, p 112ff.
(31) Danopoulos, A. A.; Hankin, D. M.; Wilkinson, G.; Cafferkey, S. M.; Sweet, T. K. N.; Hursthouse, M. B. *Polyhedron* **1997**, *16*, 3879−3892.

10.1021/om0209881 CCC: $25.00
Publication on Web 03/21/2003

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and Innovative Technologies, MBraun, or Vacuum Atmospheres inert-atmosphere gloveboxes. Solvents were purified employing Grubbs' type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H,$^{31}P\{^1H\}$,$^{11}B\{^1H\}$, and ^{19}F NMR spectra were recorded on Bruker Avance 300 or 500 spectrometers. All NMR spectra were recorded in $CDCl_3$. Trace amounts of protonated solvents were used as references for the ^1H NMR data, and chemical shifts are reported relative to $SiMe_4$. ^{31}P, ^{19}F, and ^{11}B NMR spectra are referenced to 85% H_3PO_4, $CFCl_3$, and $NaBH_4$, respectively. Magnetic susceptibility was determined by the Evans method.[32] Guelph Chemical Laboratories or in-house elemental analysis services were employed to perform combustion analyses. The species $(Cp^*CrCl(\mu\text{-}Cl))_2$ (**1**) and $(Cp^*CrMe(\mu\text{-}Cl))_2$ (**2**) were generated as previously described in the literature.[15,33]

Synthesis of $[(Cp^*Cr)_2(\mu\text{-}Cl)_3]X$ ($X = [AlCl_4]$ (3), $[GaCl_4]$ (4), $[B(C_6F_5)_4]$ (5)). These compounds were prepared in a similar manner using $AlCl_3$, $GaCl_3$, and $[Ph_3C][B(C_6F_5)_4]$, respectively. To a stirred THF suspension of $CrCl_3{\cdot}3THF$ (0.108 g, 0.29 mmol) was added Cp*Li (0.041 g, 0.29 mmol) in THF. The mixture was stirred for 1 h at 25 °C, and the volatiles were removed under vacuum. To the residue was added CH_2Cl_2 followed by $AlCl_3$ (0.020 g, 0.145 mmol). The solution was stirred for 2 days and filtered through Celite. The addition of hexane gave dark blue crystals. **3**: yield 0.040 g, 43%. Anal. Calcd (found) for $C_{20}H_{30}Cr_2AlCl_7$: C, 36.98 (37.20); H, 4.65 (5.12). ^1H NMR: δ −12.10 (br, Cp*). X-ray unit cell data: orthorhombic, $a = 12.630(7)$ Å, $b = 20.85(1)$ Å, $c = 23.07(1)$ Å, $V = 6078(1)$ Å^3, **4**: yield 0.045 g, 46%. Anal. Calcd (found) for $C_{20}H_{30}Cr_2GaCl_7$: C, 34.70 (34.50); H, 4.37 (3.61). ^1H NMR: δ −12.30 (br, Cp*). X-ray unit cell data: orthorhombic, $a = 20.81(1)$ Å, $b = 12.661(7)$ Å, $c = 23.08(1)$ Å, $V = 6082$ (1) Å^3. **5**: yield 0.066 g, 40%. Anal. Calcd (found) for $C_{44}H_{30}F_{20}Cr_2BCl_3$: C, 45.57 (45.80); H, 2.61 (2.49). ^1H NMR: δ −12.0 (br, Cp*). ^{11}B NMR: δ −20.7. ^{19}F NMR: δ −132.8, −163.3, −167.0.

Synthesis of $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][MeB(C_6F_5)_3]$ (6). To a stirred THF suspension of $CrCl_3{\cdot}3THF$ (0.094 g, 0.25 mmol) was added Cp*Li (0.036 g, 0.25 mmol) in THF. The mixture was stirred for 1 h at 25 °C. MeLi (1.4 M; 0.080 mL, 0.125 mmol) was added. After the volatiles were removed under vacuum, to the residue was added CH_2Cl_2 followed by $B(C_6F_5)_3$ (0.064 g, 0.125 mmol). The solution was stirred for 2 days and filtered through Celite. The addition of hexane gave dark blue crystals. Yield: 0.045 g, 37%. Anal. Calcd (found) for $C_{39}H_{33}F_{15}Cr_2BCl_3{\cdot}0.5C_6H_6$: C, 48.19 (47.78); H, 3.47 (3.31). ^1H NMR: δ 0.5 (br, Me−B), −12.03 (br, Cp*). ^{11}B NMR: δ −19.0. ^{19}F NMR: δ −133.2, −165.2, −167.6.

