Organometallics **2003,** *22,* 1657−1662

Phosphinidene- and Phosphido-Bridged Complexes from a η^2-Arylthioxophosphane Cyclopentadienylchromium Complex

Zhiqiang Weng, Weng Kee Leong, Jagadese J. Vittal, and Lai Yoong Goh*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260

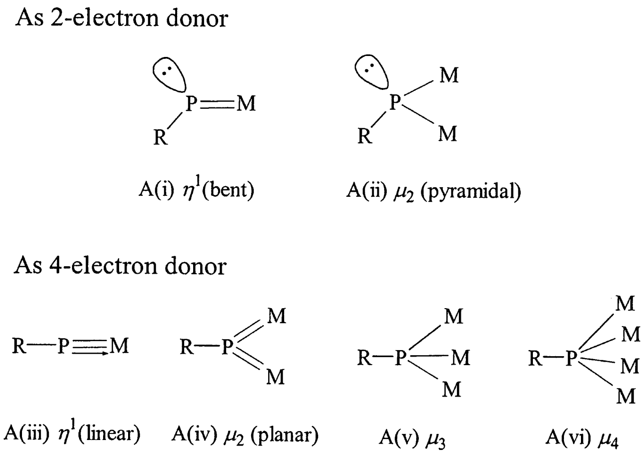
Received November 12, 2002

The reaction of the η^2-arylthioxophosphane complex $CpCr(CO)_2(SP(H)Ar)$ (**2**; Ar = C_6H_4-OCH_3) with $[CpCr(CO)_3]_2$ (**1**) at 110 °C led to the isolation of new structurally characterized complexes: hydridophosphido-bridged $Cp_2Cr_2(CO)_4(\mu_2\text{-}H)(\mu_2\text{-}P(H)Ar)$ (**3**), bis(phosphido)-bridged Cr=Cr doubly bonded $Cp_2Cr_2(CO)_2(\mu_2\text{-}P(H)Ar)_2$ (**4**), and μ_3-phosphinidene cubanes $Cp_4Cr_4S_3(\mu_3\text{-}PAr)$ (**5**) and $Cp_4Cr_4S_2(\mu_3\text{-}PAr)_2$ (**6**), together with $CpCr(CO)_3H$ (**7**) and $Cp_4Cr_4S_4$ (**9**) with yields of 4, 11, 16, 32, 5, and 19%, respectively.

Introduction

The rich chemistry of metal−carbon, −nitrogen, −oxygen, and −sulfur multiple bonds, particularly with respect to synthetic applications,[1] has spurred interest in transition-metal phosphinidenes.[2] The phosphinidene ligand is capable of binding to transition metals in a variety of coordination modes—as a two-electron donor in the bent (η_1) form A(i) and the pyramidal (μ_2) form A(ii) and as a four-electron donor in forms A(iii)−A(vi) (Chart 1).

Chart 1. Coordination Modes of Phosphinidene



Terminal phosphinidene metal complexes of the type A(i) are the analogues of carbene complexes and, like metal carbenes, have been shown to possess rich reactivity features of both electrophilic and nucleophilic character.[3] While many examples of μ_2-bridging phosphinidene complexes are known of groups 5 and 6 metals,[4a,b,d,h] and there are odd examples of Zr,[4e,f] Co,[4c,d] and Pt,[4g] μ_3- and μ_4-phosphinidene complexes are limited in number. The majority of these μ_3 complexes contain the $M_3(CO)_n$ (n = 6, 8, 9) cluster moieties of group 8 metals (M = Fe,[5] M = Ru, Os[6a,b]), with some containing bis μ_3 or μ_4 ligands, e.g. $Fe_3(CO)_9(\mu_3\text{-}PR)_2$,[5h] $Fe_4(CO)_{11}(\mu_3\text{-}PR)_2$,[5i] $(cod)_4Rh_4(\mu_4\text{-}PPh)_2$,[6d] and $Ru_4(CO)_{10}$-$(\mu\text{-}CO)(\mu_4\text{−}PPh)_2$.[8a] Heterometallic examples include $MCo_2(\mu_3\text{-}PCy)(CO)_9$ (M = Fe, Ru),[7a] $MnFeCo(CO)_{10}(\mu\text{-}PR)$,[7b] $Cp/Cp^*WRu_n(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ (n = 2, 3),[7c and] $Ru_3(CO)_9(\mu\text{-}Au(PMe_2Ph))(\mu\text{-}H)(\mu_3\text{-}PPh)$.[7d] There are some μ_3- and μ_4-aminophosphinidene complexes: e.g., $(Ph_3P{=}N{=}PPh_3)Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PN^iPr_2)$,[8b] $Ru_5(CO)_{10}$-$(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_3\text{-}PN^iPr_2)(\mu_4\text{-}NH)$,[8b] $Ru_4(CO)_{12}Pt(CO)$-

---

* To whom correspondence should be addressed. E-mail: chmgohly@nus.edu.sg.

(1) *Metal−Ligand Multiple Bonds*; Nugent, W. A., Mayer, J. M., Eds.; Wiley: New York, 1988.

(2) (a) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. (b) Mathey, F.; Huy, N. H. T.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938.

(3) (a) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445. (b) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127.

(4) (a) Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406. (b) Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.* **1984**, *263*, C33. (c) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulskl, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1267. (d) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. *Organometallics* **1988**, *7*, 309. (e) Ho, J.; Stephan, D. W. *Organometallics* **1991**, *10*, 3001. (f) Ho, J.; Rousseau, R.; Stephan, D. W. *Organometallics* **1994**, *13*, 1918. (g) Kourkine, I. V.; Glueck, D. S. *Inorg. Chem.* **1997**, *36*, 5160. (h) Hadi, G. A. A.; Fromm, K.; Blaurock, S.; Jelonek, S.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 721.

