

# An Organometallic Radical Route to Bis(phosphido)- and Hydrido–Phosphido-Bridged Metal–Metal-Bonded Complexes of Cyclopentadienylchromium via Desulfurization of Thiophosphinito Ligands

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The reaction of  $[\text{CpCr}(\text{CO})_3]_2$  (**1**, Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) with 1 mol equiv of the tetraalkyldiphosphine disulfide  $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2$  (R = Me, Et) at 60 °C for 24 h led to the isolation of the thiophosphinito complexes  $\text{CpCr}(\text{CO})_2(\text{SPR}_2)$  (**2a**, R = Me; **2b**, R = Et) as dark red solids in ca. 24% yield. Desulfurization of **2a** by the organometallic radical  $\text{CpCr}(\text{CO})_3^\bullet$  (**1A**) gave the hydrido–phosphido-bridged complex  $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-PMe}_2)$  (**3a**), the bis( $\mu$ -phosphido) metal–metal doubly bonded complex  $\text{Cp}_2\text{Cr}_2(\text{CO})_2(\mu\text{-PMe}_2)_2$  (**4a**), and the triangulo trinuclear complex  $\text{Cp}_3\text{Cr}_3(\text{CO})_3(\text{S})(\text{PMe}_2)$  (**5a**). The solid-state structures of all of the complexes have been determined by single-crystal X-ray diffraction analysis.

## Introduction

The chemistry of organometallic radical species, especially of the 17-electron type, is of continuing current interest.<sup>1</sup> We have been investigating the reactivity of the cyclopentadienylchromium tricarbonyl 17-electron radical species,  $\text{CpCr}(\text{CO})_3^\bullet$  (**1A**), toward cleavage of the interchalcogen bonds in homo- and heteropolynuclear inorganic compounds<sup>2</sup> and in organic substrates, e.g. diphenyl dichalcogenides,  $\text{Ph}_2\text{E}_2$  (E = S, Se, Te),<sup>3a</sup> bis(diphenylthiophosphinyl)disulfane,  $\text{Ph}_2\text{P}(\text{S})\text{SSP}(\text{S})\text{Ph}_2$ ,<sup>3b</sup> and tetraalkylthiuram disulfides.<sup>3c</sup>

In the course of these studies, we have observed that desulfurization or removal of Se had occurred under thermal activation to give new complexes possessing different nuclearities and varied structures.<sup>2,3</sup> Desulfurization processes, especially those involving carbon–sulfur bond cleavage, have biological and industrial relevance.<sup>4,5</sup> Our recent encounter with this type of bond

rupture involved thermal desulfurization of a dithiocarbamate ligand to generate thiocarbonyl and dicubane compounds.<sup>3c</sup> Subsequently, we found that these transformations were facilitated by the 17-electron species **1A**, which behaves as an avid thiophile, producing a variety of new compounds.<sup>6</sup> We were therefore prompted to investigate the probable role of **1A** in desulfurization of thiophosphinito ligands, an occurrence not reported to date for ligated P,S-containing organic moieties. We are particularly interested in examining if this will provide a viable route to phosphido ligands, since these are of continuing current interest,<sup>7</sup> on account of their stabilizing influence on di- and polynuclear complexes.<sup>8</sup> The findings are described in this paper.

## Experimental Section

**General Procedures.** Standard procedures were as described in a previous paper.<sup>3b</sup>  $[\text{CpCr}(\text{CO})_3]_2$  (**1**) and  $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$  were prepared as described in the literature.<sup>9,10</sup>  $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$  (99% purity) was obtained from Strem Chemical Co. Details for the syntheses of **2a**, **2b**, **3b**, and **5b** are given in the Supporting Information.

**Thermolytic Reaction of  $\text{CpCr}(\text{CO})_2(\text{SPMe}_2)$  (**2a**) with  $[\text{CpCr}(\text{CO})_3]_2$  (**1**) at 110 °C.** A greenish brown mixture of

(6) Goh, L. Y.; Weng, Z.; Leong, W. K.; Vittal, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 8804.

(7) (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.

(8) (a) Davies, J. E.; Mays, M. J.; Pook, E. J.; Raithby, P. R.; Tompkin, P. K. *J. Chem. Soc., Dalton Trans.* **1997**, 3283 and references therein. (b) Davies, J. E.; Feeder, N.; Gray, C. A.; Mays, M. J.; Woods, A. D. *J. Chem. Soc., Dalton Trans.* **2000**, 1695 and references therein. (c) Graf, M.; Merzweiler, K.; Bruhn, C.; Böttcher, H.-C. *J. Organomet. Chem.* **1998**, *553*, 371 and references therein.