Synthesis of $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][Me_2B(C_6F_5)_2]$ (7). To a stirred CH_2Cl_2 solution of **2** (0.035 g, 0.147 mmol) was added $HB(C_6F_5)_2$ (0.051 g, 0.147 mmol) in CH_2Cl_2. The resulting solution was stirred for 2 days at room temperature. Crystallization from benzene/hexane gave dark crystals. Yield: 0.020 g, 16%. Anal. Calcd (found) for $C_{34}H_{36}F_{10}BCr_2Cl_3$: C, 47.72 (47.28); H, 4.24 (3.87). ^1H NMR: δ −12.10 (br, Cp*). ^{11}B NMR: δ −19.1. ^{19}F NMR: δ −132.4, −164.2, −167.1.

Synthesis of $[(Cp^*Cr(\mu\text{-}Cl))_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (8). To a stirred THF solution of **5** (0.125 mmol) which was prepared in situ was added MeLi (1.4 M; 0.267 mL, 0.375 mmol). The solution was stirred for 2 days and filtered through Celite. Crystallization from CH_2Cl_2/hexane gave dark purple crystals. Yield: 0.040 g, 30%. Anal. Calcd (found) for $C_{45}H_{33}F_{20}BCr_2Cl_2$: C, 47.44 (47.90); H, 2.92 (3.20). ^1H NMR: δ −12.01 (br, Cp*). ^{11}B NMR: δ −20.7. ^{19}F NMR: δ −132.7, −162.7, −166.4. X-ray unit cell data: monoclinic, $a = 18.93(1)$ Å, $b = 34.05(2)$ Å, $c = 14.970(8)$ Å, $\beta = 99.76(1)°$, $V = 9507(1)$ Å^3.

Synthesis of $[(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2][B(C_6F_5)_4]$ (9). To a stirred toluene solution of **5** (0.125 mmol) which was prepared in situ was added Ph_2PLi (0.024 g, 0.125 mmol). The solution was stirred for 2 days and filtered through Celite. Crystallization from toluene/CH_2Cl_2/hexane gave dark crystals. Yield: 0.055 g, 34%. Anal. Calcd (found) for $C_{56}H_{40}F_{20}PBCr_2Cl_2$: C, 51.36 (50.89); H, 3.08 (2.71). ^1H NMR: δ 7.72, 7.37, 7.19, 7.12 (br, Ph H), −5.00 (br, Cp*). ^{31}P NMR: silent. ^{11}B NMR: δ −21.0. ^{19}F NMR: δ −132.3, −163.1, −166.7.

Synthesis of $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Cl)][AlMe_3Cl]$ (10). To a stirred THF suspension of $CrCl_3{\cdot}3THF$ (0.094 g, 0.25 mmol) was added Cp*Li (0.036 g, 0.25 mmol) in THF. The mixture was stirred for 1 h at room temperature. To the solution was added Ph_2PLi (0.048 g, 0.25 mmol) in THF. The resulting solution was stirred for 2 days. After the volatiles were removed under vacuum, to the residue was added benzene following $AlMe_3$ (0.045 g, 0.626 mmol). The resulting solution was stirred for 2 days and filtered through Celite. Crystallization from benzene/hexane gave dark crystals, Yield: 0.015 g, 13%. Anal. Calcd (found) for $C_{47}H_{59}P_2Cr_2AlCl_2{\cdot}0.5C_6H_6$: C, 64.79 (64.32); H, 6.74 (6.45). ^1H NMR: δ 7.63, 7.45, 7.14, 7.07 (br, Ph H), Cp* not observed. ^{31}P NMR: silent.

Synthesis of $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Me)][(Me_3Al)_2(\mu\text{-}Cl)]$ (11). To a stirred THF suspension of $CrCl_3$ (0.040 g, 0.25 mmol) was added Cp*Li (0.036 g, 0.25 mmol) in THF. The mixture was stirred overnight at room temperature. To the solution was added MeLi (1.4 M; 0.09 mL, 0.125 mmol) followed by Ph_2PLi (0.048 g, 0.25 mmol) in THF. The resulting solution was stirred for 2 days. After the volatiles were removed under vacuum, $AlMe_3$ (0.054 g, 0.750 mmol) was added to the residue. The resulting solution was stirred a further 2 days and filtered through Celite. Removal of the solvent and recrystallization of the residue from benzene/hexane gave dark crystals of **11**. Yield: 0.030 g, 25%. Anal. Calcd (found) for $C_{51}H_{71}P_2Cr_2Al_2Cl$: C, 65.20 (64.78); H, 7.62 (7.15). $\mu = 3.42\ \mu_B$. ^1H NMR: δ 7.64, 7.37, 7.16, 6.92 (br, Ph H), Cp* not observed. ^{31}P NMR: silent.