(5) (a) Fackler, J. P., Jr.; Mazany, A. M.; Seyferth, D.; Withers, H. P., Jr.; Wood, T. G.; Campana, C. F. *Inorg. Chim. Acta* **1984**, *82*, 31. (b) Lindner, E.; Weiss, G. A.; Hiller, W. W.; Fawzi, R. *J. Organomet. Chem.* **1983**, *255*, 245. (c) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367. (d) Borg-Breen, C. C.; Bautista, M. T.; Schauer, C. K.; White, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 3952. (e) Sunick, D. L.; White, P. S.; Schauer, C. K. *Organometallics* **1993**, *12*, 245. (f) Bautista, M. T.; Jordan, M. R.; White, P. S.; Schauer, C. K. *Inorg. Chem.* **1993**, *32*, 5429. (g) Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897. (h) Lang, H.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1985**, *282*, 23. (i) Jaeger, J. T.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1746.

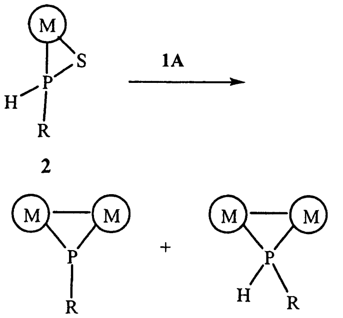
(6) (a) Iwasaki, F.; Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Wheatley, P. J. *J. Organomet. Chem.* **1981**, *213*, 185. (b) Böttcher, H.-C.; Graf, M.; Merzweiler, K. *J. Organomet. Chem.* **1997**, *531*, 107. (c) Cherkas, A. A.; Corrigan, J. F.; Doherty, S.; MacLaughlin, S. A.; van Gastel, F.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 1662. (d) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.

(7) (a) Bouherour, S.; Braunstein, P.; Rosé, J.; Toupet, L. *Organometallics* **1999**, *18*, 4908. (b) Muller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2322. (c) Lin, R.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1992**, *31*, 3818. (d) May, M. J.; Raithby, P. R.; Taylor, P. L. *J. Chem. Soc., Dalton Trans.* **1984**, 959.

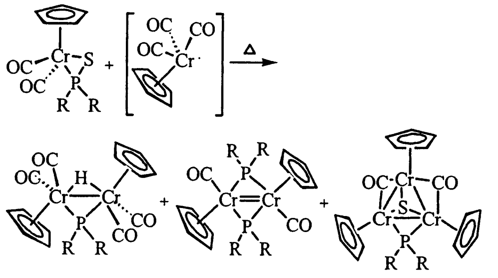
(8) (a) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Chem. Soc., Dalton Trans.* **1988**, 1315. (b) Scoles, L.; Stereberg, B. T.; Udachin, K. A.; Carty, A. J. *Chem. Commun.* **2002**, 320. (c) Scoles, L.; Yamamoto, J. H.; Brissieux, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Inorg. Chem.* **2001**, *40*, 6731.

10.1021/om020934r CCC: $25.00

PPh$_3$(μ_4-PN^{i}Pr$_2$),[8c] and Ru$_3$(CO)$_9$Pt(CO)PPh$_3$(μ_3-PN^{i}Pr$_2$).[8c] The main synthetic pathways to these complexes are represented by (i) the reaction of M$_3$(CO)$_{12}$ (e.g. for M = Fe, Ru) with RP(S)Cl$_2$,[5a] [RP(S)S]$_2$,[5a] or H$_2$PPh,[6a] (ii) the reaction of Na$_2$[Fe(CO)$_4$] with RP(S)Cl$_2$,[5b] and (iii) P−C(Ph) bond activation of the μ-phosphido complex HM$_3$(CO)$_{10}$(μ-PPh$_2$) (M = Ru, Os).[6c] The single μ_3-phosphinidene cubane reported to date is the cluster (Cp′Mo)$_2$Co(CO)$_2$S$_3$(PPh), derived from the reaction of (Cp′Mo)$_2$(Co(CO)$_2$)$_2$S$_3$ with H$_2$PPh.[9] In this study we wish to explore whether CpCr(CO)$_3^{\bullet}$-initiated desulfurization of the η^2-arylthioxophosphane complex **2** (described in the preceding paper in this issue) will provide a pathway to μ-phosphinidene or μ-phosphido complexes (eq i). The results would give a comparison to related studies that we have performed on thiophosphinito complexes, represented by eq ii.[10]



(i)



(ii)

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 inert gas system. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (^{1}H at 300.14 MHz, ^{13}C at 75.43 MHz, and ^{31}P at 121.49 MHz); ^{1}H and ^{13}C chemical shifts were referenced to residual C$_6$H$_6$ in C$_6$D$_6$ and ^{31}P chemical shifts to external H$_3$PO$_4$. IR spectra were measured in the range 4000−400 cm^{-1} on a BioRad FTS-165 FTIR instrument. Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the in-house microanalytical laboratory. [CpCr(CO)$_3$]$_2$ (**1**) was prepared according to literature procedures,[11] and CpCr(CO)$_2$(SP(H)Ar) (Ar = C$_6$H$_4$OCH$_3$) (**2**) was obtained as described in the preceding paper in this issue.[12] All solvents were dried over sodium/benzophenone and distilled before use. Silica gel (Merck Kieselgel 60, 230−400 mesh) for column chromatography was dried at 140 °C overnight before use.