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

(10) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 704.

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(1) (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. *Organometallic Radical Processes*; Troglor, W. C., Ed.; Elsevier: Amsterdam, 1990. (c) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (d) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135*, 203. (e) Huber, T. A.; Macartney, T. A.; Baird, M. C. *Organometallics* **1995**, *14*, 592. (f) Hammack, D. J.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H. *Organometallics* **1996**, *15*, 4791.

(2) (a) Goh, L. Y. *Coord. Chem. Rev.* **1999**, *185–186*, 257 and references therein. (b) Goh, L. Y.; Chen, W.; Wong, R. C. S.; Karaghiosoff, K. *Organometallics* **1995**, *14*, 3886. (c) Goh, L. Y.; Chen, W.; Wong, R. C. S. *Organometallics* **1999**, *18*, 306. (d) Goh, L. Y.; Chen, W.; Wong, R. C. S. *Chem. Commun.* **1999**, 1481.

(3) (a) Goh, L. Y.; Tay, M. S.; Chen, W. *Organometallics* **1994**, *13*, 1813 and references therein. (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.; Leung, P. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3236.

(4) *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K. Eds.; ACS Symposium Series No. 653; American Chemical Society: Washington, DC, 1996.

(5) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109.

CpCr(CO)<sub>2</sub>(SPMe<sub>2</sub>) (**2a**; 90 mg, 0.34 mmol) and **1** (136 mg, 0.34 mmol) in toluene (10 mL) was stirred at 110 °C for 1.5 h. The resultant dark brown product solution was concentrated to ca. 3 mL and filtered to remove a dark green solid of Cp<sub>4</sub>Cr<sub>4</sub>S<sub>4</sub> (8 mg, 8%). The filtrate was loaded onto a silica gel column (2 × 15 cm) prepared in *n*-hexane. Elution gave five fractions: (i) a deep green eluate in *n*-hexane/toluene (4:1, 5 mL), from which was obtained deep green crystals of [CpCr(CO)<sub>2</sub>]<sub>2</sub> (8 mg, 7% yield); (ii) a cherry red eluate in *n*-hexane/toluene (2:1, 5 mL), which on concentration gave deep red crystals of Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>2</sub>(μ-PMMe<sub>2</sub>)<sub>2</sub> (**4a**; 16 mg, 12%); (iii) a dark red eluate in *n*-hexane/toluene (1:2, 10 mL), which gave deep red crystals of Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PMMe<sub>2</sub>) (**3a**; 32 mg, 23%); (iv) a dark green eluate in toluene (5 mL), which yielded an additional amount of Cp<sub>4</sub>Cr<sub>4</sub>S<sub>4</sub> (4 mg, 4%); (v) a red-brown eluate in toluene (10 mL), which yielded a brown solid of Cp<sub>3</sub>Cr<sub>3</sub>(μ-CO)<sub>2</sub>(μ<sub>3</sub>-S)(μ-PMMe<sub>2</sub>) (**5a**; 51 mg, 45%).

**Thermolysis of Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PMMe<sub>2</sub>) (**3a**).** A red solution of **3a** (81 mg, 0.20 mmol) in toluene (5 mL) was maintained at 90 °C for 6 h. The resultant dark red solution was filtered to remove a dark green insoluble precipitate (21 mg) of an unidentified compound. The filtrate was concentrated to ca. 1 mL and loaded onto a silica gel column (1.5 × 8 cm) prepared in *n*-hexane. Two fractions were eluted: (i) a purple red eluate in *n*-hexane/toluene (1:1, 8 mL), which gave a red solid of **4a** (12 mg, 15% yield); (ii) a red eluate in *n*-hexane/toluene (1:4, 10 mL), from which was obtained a dark red crystalline solid of **3a** (42 mg, 51% recovery).

**Data for 3a.** IR (toluene, cm<sup>-1</sup>): ν(CO) 1925 s, 1886 s. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.15 (s, 10H, 2 × C<sub>5</sub>H<sub>5</sub>), 1.62 (d, *J* = 9 Hz, 6H, 2 × CH<sub>3</sub>), -12.88 (d, *J* = 70 Hz, 1H, CrHCr). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 88.1 (C<sub>5</sub>H<sub>5</sub>), 26.2 (d, *J* = 18 Hz, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 201.7 (s; H-coupled, d of unresolved multiplet, *J* = 70, ca. 9 Hz). Anal. Calcd for C<sub>16</sub>H<sub>17</sub>Cr<sub>2</sub>O<sub>4</sub>P: C, 47.1; H, 4.2; P, 7.6. Found: C, 46.6; H, 4.1; P, 7.4. MS FAB<sup>+</sup> (*m/z*): 408 [M]<sup>+</sup>, 379 [M - CO]<sup>+</sup>, 351, [M - 2CO]<sup>+</sup>, 324 [M - 3CO]<sup>+</sup>, 296 [M - 4CO]<sup>+</sup>, 117 [CpCr]<sup>+</sup>, 52 [Cr]<sup>+</sup>. HR-MS ESI<sup>+</sup> (*m/z*): for M<sup>+</sup> 407.968 (found), 407.967 (calcd).