Synthesis of $(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}CH_2)$ (12) and $(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(\mu\text{-}CH_2)$ (13). To a stirred THF suspension of $CrCl_3{\cdot}3THF$ (0.108 g, 0.29 mmol) was added Cp*Li (0.041 g, 0.29 mmol) in THF. The mixture was stirred for 1 h at room temperature. To the solution was added MeLi (1.4 M; 0.207 mL, 0.29 mmol) followed by Ph_2PLi (0.056 g, 0.29 mmol) in THF. The resulting solution was stirred for 2 days and then filtered through Celite. Crystallization from benzene gave dark crystals of **12**. Yield: 0.055 g, 50%. Upon standing for extended period of time, **13** was obtained in very low yield (<6%). **12**: $\mu = 4.09\ \mu_B$; ^1H NMR δ 7.90, 7.57, 6.89, 6.76 (br, Ph H), Cp* silent; ^{31}P NMR silent. Anal. Calcd (found) for $C_{45}H_{52}Cr_2P_2$: C, 71.23 (70.80); H, 6.91 (7.15). **13**: yield 0.006 g, 6%; ^1H NMR δ 7.61, 7.43, 7.17, 6.92 (br, Ph H), Cp* silent; ^{31}P NMR silent. Anal. Calcd (found) for $C_{33}H_{42}Cr_2PCl$: C, 65.07 (64.59); H, 6.95 (6.47).

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

---

(32) Evans., D. F. *J. Chem. Soc.* **1959**, 2003.

(33) Noh, S. K.; Sendlinger, S. C.; Janiak, C.; Theopold, K. H. *J. Am. Chem. Soc.* **1989**, *111*, 9127−9129.

Table 1. Crystallographic Data[a]

	5	**6**	**7**	**9**
formula	$C_{88}H_{60}B_2Cl_6Cr_4F_{40}$	$C_{42}H_{36}BCl_3Cr_2F_{15}$	$C_{34}H_{36}BCl_3Cr_2F_{10}$	$C_{56}H_{40}BCl_2Cr_2F_{20}P$
fw	2319.68	1046.87	855.79	1309.56
a (Å)	18.914(9)	11.815(6)	11.251(8)	31.57(5)
b (Å)	34.087(17)	12.065(6)	12.519(9)	11.852(19)
c (Å)	15.051(7)	17.292(9)	14.347(10)	30.80(5)
α (deg)		87.968(10)	98.905(13)	
β (deg)	100.407(10)	70.213(10)	102.621(13)	103.54(4)
γ (deg)		78.280(10)	90.142(13)	
cryst syst	monoclinic	triclinic	triclinic	monoclinic
V (Å^3)	9544(8)	2270(2)	1947(2)	11204(32)
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
δ(calcd) (g cm^{-3})	1.614	1.532	1.460	1.553
Z	4	2	2	8
abs coeff, μ (cm^{-1})	0.734	0.747	0.913	0.616
no. of data collected	13 609	9863	8197	20 107
no. of data, $F_o^2 > 3\sigma(F_o^2)$	13 609	6496	5550	8287
no. of variables	1282	589	451	697
R	0.0424	0.0571	0.0608	0.0748
R_w	0.0822	0.1322	0.1084	0.1609
GOF	0.763	0.895	1.044	1.014

	10	**11**	**12**	**13**
formula	$C_{50}H_{62}AlCl_2Cr_2P_2$	$C_{51}H_{71}Al_2ClCr_2P_2$	$C_{45}H_{51}CrP$	$C_{33}H_{40}ClCr_2P$
fw	926.82	939.43	378.90	607.07
a (Å)	11.114(6)	11.136(5)	19.770(8)	11.266(6)
b (Å)	28.983(15)	15.005(7)	10.659(4)	12.028(6)
c (Å)	16.187(8)	16.986(8)	20.997(9)	12.536(7)
α (deg)		88.346(10)		86.238(10)
β (deg)	101.902(12)	73.993(9)	116.384(7)	80.103(9)
γ (deg)		81.270(10)		71.857(9)
cryst syst	monoclinic	triclinic	monoclinic	triclinic
V (Å^3)	5102(5)	2696(2)	3964(3)	1590.1(14)
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
δ(calcd) (g cm^{-3})	1.207	1.157	1.270	1.317
Z	4	2	4	2
abs coeff, μ (cm^{-1})	0.641	0.575	0.659	0.921
no. of data collected	21 842	11 611	6839	6906
no. of data, $F_o^2 > 3\sigma(F_o^2)$	7327	7703	2791	4534
no. of variables	514	535	222	352
R	0.0664	0.0389	0.0567	0.0348
R_w	0.1714	0.0783	0.1357	0.0847
GOF	0.898	0.802	0.758	0.817

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.710\ 69$ Å), $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[34] The heavy-atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. In cases where disorder was implied by the difference maps or the thermal parameters, attempts to model the disorder were undertaken. Such a model was deemed acceptable if the thermal parameters were typical and the geometry was chemically reasonable. In such cases the disordered atoms were treated isotropically. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated but not refined.