Reaction of CpCr(CO)$_2$(SPAr) (2) with [CpCr(CO)$_3$]$_2$ (1). A brown mixture of CpCr(CO)$_2$(SP(H)Ar) (**2**; 48 mg, 0.14 mmol) and [CpCr(CO)$_3$]$_2$ (**1**; 56 mg, 0.14 mmol) in toluene (6 mL) was stirred at 110 °C for 1 h. The resultant dark brown product solution was concentrated to ca. 2 mL and loaded onto a silica gel column (2 × 10 cm) prepared in *n*-hexane. Elution gave seven fractions. (i) A yellow eluate in *n*-hexane/toluene (4:1, 5 mL) was obtained, which yielded greenish yellow solids of CpCr(CO)$_3$H (**7**) (ca. 3 mg, 0.01 mmol, 5%), diagnosed by its proton NMR characteristics (δ(Cp) 4.02 and δ(Cr−H) 5.56).[13] (ii) A deep green eluate in *n*-hexane/toluene (1:1, 5 mL) was obtained, which yielded highly air-sensitive dark brown crystals of Cp$_2$Cr$_2$(CO)$_4$(H)(P(H)Ar) (**3**; ca. 3 mg, 0.006 mmol, 4% yield). (iii) A dark green eluate in toluene (8 mL) was obtained, which on concentration yielded dark green solids of Cp$_4$Cr$_4$S$_4$ (**9**; 8 mg, 0.013 mmol, 19%). (iv) A red eluate in toluene (8 mL) was obtained, which gave dark red crystals of Cp$_2$Cr$_2$(CO)$_2$(P(H)Ar)$_2$ (**4**; 9 mg, 0.02 mmol, 11%). (v) A red-brown eluate in toluene (10 mL) was obtained, which gave dark brown crystals of Cp$_4$Cr$_4$S$_3$(PAr) (**5**; 8 mg, 0.01 mmol, 16%). (vi) A brown eluate in toluene/THF (5:1, 10 mL) was obtained, which yielded dark brown solids of Cp$_4$Cr$_4$S$_2$(PAr)$_2$ (**6**; 18 mg, 0.02 mmol, 32%). (vii) A brown eluate in THF (5 mL) was obtained, which yielded an uncharacterizable dark brown oily compound (3 mg).

Data. Compound 3. IR (toluene, ν(CO)/cm^{-1}): 1930 s, 1880 s. ^{1}H NMR (C$_6$D$_6$): δ 4.16 (s, 10H, C$_5$H$_5$), 6.72 (d, J = 8 Hz, 2H, C$_6$H$_4$), 7.38 (m, 2H, C$_6$H$_4$), 3.25 (s, 3H, OCH$_3$), 6.73 (d, J = 340 Hz, 1H, PH). −12.84 (d, J = 73 Hz, 1H, CrHCr). ^{13}C NMR (C$_6$D$_6$): δ 89.0 (C$_5$H$_5$), 134.9, 134.8, 115.0 and 114.9 (C$_6$H$_4$), 55.4 (OCH$_3$); no CO signals were observed, presumably because of their long relaxation times. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 191.7. MS FAB$^+$ (*m*/*z*): 486 [M]$^+$, 430 [M − 2CO]$^+$, 374 [M − 4CO]$^+$. HR-MS FAB$^+$ (*m*/*z*): for [M]$^+$ 485.9783 (found), 485.9780 (calcd). Microanalytical data are not available, on account of the extremely low yield and high air sensitivity. The proton NMR spectrum is submitted in the Supporting Information as proof of purity.

Compound 4. IR (KBr, ν(CO)/cm^{-1}): 1913 m, 1845 s. ^{1}H NMR (C$_6$D$_6$): δ 4.34 (s, 10H, C$_5$H$_5$), 6.77 (d, J = 8 Hz, 4H, C$_6$H$_4$), 7.66 (m, 4H, C$_6$H$_4$), 3.29 (s, 6H, OCH$_3$), 5.04 (d, J = 318 Hz, 1H, PH). ^{13}C NMR (C$_6$D$_6$): δ 91.4 (C$_5$H$_5$), 134.7, 130.0, and 115.1 (C$_6$H$_4$), 55.4 (OCH$_3$); as in complex **3**, no CO signals were observed. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 131.2. Anal. Calcd for C$_{26}$H$_{26}$Cr$_2$O$_4$P$_2$: C, 55.0; H, 4.6. Found: C, 55.5; H, 4.2. MS FAB$^+$ (*m*/*z*): 568 [M]$^+$, 540 [M − CO]$^+$, 510 [M − 2CO]$^+$. HR-MS FAB$^+$ (*m*/*z*): for [M]$^+$ 568.0104 (found), 568.0116 (calcd).

Compound 5. ^{1}H NMR (C$_6$D$_6$): δ 5.06 (s, 5H, C$_5$H$_5$), 4.82 (s, 15H, C$_5$H$_5$), 6.78 (d, J = 8 Hz, 2H, C$_6$H$_4$), 7.42 (m, 2H, C$_6$H$_4$), 3.37 (s, 3H, OCH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 90.2 and 89.2 (C$_5$H$_5$), 135.0, 132.7, 130.8, and 115.1 (C$_6$H$_4$), 55.6 (OCH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 508.4. Anal. Calcd for C$_{27}$H$_{27}$Cr$_4$OPS$_3$: C, 46.2; H, 3.9. Found: C, 46.5; H, 3.9. MS FAB$^+$ (*m*/*z*): 702 [M]$^+$, 637 [M − Cp]$^+$. HR-MS ESI$^+$ (*m*/*z*): for [M]$^+$ 701.8589 (found), 701.8589 (calcd).

Compound 6. ^{1}H NMR (C$_6$D$_6$): δ 5.01 (s, 10H, C$_5$H$_5$), 4.73 (s, 10H, C$_5$H$_5$), 6.80 (d, J = 8 Hz, 4H, C$_6$H$_4$), 7.40 (br, 4H, C$_6$H$_4$), 3.38 (s, 6H, OCH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 88.7 (C$_5$H$_5$), 88.1 (C$_5$H$_5$), 134.8, 130.8, and 115.0 (C$_6$H$_4$), 55.5 (OCH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 1296. Anal. Calcd for C$_{34}$H$_{34}$Cr$_4$O$_2$P$_2$S$_2$: C, 50.5; H, 4.3. Found: C, 49.9; H, 4.9. MS FAB$^+$ (*m*/*z*): 808 [M]$^+$, 743 [M − Cp]$^+$. HR-MS ESI$^+$ (*m*/*z*): for [M]$^+$ 807.9099 (found), 807.9096 (calcd).