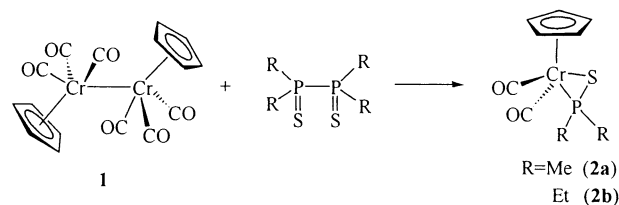
**Data for 4a.** IR (toluene, cm<sup>-1</sup>): ν(CO) 1844 s. <sup>1</sup>H{<sup>31</sup>P} NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.72 (s, 10H, 2 × C<sub>5</sub>H<sub>5</sub>), 1.85 (s, 12H, 4 × CH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 90.2 (C<sub>5</sub>H<sub>5</sub>), 23.3 (CH<sub>3</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 131.3. Anal. Calcd for C<sub>16</sub>H<sub>22</sub>Cr<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 46.6; H, 5.4; P, 15.0. Found: C, 46.6; H, 5.4; P, 15.3. MS FAB<sup>+</sup> (*m/z*): 412 [M]<sup>+</sup>, 384 [M - CO]<sup>+</sup>, 356 [M - 2CO]<sup>+</sup>. HR-MS ESI<sup>+</sup> (*m/z*): for M<sup>+</sup> 411.990 (found), 411.991 (calcd).

**Data for 5a.** IR (toluene, cm<sup>-1</sup>): ν(CO) 1799 s, 1750 s. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 14.0 (br, ν<sub>1/2</sub> = 140 Hz, 10H, 2 × C<sub>5</sub>H<sub>5</sub>), 13.6 (br, ν<sub>1/2</sub> = 120 Hz, 5H, C<sub>5</sub>H<sub>5</sub>), 0.31 (br, ν<sub>1/2</sub> = 120 Hz, 3H, CH<sub>3</sub>), -3.43 (br, ν<sub>1/2</sub> = 120 Hz, 3H, CH<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>21</sub>Cr<sub>3</sub>O<sub>2</sub>PS: C, 45.6; H, 4.2; P, 6.2, S, 6.4. Found: C, 44.9; H, 4.2; P, 5.9, S, 6.7. MS ESI<sup>+</sup> (*m/z*): 500 [M]<sup>+</sup>, 444 [M - 2CO]<sup>+</sup>, 117 [CpCr]<sup>+</sup>, 52 [Cr]<sup>+</sup>.

## Results and Discussion

**Products and Reaction Pathways.** The reaction of [CpCr(CO)<sub>3</sub>]<sub>2</sub> (**1**) with 1 mol equiv of the tetraalkyl-diphosphine disulfides R<sub>2</sub>P(S)P(S)R<sub>2</sub> (R = Me, Et) in toluene at 60 °C for 24 h led to the isolation of the η<sup>2</sup>-thiophosphinito complex CpCr(CO)<sub>2</sub>(SPR<sub>2</sub>) (**2a**, R = Me, 25% yield; **2b**, R = Et, 22% yield), together with recovered **1** (ca. 30%), [CpCr(CO)<sub>2</sub>]<sub>2</sub>(Cr≡Cr) (28%), [CpCr(CO)<sub>2</sub>]<sub>2</sub>S (12%), and recovered ligand (ca. 40%). Since a substantial amount of **1** remained unreacted, the reactions were repeated at 90 °C until **1** had completely reacted (2 h). These altered conditions did not cause any change to the yields of **2a/2b** (both 24% yield) but also gave additional products, viz. the hydrido-phosphido-bridged complexes Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>4</sub>(μ-H)-