Results and Discussion

The species $(Cp^*CrCl(\mu\text{-}Cl))_2$ was generated and reacted with a chloride abstraction reagent such as $AlCl_3$, $GaCl_3$, or $[Ph_3C][B(C_6F_5)_4]$. Subsequent workup and recrystallization gave the salts formulated as $[(Cp^*Cr)_2(\mu\text{-}Cl)_3]X$ (X = $[AlCl_4]$ (**3**), $[GaCl_4]$ (**4**), $[B(C_6F_5)_4]$ (**5**)). The formulations of these compounds were consistent with the observation of a single resonance in the ^1H NMR spectra. In the last case, ^{11}B and ^{19}F NMR confirmed the presence of the perfluorinated borate anion. Recrystallization of these species gave dark blue crystals in each case. Crystallographic data were obtained for each of these species. In the case of **3** and **4**, initial solutions were consistent with the formulations; however, disorder issues were evident in both the anions and cations. Extensive attempts to model the disorders were problematic. In the case of **5**, a satisfactory solution was obtained and refined where the asymmetric unit contained two anions and cations. The borate anions were as expected. The cations were formulated as $[(Cp^*Cr)_2(\mu\text{-}Cl)_3]^+$ with the two Cp* rings oriented in a parallel fashion perpendicular to the Cr−Cr vector (Figure 1). For one of the cations in the asymmetric unit it was necessary to model a 4-fold disorder of the bridging chloride atoms. On the other hand, the second

---

(34) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321−324.

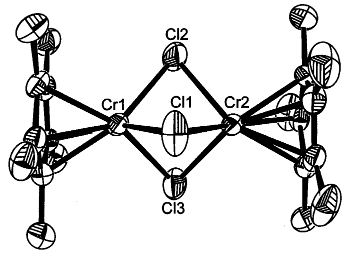


Figure 1. ORTEP drawing of one of the two cations of **5** in the asymmetric unit. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−Cl(2) = 2.3392(18), Cr(1)−Cl(1) = 2.3526(18), Cr(1)−Cl(3) = 2.3563(17), Cr(2)−Cl(1) = 2.3534(18), Cr(2)−Cl(2) = 2.3550(17), Cr(2)−Cl(3) = 2.3582(19), Cr(1)−Cr(2) = 2.8157(13); Cl(1)−Cr(2)−Cl(2) = 87.41(7), Cl(1)−Cr(2)−Cl(3) = 88.37(6), Cl(2)−Cr(2)−Cl(3) = 87.38(7), Cr(1)−Cl(1)−Cr(2) = 73.50(5), Cr(1)−Cl(2)−Cr(2) = 73.71(5), Cr(1)−Cl(3)−Cr(2) = 73.35(5).

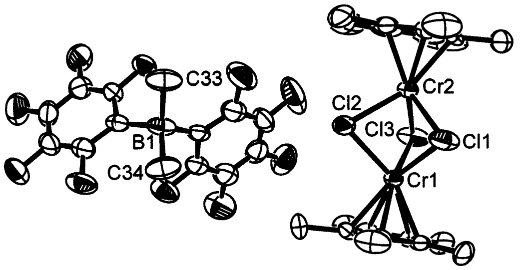


Figure 2. ORTEP drawing of **7**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

cation was refined without such a disorder. The latter case offers a more reliable metric of the Cr−Cl distances, which was found to be 2.3524(20) Å. On the other hand, the Cr−Cr separations are very similar in the two models (ordered cation, 2.8157(13) Å; disordered cation, 2.825(2) Å).

Using a similar synthetic route, the reaction of **1** generated in situ with MeLi and the borane $B(C_6F_5)_3$ gave crystals of the salt $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][MeB(C_6F_5)_3]$ (**6**). X-ray crystallography revealed that this species also crystallized in a disordered fashion. This disorder involved a 4-fold disorder of the Cl. This was satisfactorily modeled with 12 partial Cl positions located in the plane bisecting the Cr−Cr vector. The Cr−Cr separation was found to be similar to that in **5** (2.820(5) Å). A completely ordered structure was obtained for the complex $[(Cp^*Cr)_2(\mu\text{-}Cl)_3][Me_2B(C_6F_5)_2]$ (**7**) (Figure 2). This species was derived, albeit in low yield, from the reaction of $[Cp^*CrMe(\mu\text{-}Cl)]_2$ with $HB(C_6F_5)_2$ in CH_2Cl_2. In this case, the Cr−Cl distances and the Cl−Cr−Cl angles averaged 2.363(4) Å and 74.4(1)°, respectively, while the Cr−Cr separation was found to be 2.859(2) Å, a metric similar to those seen in the previous salts.

The compound $[(Cp^*Cr)_2(\mu\text{-}Me)_3][BF_4]$,[12] which represents the only previously known triply bridged dinuclear Cr salt, was generated via protonation of $(Cp^*Cr(\mu\text{-}Me))_2(\mu\text{-}CH_2)$. Although crystallographic data have not been published to our knowledge, the Cr−Cr distance is described as 2.42 Å, significantly shorter than those found in **5**−**7**.