Thermolysis of CpCr(CO)$_2$(SP(H)Ar) (2). An NMR-Tube Reaction. A dark red solution of **2** (8 mg, 0.02 mmol) in toluene-d_8 (0.5 mL) in a septum-capped 5 mm NMR tube under argon was maintained at ca. 110 °C, and its proton NMR spectrum was scanned at intervals up to 2 h.

---

(9) Curnow, O. J.; Kampf, J. W.; Curtis, M. D. *Organometallics* **1991**, *10*, 2546.

(10) Goh, L. Y.; Weng, Z.; Leong, W. K.; Vittal, J. J. *Organometallics* **2002**, *21*, 5287.

(11) Manning, A. R.; Hackett, P.; Birdwhistell, R.; Soye, P. *Inorg. Synth.* **1990**, *28*, 148.

(12) Goh, L. Y.; Weng, Z.; Leong, W. K.; Vittal, J. J. *Organometallics* **2003**, *22*, 1645.

(13) (a) Goh, L. Y.; Chen, W.; Wong, R. C. S.; Karaghiosoff, K. *Organometallics* **1995**, *14*, 3886. (b) Goh, L. Y.; Chen, W.; Wong, R. C. S. *Organometallics* **1999**, *18*, 306.

Table 1. Data Collection and Processing Parameters

	4	**5**	**6**
formula	$C_{26}H_{26}Cr_2O_4P_2$	$C_{27}H_{27}Cr_4OPS_3 \cdot {}^1/_4C_7H_8$	$C_{34}H_{34}Cr_4O_2P_2S_2$
M_r	568.41	725.67	808.67
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$C2/c$	$C2/c$	$Cmcm$
a, Å	13.618(2)	43.214(6)	10.7471(13)
b, Å	9.4510(15)	9.7364(13)	16.1172(18)
c, Å	19.492(3)	14.971(2)	18.290(2)
α, deg	90	90	90
β, deg	98.305(4)	110.106(3)	90
γ, deg	90	90	90
V, Å^3	2482.4(7)	5915.3(14)	3168.1(6)
Z	4	8	4
density, g cm^{-3}	1.521	1.630	1.695
abs coeff, mm^{-1}	1.035	1.719	1.601
F(000)	1168	2948	1648
θ range for data collecn, deg	2.11 to 25.00	2.01 to 25.00	2.23 to 24.71
index ranges			
h	−16 to +13	−31 to +51	0 to +12
k	−11 to +11	−11 to +11	0 to +18
l	−21 to +23	−17 to +17	0 to +21
no. of rflns collected	6934	16 175	26 166
no. of indep rflns	2184	5208	1486
no. of data/restraints/params	2184/0/186	5208/5/250	1486/6/65
final R indices [$I > 2\sigma(I)$][a,b]			
R1	0.0484	0.0748	0.0493
wR2	0.1056	0.2088	0.1269
R indices (all data)			
R1	0.0660	0.0977	0.0586
wR2	0.1114	0.2274	0.1319
goodness of fit on F^2 [c]	1.025	1.093	1.038
large diff peak, hole, e Å^{-3}	0.527, −0.249	1.371, −1.431	0.738, −0.509

[a] $R1 = (\Sigma|F_o| - |F_c|)\Sigma|F_o|$. [b] $wR2 = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $GOF = [(\Sigma w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Crystal Structure Analyses. Diffraction-quality single crystals were obtained from solutions at −29 °C after 4−5 days as follows: **4** and **5** as red rhombuses and dark brown prisms, respectively, from *n*-hexane−toluene, and **6** as dark brown prisms from *n*-hexane−THF.

The crystals were mounted on quartz fibers. X-ray data were collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo Kα radiation ($\lambda = 0.710\ 73$ Å).

The data were corrected for Lorentz and polarization effcts with the SMART suite of programs[14] and for absorption effects with SADABS.[15] Structure solution and refinement were carried out with the SHELXTL suite of programs.[16] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The Cp and alkyl hydrogens were placed in calculated positions. For **5**, two of the four Cp rings were found to be disordered. Two Cp models (occupancies 0.55 and 0.45) with common isotropic thermal parameters were refined for these two disordered rings. The *p*-methoxyphenyl ring was also found to have two different orientations in the crystal lattice with 50:50 occupancies, and individual U values were refined for each non-hydrogen atom. The Fourier difference map revealed the presence of a toluene solvate in the lattice. All the rings were constrained to regular shapes in the least-squares cycles. For **6**, Cp rings were each disordered over two alternative sites related by symmetry; each unique ring was modeled as a regular pentagon. The *p*-methoxyphenyl ring was also disordered over two sites; these were modeled with equal occupancies, with the rings constrained as regular hexagons and the oxygen atoms in the planes of the rings. P−C(ring), C(ring)−O, and C(methyl)−O distances were restrained to be the same. Heavy atoms, viz., Cr, S, and P, were refined anisotropically; all others were isotropic. All phenyl carbons were given one common isotropic thermal parameter; the corresponding atoms for the two sites were also given equivalent isotropic thermal parameters. All carbon atoms in the Cp rings were assigned a common isotropic thermal parameter. Hydrogen atoms were placed in calculated positions and refined with a riding model. The crystal data and refinement details are given in Table 1.