## Scheme 1



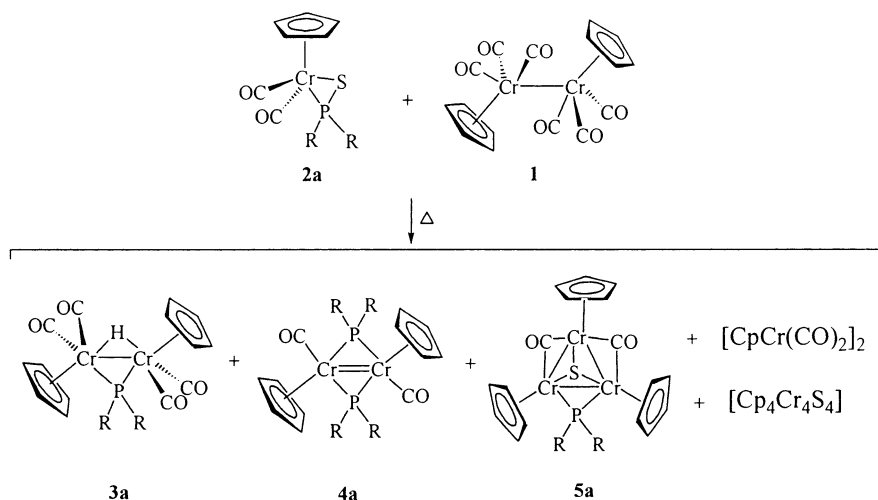
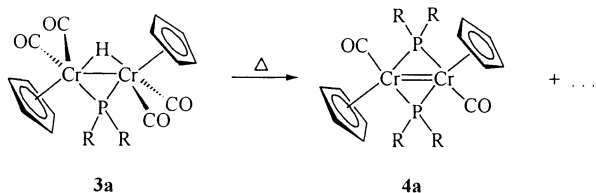
(μ-PR<sub>2</sub>) (**3a**, R = Me, 27% yield; **3b**, R = Et, 17% yield) and the trinuclear complexes Cp<sub>3</sub>Cr<sub>3</sub>(CO)<sub>2</sub>(S)(μ-PR<sub>2</sub>) (**5a**, R = Me, 11% yield; **5b**, R = Et, 6% yield), together with [CpCr(CO)<sub>2</sub>]<sub>2</sub>(Cr≡Cr) (14% yield) and Cp<sub>4</sub>Cr<sub>4</sub>S<sub>4</sub> (ca. 12% yield).

The formation of the η<sup>2</sup>-thiophosphinito complexes CpCr(CO)<sub>2</sub>(SPR<sub>2</sub>) (**2**) (Scheme 1) is in agreement with the established reaction mode of the 17-electron CpCr(CO)<sub>3</sub><sup>•</sup> radical species in the cleavage of element–element bonds of groups 15 and 16. The isolation of additional products, **3** and **5**, from a reaction at a higher temperature, is suggestive of secondary reactions, which may be subsequent thermolysis of **2** and/or its interaction with **1**. An NMR tube reaction in *d*<sub>8</sub>-toluene showed that the complex **2a** underwent only 40% decomposition after 2 h at 100–110 °C, producing Cp<sub>4</sub>Cr<sub>4</sub>S<sub>4</sub> (ca. 35% yield) and other insoluble noncharacterizable compounds, thus ruling out a direct thermolytic degradation pathway. However, when cothermolized with 1 mol equiv of **1** for 1.5 h at 110 °C, the complex **2a** gave **3a** (23%), **4a** (12%), and **5a** (45%), together with [CpCr(CO)<sub>2</sub>]<sub>2</sub>(Cr≡Cr) (7%) and Cp<sub>4</sub>Cr<sub>4</sub>S<sub>4</sub> (12%), as illustrated in Scheme 2. Additionally, a separate experiment showed that **3a** underwent ca. 50% conversion after 6 h at 90 °C, yielding **4a** as the only isolable product in ca. 29% yield, based on reacted **3a** (Scheme 3).

Phosphido complexes of the types **3** and **4** have mainly been prepared from the reaction of metal carbonyls with diphosphanes R<sub>2</sub>PPR<sub>2</sub><sup>11a</sup> and phenylphosphines PPh<sub>2</sub>H and PPhH<sub>2</sub>.<sup>11b,c</sup> Recently, cyclopentadienyl complexes of group 6 metals, Cp<sub>2</sub>M<sub>2</sub>(CO)<sub>4</sub>(μ,η<sup>2</sup>-P<sub>2</sub>), have been found to be precursors to phosphanido (μ-PH<sub>2</sub>) complexes, via cleavage of the P–P bond with hydroxide followed by acid treatment (M = Mo, W)<sup>12a</sup> or with the LiBEt<sub>3</sub>H superhydride (M = Cr).<sup>12b</sup> Our present results show that desulfurization of a thiophosphinito ligand at a chromium center provides an additional pathway to these μ-phosphido complexes. Surprisingly, we found that **1** did not react readily with R<sub>2</sub>PPR<sub>2</sub> (R = Ph) and after 24 h at 90 °C gave uncharacterizable products, consisting of an oil (ca. 10% yield) and an insoluble dark red solid (ca. 70% yield), the FAB<sup>+</sup>-MS of which shows a very high mass peak at *m/z* 1589. The origin of the bridging hydride in **3** remains unclear; the hydride signal of **3a** is still detected in the NMR spectrum of the product solution from a reaction of **2a** with **1** in the deuterio solvents C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>. It is tempting to