Attempts to alkylate **5** with MeLi afforded the species formulated as $[(Cp^*Cr(\mu\text{-}Cl))_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**8**), which was isolated as dark, purple crystals in 30% yield. The bridging methyl resonances were not observed in the ^1H NMR spectrum. Although crystallographic data were obtained, a complete and satisfactory solution was not. Nonetheless, the data appeared consistent with the presence of the Cp*Cr fragments and the anion, although the nature and positions of the bridging atoms could not unambiguously be determined, as a result of disorder. Nonetheless, one piece of preliminary metric information that supports the above formulation was the observed Cr−Cr distance of 2.59(1) Å. This distance is markedly shorter than that seen in **5**−**7**, while being longer than that alluded to by Theopold et al. for $[(Cp^*Cr)_2(\mu\text{-}Me)_3][BF_4]$ (2.42 Å).[12] This, together with elemental analyses, was consistent with monomethylation of the bridging positions.

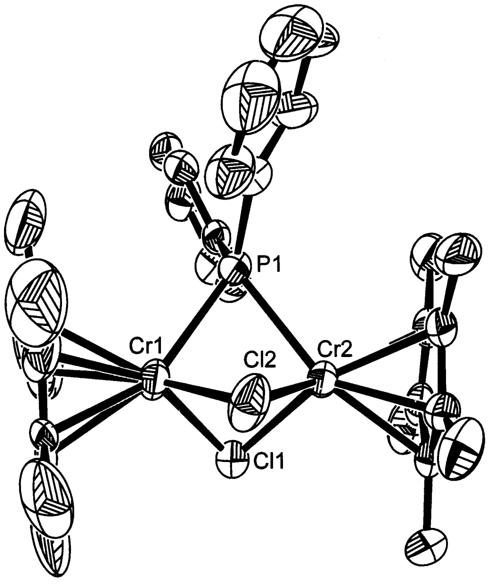


Figure 3. ORTEP drawing of the cation of **9**. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Cr(1)−Cl(2) = 2.323(4), Cr(1)−Cl(1) = 2.340(4), Cr(1)−P(1) = 2.390(5), Cr(1)−Cr(2) = 2.802(4), Cr(2)−Cl(1) = 2.324(4), Cr(2)−Cl(2) = 2.340(4), Cr(2)−P(1) = 2.404(4); Cl(2)−Cr(1)−Cl(1) = 88.74(15), Cl(2)−Cr(1)−P(1) = 87.90(11), Cl(1)−Cr(1)−P(1) = 88.16(11), Cl(1)−Cr(2)−Cl(2) = 88.74(16), Cl(1)−Cr(2)−P(1) = 88.24(12), Cl(2)−Cr(2)−P(1) = 87.20(10), Cr(2)−Cl(1)−Cr(1) = 73.86(14), Cr(1)−Cl(2)−Cr(2) = 73.88(10), Cr(1)−P(1)−Cr(2) = 71.55(8).

Related phosphide-bridged cationic species were derived from the reaction of **5** with the phosphide Ph_2PLi. Following workup the species formulated as $[(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2][B(C_6F_5)_4]$ (**9**) was isolated in 34% yield. The X-ray structure (Figure 3) of **9** confirmed the formulation, revealing a structure of the cation that is analogous to that seen in **5**−**7**, with a phosphide replacing one of the bridging chloride atoms. The bridging Cr−Cl and Cr−P distances averaged 2.332(5) and 2.397(5) Å, respectively, while the Cr−Cl−Cr and Cr−P−Cr angles at the bridging atoms were found to be 73.87(14) and 71.55(8)°, respectively. The Cr−Cr distance of 2.802(1) Å was slightly shorter than those found in **5**−**7**.

In attempts to isolate related neutral phosphide-bridged species, the reaction of **1** with Ph_2PLi was undertaken. Although reaction was evident from the observed color change, repeated attempts under various