Results and Discussion

Products and Reaction Pathways. Reaction of $CpCr(CO)_2(SP(H)Ar)$ (**2**) with $[CpCr(CO)_3]_2$ (**1**) in toluene at 110 °C for 1 h led to the isolation of deep brown crystals of the hydridophosphido-bridged complex $Cp_2Cr_2(CO)_4(H)(P(H)Ar)$ (**3**; 4% yield), dark red crystals of $Cp_2Cr_2(CO)_2(P(H)Ar)_2$ (**4**; 11%), deep brown crystals of the phosphinidene cubane complexes $Cp_4Cr_4S_3(PAr)$ (**5**; 16%) and $Cp_4Cr_4S_2(PAr)_2$ (**6**; 32%), greenish yellow solids of $CpCr(CO)_3H$ (**7**; 5%), and dark green solids of $Cp_4Cr_4S_4$ (**9**; 19%) (Scheme 1).

Thermolysis of **2** alone in refluxing toluene-d_8 for 2 h did not produce any of the compounds **3**−**6**, but only **9** in ca. 13% yield together with some insoluble noncharacterizable compounds, thus ruling out a direct thermolytic degradation pathway and demonstrating that desulfurization of **2** is effected by the 17-electron species $CpCr(CO)_3^{\bullet}$(**1A**), the incumbent monomer of **1** arising from its facile dissociation.[17] The formation of the products can be rationalized by pathways illustrated in Scheme 2. Congruent with the observed thiophilicity of

---

(14) SMART, version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 2000.

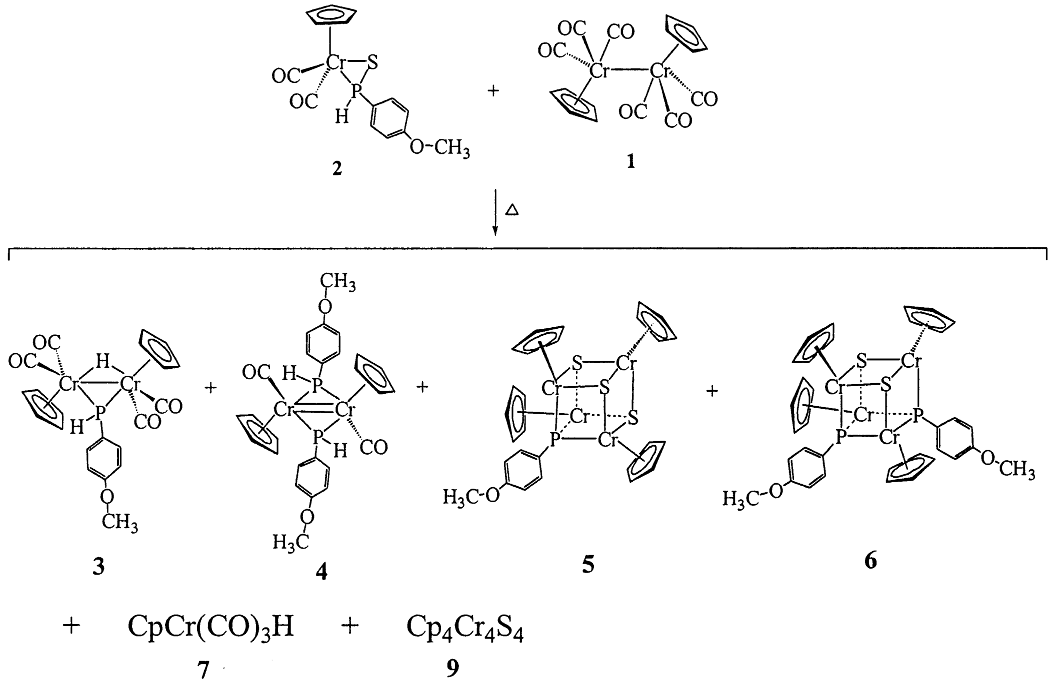
(15) Sheldrick, G. M. SADABS, a Program for Empirical Absorption Correction, University of Göttingen, Göttingen, Germany, 2000.

(16) SHELXTL, version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

(17) (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Goh, L. Y.; Lim, Y. Y. *J. Organomet. Chem.* **1991**, *402*, 209.

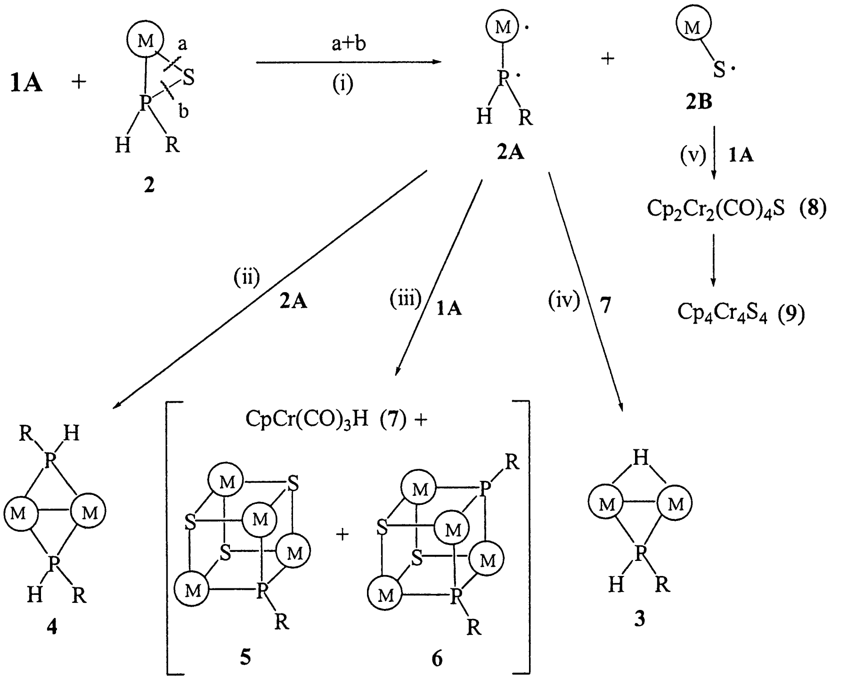
(18) (a) Goh, L. Y.; Hambley, T. W.; Robertson, G. B. *Organometallics* **1987**, *6*, 1051. (b) Chen, W.; Goh, L. Y.; Bryan, R. F.; Sinn, E. *Acta Crystallogr.* **1986**, *C42*, 796.