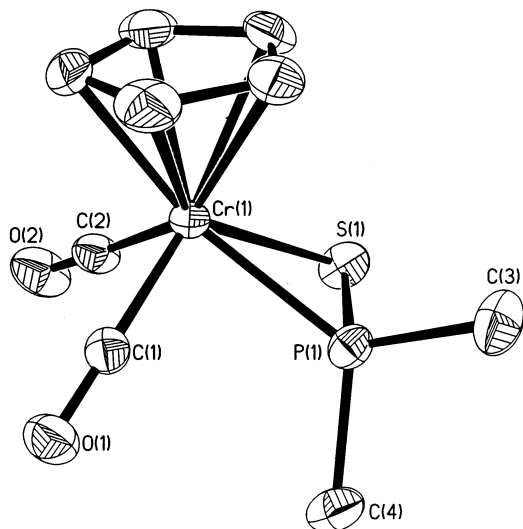
(11) (a) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555 and references therein. (b) Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083. (c) Iggo, A. J.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1983**, 205.

(12) (a) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Shields, G. P.; Tompkin, P. K. *J. Chem. Soc., Chem. Commun.* **1997**, 361. (b) Sekar, P.; Scheer, M.; Voigt, A.; Kirmse, R. *Organometallics* **1999**, *18*, 2833.

Scheme 2<sup>a</sup><sup>a</sup> R = Me.Scheme 3<sup>a</sup><sup>a</sup> R = Me.

suggest that the hydride originates from the Cp ligand via thermal C–H bond activation, similar to the photochemical process demonstrated by Riera and Jeannin for  $[\text{CpM}(\text{CO})_3]_2$  (M = Mo, W), in which case they obtained crystal structure evidence for the presence of a  $(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)$  ligand in the products.<sup>13</sup> Though we have not been able to detect this derived Cp ligand, we have previously isolated  $\text{CpCr}(\text{CO})_3\text{H}$  from reactions of **1** with  $\text{P}_4\text{X}_3$  (X = S, Se) even in deuterio solvents<sup>2b,c</sup> and have detected the hydride species in the proton NMR spectra of product solutions from reactions of **1** with  $\text{Ph}_2\text{S}_2$ .<sup>3a,14</sup>

**Properties and Spectral Characteristics.** In the solid state the Cr=Cr doubly bonded complex **4** is stable



**Figure 1.** Molecular structure of **2a**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for **2**

dist	<b>2a</b>	<b>2b</b>	angle	<b>2a</b>	<b>2b</b>
Cr–S	2.5155(7)	2.5038(18)	P–Cr–S	48.986(19)	49.13(6)
Cr–P	2.2704(6)	2.2738(18)	Cr–P–S	71.92(2)	71.45(7)
P–S	1.9966(8)	1.997(2)	Cr–S–P	59.09(2)	59.42(6)