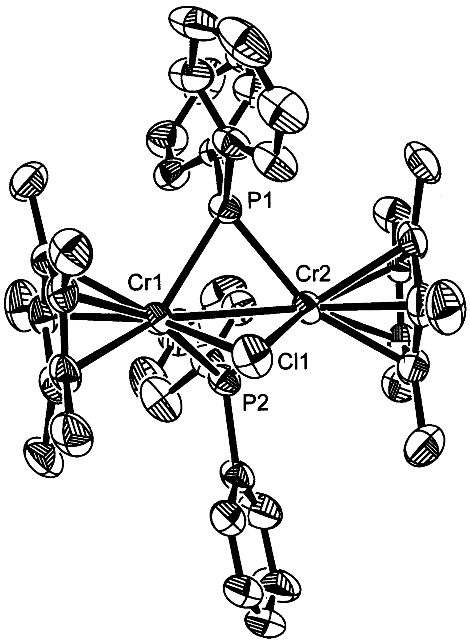
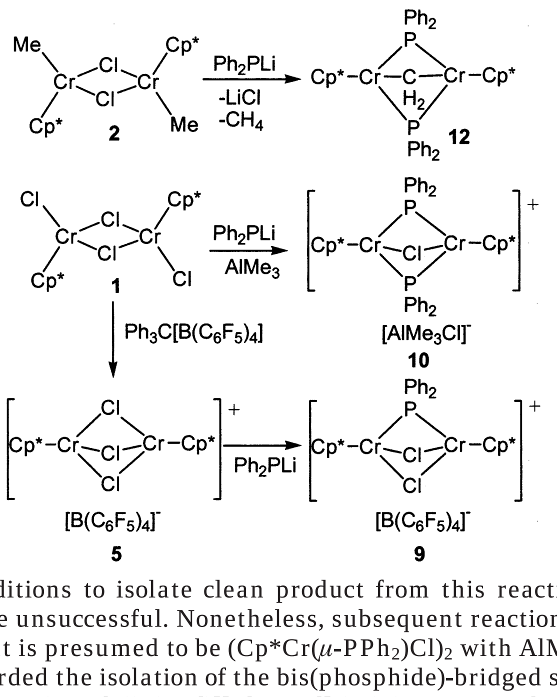


Figure 4. ORTEP drawing of the cation of **10**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−Cl(1) = 2.353(2), Cr(1)−P(1) = 2.392(2), Cr(1)−P(2) = 2.393(3), Cr(1)−Cr(2) = 2.7984(19), Cr(2)−Cl(1) = 2.346(3), Cr(2)−P(1) = 2.385(2), Cr(2)−P(2) = 2.398(2); Cl(1)−Cr(1)−P(1) = 86.14(8), Cl(1)−Cr(1)−P(2) = 86.24(8), P(1)−Cr(1)−P(2) = 93.78(7), Cl(1)−Cr(2)−P(1) = 86.45(9), Cl(1)−Cr(2)−P(2) = 86.30(8), P(1)−Cr(2)−P(2) = 93.84(8), Cr(2)−Cl(1)−Cr(1) = 73.09(7), Cr(2)−P(1)−Cr(1) = 71.73(7), Cr(1)−P(2)−Cr(2) = 71.48(7).

Scheme 1



conditions to isolate clean product from this reaction were unsuccessful. Nonetheless, subsequent reaction of what is presumed to be $(Cp^*Cr(\mu\text{-}PPh_2)Cl)_2$ with $AlMe_3$ afforded the isolation of the bis(phosphide)-bridged salt $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Cl)][AlMe_3Cl]$ (**10**) (Figure 4, Scheme 1). The anion was unexceptional, while the average Cr−P and Cr−Cl distances in the cation of **10** were found to be 2.392(2) and 2.350(2) Å, respectively. The Cr−Cr distance in **10** is 2.7984(19) Å, slightly less than that seen in **9**, while the Cr−P−Cr angle of 71.50(9)° is similar to that seen in **9**.

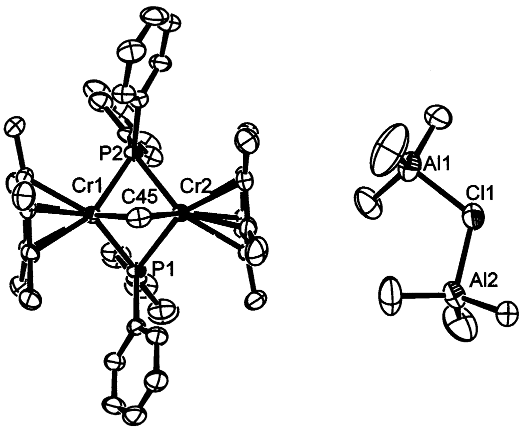


Figure 5. ORTEP drawing of **11**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−C(45) = 2.215(5), Cr(1)−P(2) = 2.3559(14), Cr(1)−P(1) = 2.3672(14), Cr(1)−Cr(2) = 2.6392(12), Cr(2)−C(45) = 2.238(5), Cr(2)−P(1) = 2.3516(13), Cr(2)−P(2) = 2.3739(15), Al(1)−Cl(1) = 2.382(2), Al(2)−Cl(1) = 2.378(2); C(45)−Cr(1)−P(2) = 87.25(14), C(45)−Cr(1)−P(1) = 87.99(16), P(2)−Cr(1)−P(1) = 97.28(4), C(45)−Cr(2)−P(1) = 87.84(15), C(45)−Cr(2)−P(2) = 86.28(15), P(1)−Cr(2)−P(2) = 97.21(4), P(1)−Cr(2)−Cr(1) = 56.27(3), P(2)−Cr(2)−Cr(1) = 55.76(4), Al(2)−Cl(1)−Al(1) = 116.02(7), Cr(2)−P(1)−Cr(1) = 68.01(4), Cr(1)−P(2)−Cr(2) = 67.83(3), Cr(1)−C(45)−Cr(2) = 72.68(12).