Scheme 1[a]



[a] The Cr–Cr bonds in the cubane cores of **5** and **6** are omitted for clarity.

Scheme 2. Proposed Fragmentation and Aggregation Pathways[a]



[a] Legend: Ⓜ = CpCr(CO)$_n$ metal fragment; **1A** = CpCr(CO)$_3$; R = C$_6$H$_4$OCH$_3$; a, b = bond scissions.

1A, a probable mechanism would involve an initial radical cleavage of M–S and P–S bonds in **2** (route i), generating the P- and Cr-centered diradical **2A** and the S-centered radical **2B**. Dimerization of **2A** with concomitant loss of CO will yield the Cr–Cr-bonded diphosphido complex **4** (route ii). The interaction of **2A**, **2B**, and **1A** with concurrent hydrogen abstraction from **2A** would generate hydride **7** and phosphinidene cubanes **5** and **6** (route iii), while the coupling of **2A** with **7** would give **3**. (As discussed in the previous paper, **7** could probably be derived via H abstraction from a Cp ligand by **1A**.) The interaction of **2B** with **1A** (route v) would yield [CpCr(CO)$_2$]$_2$S (**8**),[18a] the precursor complex to the previously characterized cubane Cp$_4$Cr$_4$S$_4$ (**9**).[18b]

Properties and Spectral Characteristics. Complexes **3** and **4** are both 36-electron species of Cr(II), with the phosphido ligand bridging two 15-electron CpCr(CO)$_2$ and two 13-electron CpCr(CO) fragments, respectively, while **5** and **6** possess 52-electron cubane cores and chromium in the +3 oxidation state.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Bond Lengths (Å)			
Cr(1)−Cr(1A)	2.5786(11)	Cr(1)−P(1)	2.2551(12)
Cr(1)−P(1A)	2.2665(13)	P(1)−C(7)	1.824(4)
C(10)−O(2)	1.366(4)	C(13)−O(2)	1.411(7)
C(1)−O(1)	1.158(4)		

Bond Angles (deg)			
P(1)−Cr(1)−P(1A)	110.46(4)	P(1)−Cr(1)−Cr(1A)	55.44(4)
P(1A)−Cr(1)−Cr(1A)	55.02(3)	C(7)−P(1)−Cr(1)	124.75(12)
C(7)−P(1)−Cr(1A)	126.78(13)	Cr(1)−P(1)−Cr(1A)	69.54(4)
C(10)−O(2)−C(13)	117.8(4)		

In the crystalline state complexes **4**−**6** are stable in air over an extended period, whereas the hydridophosphido-bridged complex **3** is very air-sensitive.

The solution IR spectrum of complex **3** shows two terminal carbonyl stretching absorptions at 1930 and 1880 cm^{-1} (cf. 1935 and 1881 cm^{-1} in $Cp_2Cr_2(CO)_4(\mu\text{-H})(\mu\text{-PH}_2)$).[19] In the NMR spectra of **3** are found the resonances for the Cp protons at δ 4.16 and the ring carbons at δ 89.0, within the normal range observed for the CpCr moiety, and the bridging hydride as a doublet at δ −12.84 (J_{PH} = 73 Hz); the PH moiety shows a proton resonance at δ 6.73 with strong coupling to the P atom (J = 340 Hz) and a ^{31}P signal at δ 191.7. The NMR spectra of **4** show δ(Cp) at 4.34 in the ^{1}H spectrum and at δ 91.4 in the ^{13}C spectrum and a ^{31}P signal at δ 131.2 and the PH proton resonance at δ 5.04 (J = 318 Hz). Complex **5** possesses two Cp proton resonances at δ 5.06 and 4.82 with relative intensity 1:3, which are consistent with the molecular structure discussed below, and a ^{31}P signal at δ 508.4. Complex **6** also shows two Cp proton resonances (δ 5.01 and 4.73) with relative intensity 1:1 and a ^{31}P signal at δ 1296; we are not aware of the occurrence of ^{31}P resonances at such unusually low chemical shifts, though large low-field shifts of Cp resonances of paramagnetic CpCr complexes have been observed in both the proton and ^{13}C spectra.[17b,20]

Crystal Structures. The molecular structures of **4**−**6** have been determined and are shown in Figures 1−3, respectively. Selected bond parameters of the complexes are given in Tables 2−4.

The complex **4** belongs to the class of dinuclear bis(μ-phosphido) complexes containing a planar M_2P_2 unit.[21] The molecule (Figure 1) possesses a center of inversion at the middle of the Cr−Cr bond, the length of which (2.5786(11) Å) lies between values observed for a single Cr−Cr bond[22] and that of a Cr≡Cr bond, e.g. 2.30 Å, as found in $[CpCr(CO)_2]_2$.[23] It is very close to that found in the complex $Cp_2Cr_2(CO)_2(\mu\text{-PMe}_2)_2$ (2.5776(7) Å).[10] The two Cr−P distances (2.2551(12) and 2.2665(13) Å) are close to that found in **2** (2.2608(8) Å).[12]

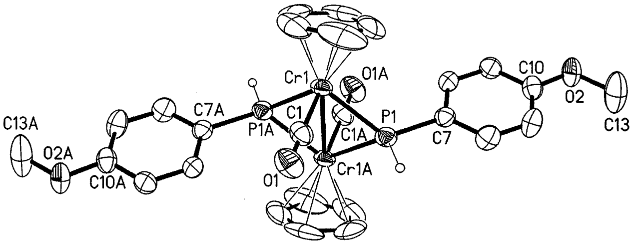


Figure 1. Molecular structure of **4** (C−H hydrogen atoms are not shown). Thermal ellipsoids are drawn at the 50% probability level.