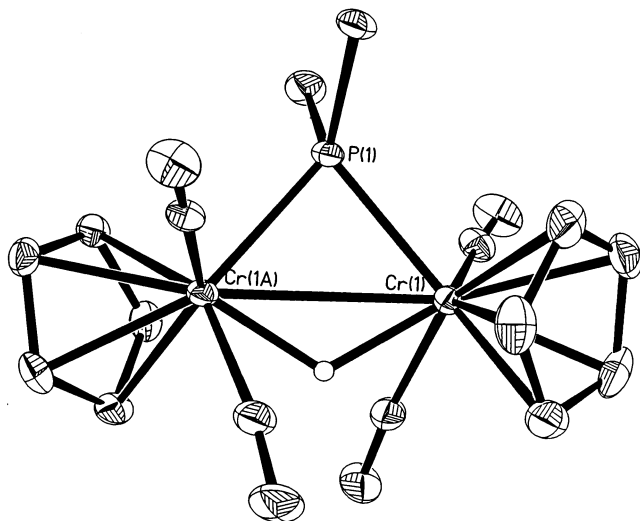
in air over an extended period and **2** is fairly stable, whereas the complexes **3** and **5** are extremely air-sensitive; in solution under nitrogen, **4** is stable for an extended period at ambient temperature, while **2**, **3**, and **5** are stable for several days at 0 °C. The 18-electron complexes **2**, 34-electron complexes **3**, and 32-electron complex **4a** are diamagnetic and possess proton Cp chemical shifts ( $\delta$  4.15–4.72) in the normal range observed for CpCr species, while that of the 43-electron paramagnetic complex **5** is observed as very broad peaks at unusually low field ( $\delta$  14–15). The proton NMR spectrum of **3a** shows the presence of equivalent methyl groups of the  $\mu\text{-PMe}_2$  ligands; that of **3b** shows that the  $\mu\text{-PEt}_2$  ligand possesses equivalent methyl protons and two pairs of methylene protons. The proton resonance of the  $\mu\text{-PMe}_2$  ligand in **4a** shows equivalent Me groups; these groups, however, are nonequivalent in the paramagnetic triangular trichromium complex **5a**. In the <sup>13</sup>C NMR spectra, the diamagnetic complexes **2–4** possess resonances for the Cp ring carbons in the expected range. Detailed NMR and IR spectral data are given in the Supporting Information.

**Crystal Structures.** The structure of the molecule of **2a** (Figure 1) contains a CpCr moiety bonded to two CO ligands and a  $\eta^2$ -thiophosphinito ligand. This side-on mode of bonding has been structurally established for only a few complexes.<sup>15</sup> The P–S bond distances in **2a,b** (see Table 1), slightly shorter than those in the literature examples, are intermediate between those of the typical P=S (range 1.926(1)–1.966(2) Å) and the P–S (2.122(1) Å) single bond in such ligands.<sup>16</sup>

**3a** (Figure 2) and **3b** belong to the  $\mu$ -hydrido  $\mu$ -phosphido subclass of homobimetallic<sup>17</sup> and heterobimetallic<sup>18</sup> compounds, some of which resemble **3** in possessing an additional metal–metal bond. Close analogues of **3**

(13) Alvarez, M. A.; Garcia, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1324.

(14) Goh, L. Y.; Tay, M. S. Unpublished observations, 1992.

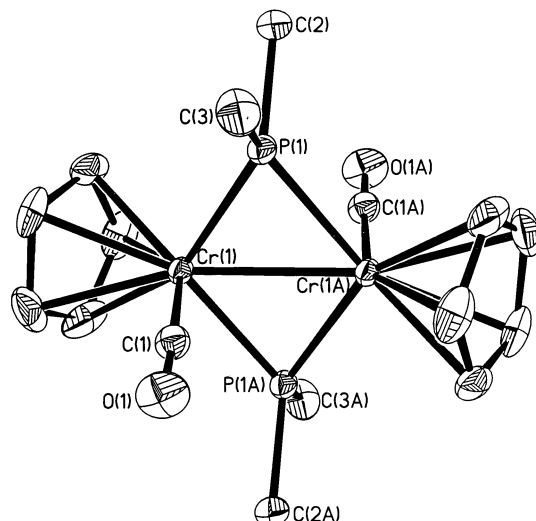


**Figure 2.** Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3 and 4**

dist or angle	3a	3b	4a
Cr(1)–Cr(1A)	2.9515(10)	2.8985(11)	2.5776(7)
Cr(1)–P(1)	2.2816(14)	2.2780(15)	2.2540(7)
Cr(1)–P(1A)			2.2555(7)
Cr(1)–P(1)–Cr(1A)	80.39(4)	78.85(5)	69.72(2)
P(1)–Cr(1)–Cr(1A)	49.95(4)	50.69(4)	55.167(19)
P(1)–Cr(1)–P(1A)			110.28(2)
P(1)–Cr(1A)–Cr(1)	49.66(4)	50.45(4)	
P(1A)–Cr(1)–Cr(1A)			55.111(19)

include  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-PPh}_2)$  and its phosphite derivative  $\text{Cp}_2\text{Mo}_2(\text{CO})_3(\mu\text{-H})(\mu\text{-PPh}_2)(\text{P}(\text{OMe})_3)^{11\text{b},17\text{e}}$  and the  $\mu$ -phosphanido M–M-bonded complexes  $\text{Cp}_2\text{M}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-PH}_2)$  of Mn, Re, Mo, and W<sup>12a</sup> and of Cr;<sup>12b</sup> the Cr–Cr distance of the latter was found to be 3.104(1) Å, very much longer than the corresponding distances in **3a,b**, which are 2.9515(10) and 2.8985(11) Å, respectively (Table 2), although all lie within the observed range for Cr–Cr bonds, with the longest bond being found in  $[\text{CpCr}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ .<sup>2a,19</sup> The Cr–P



**Figure 3.** Molecular structure of **4a**. Thermal ellipsoids are drawn at the 50% probability level.

distances (2.2816(14), 2.2780(15) Å) resemble closely those in complexes **2** (range 2.2704(6)–2.2738(18) Å).