Alkylation of **1** with MeLi in situ followed by treatment with 2 equiv of Ph_2PLi and subsequent excess $AlMe_3$ yielded $[(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}Me)][(Me_3Al)_2(\mu\text{-}Cl)]$ (**11**) in 25% yield (Figure 5). The anion was found to contain a chloride ion bridging two $AlMe_3$ fragments with an average Al−Cl distance of 2.380(2) Å. The cation of **11** was similar to that seen in **10**, with a methyl group replacing the bridging chloride. The Cr−P distances average 2.3586(16) Å, while the Cr−C bond lengths to the bridging methyl group average 2.226(5) Å. The corresponding Cr−C−Cr angle is 72.68(12)°. The result of methyl replacing Cl appears to be a slightly shorter Cr−Cr distance of 2.6392(12) Å in **11** and a decrease in the Cr−P−Cr angle to 67.92(4)°.

The neutral phosphide- and methylene-bridged species $(Cp^*Cr(\mu\text{-}PPh_2))_2(\mu\text{-}CH_2)$ (**12**) was isolated from the reaction of **2** with 2 equiv of Ph_2PLi by elimination of LiCl and methane in 50% yield (Figure 6, Scheme 1). Although not determined quantitatively, a ^1H NMR resonance attributable to methane was observed. In addition, an extremely small yield of a few crystals of $(Cp^*Cr)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(\mu\text{-}CH_2)$ (**13**) was also obtained (Figure 7). Crystallographic data confirmed the neutral formulations, although the data for **13** revealed a disorder of the bridging Cl and CH_2 ligands. In **12** the bridging Cr−P and Cr−C distances were found to be 2.3148(13) and 2.253(3) Å, respectively. The corresponding Cr−P distances in **13**, averaging 2.3613(15) Å, are slightly longer than in **12**. The presence of the bridging methylene group in these species resulted in relatively short Cr−Cr separations of 2.5517(13) Å in **12** and 2.6134(11) Å in **13**. The angles at the bridging P and Cr centers (Cr−P−Cr: **12**, 66.89(3)°; **13**, 67.20(3)°) are similar but smaller than those seen in **9** and **10**.

The data presented above describe neutral and phosphido-bridged Cr dimers. The Cr−P bonds found in

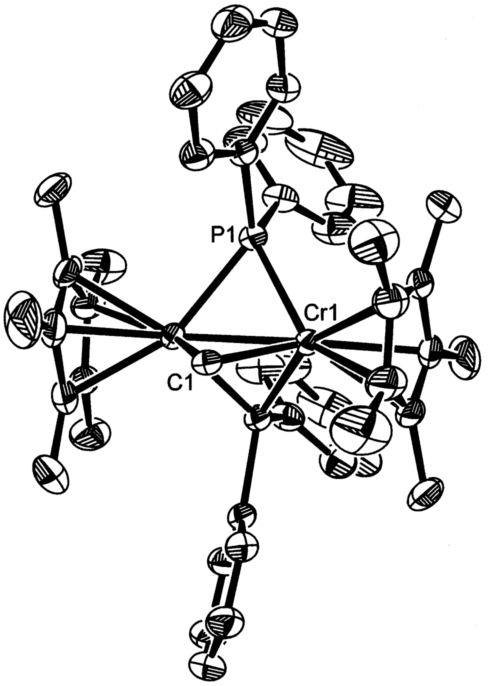


Figure 6. ORTEP drawing of **12**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−C(1) = 2.253(3), Cr(1)−P(1) = 2.3130(13), Cr(1)−P(1) = 2.3167(13), Cr(1)−Cr(1) = 2.5517(13); C(1)−Cr(1)−P(1) = 91.36(6), C(1)−Cr(1)−P(1) = 91.26(5), P(1)−Cr(1)−P(1) = 93.56(4), Cr(1)−P(1)−Cr(1) = 66.89(3), Cr(1)−C(1)−Cr(1) = 68.98(12).