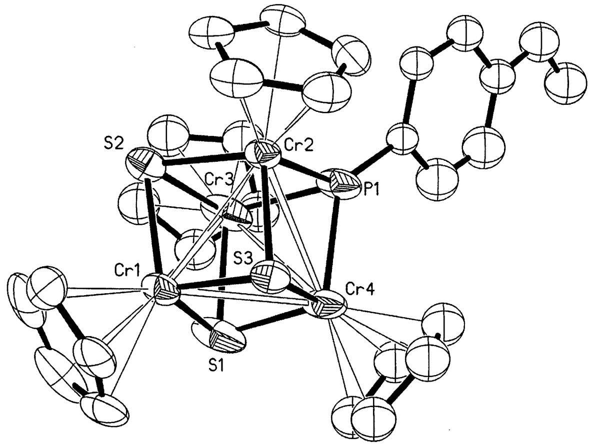


Figure 2. Molecular structure of **5** (C−H hydrogen atoms are not shown). Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

Bond Lengths (Å)			
Cr(1)−Cr(2)	2.8299(14)	Cr(1)−Cr(3)	2.8612(15)
Cr(1)−Cr(4)	2.8295(17)	Cr(2)−Cr(3)	2.8722(16)
Cr(2)−Cr(4)	2.9087(15)	Cr(1)−S(1)	2.237(2)
Cr(1)−S(2)	2.2477(19)	Cr(1)−S(3)	2.236(2)
Cr(2)−S(2)	2.248(2)	Cr(2)−S(3)	2.2431(18)
Cr(3)−S(1)	2.243(2)	Cr(3)−S(2)	2.233(2)
Cr(4)−S(1)	2.244(3)	Cr(4)−S(3)	2.252(2)
Cr(2)−P(1)	2.232(2)	Cr(3)−P(1)	2.234(3)
Cr(4)−P(1)	2.232(2)		

Bond Angles (deg)			
Cr(2)−Cr(1)−Cr(3)	60.62(4)	Cr(4)−Cr(1)−Cr(2)	61.86(4)
Cr(3)−Cr(2)−Cr(4)	59.03(5)	Cr(1)−Cr(2)−Cr(4)	59.06(4)
Cr(1)−Cr(2)−Cr(3)	60.23(4)	S(1)−Cr(1)−S(2)	99.05(8)
S(3)−Cr(1)−S(1)	101.27(10)	S(3)−Cr(1)−S(2)	101.22(7)
S(3)−Cr(2)−S(2)	100.99(7)	S(2)−Cr(3)−S(1)	99.32(8)
P(1)−Cr(2)−S(2)	99.07(9)	P(1)−Cr(2)−S(3)	97.87(8)
P(1)−Cr(2)−Cr(1)	96.44(6)	S(2)−Cr(2)−Cr(4)	96.10(6)
S(2)−Cr(3)−P(1)	99.47(8)	P(1)−Cr(3)−S(1)	100.33(11)
P(1)−Cr(4)−S(3)	97.58(8)	P(1)−Cr(4)−S(1)	100.35(11)
Cr(1)−S(1)−Cr(3)	79.39(7)	S(1)−Cr(4)−S(3)	100.53(8)
Cr(3)−S(1)−Cr(4)	78.81(8)	Cr(1)−S(1)−Cr(4)	78.32(8)
Cr(3)−S(2)−Cr(1)	79.38(7)	Cr(3)−S(2)−Cr(2)	79.74(7)
Cr(1)−S(3)−Cr(2)	78.37(7)	Cr(2)−S(2)−Cr(1)	78.03(7)
Cr(2)−S(3)−Cr(4)	80.64(7)	Cr(1)−S(3)−Cr(4)	78.17(8)
Cr(4)−P(1)−Cr(3)	79.25(8)	Cr(2)−P(1)−Cr(3)	80.06(8)

Complexes **5** and **6** contain one and two μ_3-phosphinidene ligands, respectively, at the corners of cubanes. There are several instances of the occurrence of μ_3-phosphinidene in clusters of Fe[5] and Ru,[6b,c] but only one reported example of a μ_3-phosphinidene cubane, viz. $(Cp'Mo)_2(Co(CO)_2S_3(PPh)$.[9] The molecular structures of **5** and **6** are illustrated in Figures 2 and 3, respectively. In **5**, the Cr−Cr bonds (2.8295(17)−2.9087(15) Å) and the Cr−S bonds (2.233(2)−2.252(2) Å) are comparable

---

(19) Sekar, P.; Scheer, M.; Voigt, A.; Kirmse, R. *Organometallics* **1999**, *18*, 2833.

(20) (a) Goh, L. Y.; Khoo, S. K.; Lim, Y. Y. *J. Organomet. Chem.* **1990**, *399*, 115. (b) Goh, L. Y.; Leong, W. K.; Leung, P. H.; Weng, Z.; Haiduc, I. *J. Organomet. Chem.* **2000**, *607*, 64. (c) Goh, L. Y.; Weng, Z.; Leong, W. K.; Haiduc, I.; Lo, K. M.; Wong, R. C. S. *J. Organomet. Chem.* **2001**, *631*, 67.

(21) (a) Reinhold, J.; Muller, B.; Eichler, U. *Organometallics* **1997**, *16*, 1497. (b) Seyferth, D.; Brewer, K. S.; Wood, T. G.; Cowie, M.; Hilts, R. W. *Organometallics* **1992**, *11*, 2570. (c) King, J. D.; Mays, M. J.; Mo, C.-Y.; Solan, G. A.; Conole, G.; McPartlin, M. *J. Organomet. Chem.* **2002**, *642*, 227.