The complex **4a** (Figure 3) belongs to the class of bis( $\mu$ -phosphido) complexes containing planar  $\text{M}_2\text{P}_2$  units, which were first prepared in the 1960s,<sup>20</sup> were extensively studied by Vahrenkamp and Dahl,<sup>21</sup> and continue to attract interest to the present.<sup>7</sup> In these compounds the M–M bond order varies from 0 to 2.<sup>7a</sup> The molecule **4a** possesses a center of inversion at the middle of the Cr–Cr bond, the length of which (2.5776(7) Å) lies between values observed for the single Cr–Cr bond (2.905 Å) in  $\text{Cr}_2(\text{CO})_8(\mu\text{-PMe}_2)_2$ <sup>21a</sup> and that of a Cr=Cr bond, e.g. 2.30 Å as found in  $[\text{CpCr}(\text{CO})_2]_2$ ;<sup>22</sup> in fact, the M–M distance in **4a** is close to the Cr=Cr bond length (2.590(2) Å) in  $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)(\mu_3\text{-S})_2\text{Co}(\text{CO})_3$ .<sup>23</sup> The Cr–P distances (2.2540(7), 2.2555(7) Å) are slightly shorter than those in **2** and **3**. A close analogue of **4a** is the Mo=Mo-bonded complex  $\text{Cp}_2\text{Mo}_2(\text{CO})_2(\text{PPh}_2)_2$ , which possesses a trans arrangement of the ligands.<sup>11a</sup>

The structure of **5a** contains two independent molecules in the unit cell. The ORTEP plot of one of the molecules is shown in Figure 4. This trinuclear compound belongs to the class of chromium–chromium-bonded carbonyl clusters, examples of which are rare.<sup>24</sup> In fact, to date only a few instances of homometallic Cr<sub>3</sub> clusters have been structurally characterized, all containing stabilizing ligands such as edge-bridging S or CO ligands, face-capping  $\mu_3\text{-S}$  or  $\mu_3\text{-Se}$  atoms or a  $\mu_3\text{-}$

(15) (a) Walther, B. *Coord. Chem. Rev.* **1984**, *60*, 67 and references therein. (b) Walther, B.; Hartung, H.; Messbauer, B.; Baumeister, U.; Maschmeier, M.; Dargatz, M.; Hetzke, I. *Inorg. Chim. Acta* **1990**, *171*, 171. (c) Forniés, J.; Martínez, F.; Navarro, R.; Urriolaibeitia, E. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2147. (d) Wagner, K. P.; Hess, R. W.; Treichel, P. M.; Calabrese, J. C. *Inorg. Chem.* **1975**, *14*, 1121. (e) Alper, H.; Einstein, F. W. B.; Hartstock, F. W.; Jones, R. H. *Organometallics* **1987**, *6*, 829. (f) Lindner, E.; Käss, V.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 448.

(16) (a) Fluck, E.; González, G.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1981**, *473*, 51. (b) Kerr, K. A.; Boorman, P. M.; Misener, B. S.; Van Rooode, J. H. G. *Can. J. Chem.* **1977**, *55*, 3081.

(17) (a) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G. *Organometallics* **2001**, *20*, 850. (b) Zhuravel, M. A.; Moncarz, J. R.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 3447. (c) Egold, H.; Schraa, M.; Flörke, U. *J. Organomet. Chem.* **1999**, *582*, 345 and references therein. (d) Hogarth, G.; Lavender, M. H.; Shukri, K. *Organometallics* **1995**, *14*, 2325 and references therein. (e) Hartung, H.; Walther, B.; Baumeister, U.; Boettcher, H. C.; Krug, A.; Rosche, F.; Jones, P. G. *Polyhedron* **1992**, *11*, 1563.

(18) (a) Lavastre, O.; Bonnet, G.; Boni, G.; Kubicki, M. M.; Moise, C. *J. Organomet. Chem.* **1997**, *547*, 141 and references therein. (b) Mays, M. J.; Owen, S. M.; Raithby, P. R.; Reinisch, P. F.; Shields, G. P.; Solan, G. A. *J. Organomet. Chem.* **1997**, *528*, 123 and references therein. (c) Caffyn, A. J. M.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1992**, 515. (d) Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* **1990**, *9*, 387. (e) Jenkins, H. A.; Loeb, S. J.; Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1990**, *68*, 869. (f) Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 1557.