Table 2. Cr−Cr Distances (Å) in Triply Bridged Cr(III) Dimers

compd	Cr−Cr	compd	Cr−Cr
5	2.8157(13)	**13**	2.6134(11)
6	2.820(2)	**8**	2.59(1)
7	2.859(2)	**12**	2.5517(13)
9	2.802(1)	$[(Cp^*Cr)_2(\mu\text{-}Me)_3][BF_4]$	2.42[12]
10	2.7984(19)	$(Cp^*Cr)_2(\mu\text{-}Me)_2(\mu\text{-}CH_2)$	2.394(1)[37]
11	2.6392(12)		

these dimers all fall in the narrow range between 2.3130(13) and 2.393(3) Å. Although no previous reports of Cr(III) phosphides have appeared, these values can be compared with the Cr−P distances of 2.389(1), 2.396(1), 2.343(1), and 2.449(2) Å found in the dialkylphosphide-bridged heterobimetallics $(Me_3P)(OC)_4Cr(\mu\text{-}PtBu_2)Rh(COD)$, $(Me_3P)(OC)_4Cr(\mu\text{-}PtBu_2)Co(CO)(PMe_3)$,[35] $(Me_3P)(OC)_4Cr(\mu\text{-}PtBu_2)NiCl(PMe_3)$, and $(Me_3P)(OC)_4Cr(\mu\text{-}PtBu_2)Rh(CO)(PMe_3)$,[36] respectively. In addition, the structural data for dimeric Cr species show trends (Table 2) consistent with previous observations.[12] The triply bridged neutral species, containing three-center−four-electron methylene donors, give rise to shorter Cr−Cr distances than in the cationic species. In addition, variation in the Cr−Cr distances among the triply bridged cations appears to reflect the covalent radii of the bridging atoms (Cl > P > Me). While the general synthetic methods described herein provide only moderate to low yields, suggesting alternate reaction pathways may be operative, efforts are continuing to develop new synthetic strategies and to explore the chemistry of Cr phosphide complexes.

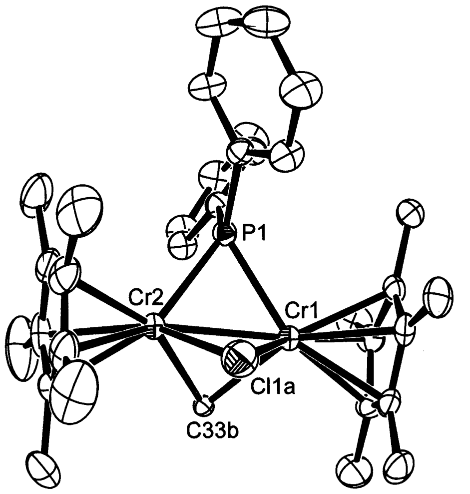


Figure 7. ORTEP drawing of **13**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−C(33) = 1.983(15), Cr(1)−C(33B) = 2.11(3), Cr(1)−Cl(1) = 2.333(3), Cr(1)−P(1) = 2.3620(12), Cr(1)−Cl(1A) = 2.393(7), Cr(1)−Cr(2) = 2.6134(11), Cr(2)−C(33B) = 2.01(3), Cr(2)−C(33) = 2.08(2), Cr(2)−Cl(1) = 2.350(3), Cr(2)−Cl(1A) = 2.353(9), Cr(2)−P(1) = 2.3606(15); C(33)−Cr(1)−C(33B) = 78.5(8), C(33)−Cr(1)−Cl(1) = 89.2(6), C(33)−Cr(1)−P(1) = 91.1(5), C(33B)−Cr(1)−P(1) = 89.8(8), C(33B)−Cr(1)−Cl(1A) = 82.7(6), Cl(1)−Cr(1)−Cl(1A) = 93.4(3), P(1)−Cr(1)−Cl(1A) = 93.2(2), C(33B)−Cr(2)−Cl(1) = 8.6(8), C(33)−Cr(2)−Cl(1) = 86.6(5), C(33B)−Cr(2)−Cl(1A) = 85.8(7), Cl(1)−Cr(2)−Cl(1A) = 94.0(2), C(33B)−Cr(2)−P(1) = 92.4(8), C(33)−Cr(2)−P(1) = 88.9(5), Cl(1)−Cr(2)−P(1) = 89.12(7), Cl(1A)−Cr(2)−P(1) = 94.3(2), Cr(2)−P(1)−Cr(1) = 67.20(3), Cr(1)−Cl(1)−Cr(2) = 67.84(8), Cr(2)−Cl(1A)−Cr(1) = 66.81(17), Cr(1)−C(33)−Cr(2) = 80.1(5), Cr(2)−C(33B)−Cr(1) = 78.7(9).

Acknowledgment. Financial support from the NSERC of Canada and the ORDCF is gratefully acknowledged. D.W.S. is grateful to the Alexander von Humboldt Stiftung for the award of a Forschungpreis.

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

OM0209881

---

(35) Chandler, D. J.; Jones, R. A.; Stuart, A. L.; Wright, T. C. *Organometallics* **1984**, *3*, 1830−1838.

(36) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stuart, A. L.; Wright, T. C.; Whittlesey, B. R. *Organometallics* **1984**, *3*, 114−119.

(37) Noh, S. K.; Heintz, R. A.; Janiak, C.; Sendlinger, S. C.; Theopold, K. H. *Angew. Chem.* **1990**, *102*, 805−807.