(22) Goh, L. Y.; Tay, M. S.; Mak, T. C. W.; Wang, R.-J. *Organometallics* **1992**, *11*, 1711 and references therein.

(23) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131.

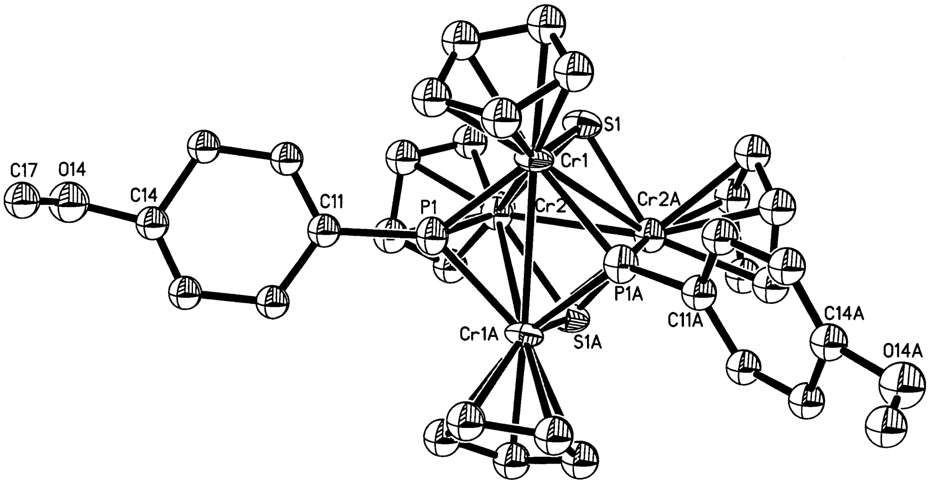


Figure 3. Molecular structure of **6** (C−H hydrogen atoms are not shown). Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6

Bond Lengths (Å)			
Cr(1)−Cr(2)	2.8871(11)	Cr(1)−Cr(1A)	2.9668(17)
Cr(2)−Cr(2A)	2.8140(18)	Cr(1)−S(1)	2.2523(17)
Cr(1)−P(1)	2.2412(13)	Cr(2)−S(1)	2.2323(13)
Cr(2)−P(1)	2.2374(17)		
Bond Angles (deg)			
Cr(2)−Cr(1)−Cr(2A)	58.33(4)	Cr(2)−Cr(1)−Cr(1A)	59.083(19)
Cr(1)−Cr(2)−Cr(1A)	61.83(4)	Cr(2A)−Cr(2)−Cr(1)	60.83(2)
S(1)−Cr(1)−P(1)	98.70(5)	S(1)−Cr(1)−Cr(1A)	96.06(4)
S(1)−Cr(1)−Cr(2)	49.62(4)	P(1)−Cr(1)−Cr(2A)	94.64(4)
P(1)−Cr(1)−Cr(1A)	48.56(3)	P(1)−Cr(1)−P(1A)	96.34(6)
P(1)−Cr(1)−Cr(2)	49.80(4)	S(1)−Cr(2)−S(1A)	100.91(6)
S(1)−Cr(2)−P(1)	99.42(5)	S(1A)−Cr(2)−Cr(1)	98.78(4)
S(1)−Cr(2)−Cr(2A)	50.93(3)	S(1)−Cr(2)−Cr(1)	50.23(4)
P(1)−Cr(2)−Cr(1)	49.92(4)	P(1)−Cr(2)−Cr(2A)	96.75(5)
Cr(1)−S(1)−Cr(2)	80.15(5)	Cr(2)−S(1)−Cr(2A)	78.14(6)
Cr(1)−P(1)−Cr(1A)	82.89(6)	Cr(1)−P(1)−Cr(2)	80.28(5)

with those found in $Cp_4Cr_4S_4$ (2.818(3)−2.891(6) Å for Cr−Cr; 2.255(7)−2.260(4) Å for Cr−S). The three Cr−P bond distances are equivalent (2.232(2), 2.234(3), 2.232(2) Å), which are slightly shorter than those found in the μ_2-bridged complex **4**. The Cr−P−Cr angles (79.25(8)−81.32(7)°) at the μ_3-P corner are smaller than those found at the μ_3-CNR_2 corner (Cr−C−Cr = 82.0(4)−86.3(4)°) in the complex $Cp_4Cr_4S_2(CO)(CNMe_2)$,[24] which we have recently reported. Complex **6** contains two μ_3-phosphinidene ligands in the cubane structure. There are two symmetry planes through Cr(1)Cr(1A)-S(1)S(1A) and Cr(2)Cr(2A)P(1)P(1A), respectively. The Cr−Cr bond lengths (2.8140(18)−2.9668(17) Å), Cr−S bond lengths (2.2323(13)−2.2523(17) Å), and Cr−P bond lengths (2.2374(17)−2.2412(13) Å) are comparable with those found in **5**.

Conclusion

The 17-electron $CpCr(CO)_3^{\bullet}$ species has effected desulfurization of the η^2-arylthioxophosphane complex $CpCr(CO)_2(SP(H)Ar)$ (**2**), providing a new route to μ_2-phosphido dinuclear complexes and μ_3-phosphinidene cubanes of cyclopentadienylchromium in fairly good yields.

Acknowledgment. Support from the Academic Research Fund (Grant No. R-143-000-077-112) of the National University of Singapore and a research scholarship to Z.W. are gratefully acknowledged. We also thank Ms. G. K. Tan for technical assistance.

Supporting Information Available: For the structures of **4**−**6**, tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and all bond lengths and angles and a figure showing the proton NMR spectrum of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020934R

---

[24] Goh, L. Y.; Weng, Z.; Hor, T. S. A.; Leong, W. K. *Organometallics* **2002**, *21*, 4408.