(19) Goh, L. Y.; D'Aniello, M. J., Jr.; Slater, S.; Muettterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192.

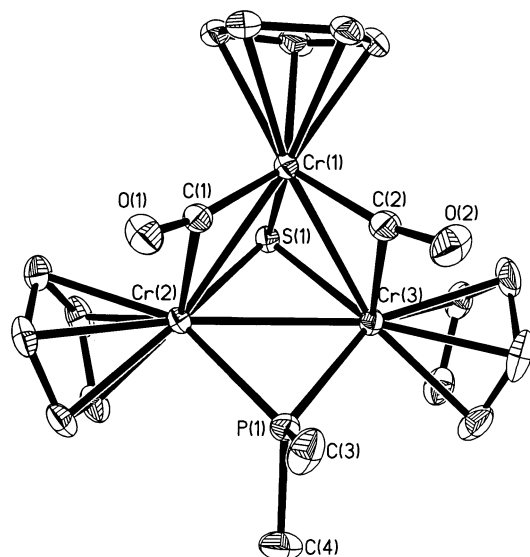
(20) (a) Chatt, J.; Thornton, D. A. *J. Chem. Soc.* **1964**, 1005. (b) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823. (c) Hieber, W.; Winter, E. *Chem. Ber.* **1964**, *97*, 1037.

(21) (a) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472. (b) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379 and references therein. (c) Ginsberg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

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

(23) Pasynskii, A. A.; Eremenko, I. L.; Oraszkhov, B.; Gasanov, G. Sh.; Novotortsev, V. M.; Ellert, O. G.; Seifulina, Z. M.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *270*, 53.

(24) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: Singapore, 1999. (b) Shriver, D. F.; Kaesz, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Complexes*; VCH: New York, 1990.



**Figure 4.** Molecular structure of **5a**. Thermal ellipsoids are drawn at the 50% probability level.

PR group.<sup>25</sup> The molecule **5a** possesses a trigonal-pyramidal structure consisting of a Cr<sub>3</sub> triangle, edge-bridged by one  $\mu$ -PR<sub>2</sub> ligand and two  $\mu$ -CO ligands and capped by a  $\mu_3$ -S atom, with Cr–Cr distances of 2.7619(5)–2.8166(5) Å (Table 3), the longest being for the edge bridged by the PR<sub>2</sub> group. As far as we are aware, this is the first example of a phosphido-bridged tri-homometal cluster of a group 6 element, though butoxide-bridged and nitrene-bridged complexes of CpCr have

(25) See for example: Shieh, M.; Ho, L.-F.; Jang, L.-F.; Ueng, C.-H.; Peng, S.-M.; Liu, Y.-H. *Chem. Commun.* **2001**, 1014 and references therein.

(26) (a) Nefedov, S. E.; Pasynskii, A. A.; Eremenko, I. L.; Orazskhatov, B.; Ellert, O. G.; Novotortsev, V. M.; Struchkov, Yu. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1990**, *385*, 277. (b) Eremenko, I. L.; Pasynskii, A. A.; Vas'utinskaya, E. A.; Katugin, A. S.; Nefedov, S. E.; Ellert, O. G.; Novotortsev, V. M.; Shestakov, A. F.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *411*, 193.

(27) Chen, W.; Goh, L. Y.; Bryan, R. F.; Sinn, E. *Acta Crystallogr.* **1986**, *C42*, 796.

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

Bond Lengths (Å)			
Cr(1)–Cr(2)	2.7767(5)	Cr(1)–Cr(3)	2.7619(5)
Cr(2)–Cr(3)	2.8166(5)	Cr(1)–S(1)	2.2948(7)
Cr(2)–S(1)	2.2283(6)	Cr(3)–S(1)	2.2292(6)
Cr(2)–P(1)	2.3210(7)	Cr(3)–P(1)	2.3115(7)
Cr(1)–C(1)	1.841(2)	Cr(1)–C(2)	1.829(2)
Cr(2)–C(1)	2.364(2)	Cr(3)–C(2)	2.362(2)
Bond Angles (deg)			
Cr(2)–Cr(1)–Cr(3)	61.134(13)	Cr(1)–Cr(2)–Cr(3)	59.173(13)
Cr(1)–Cr(3)–Cr(2)	59.693(12)	Cr(1)–S(1)–Cr(3)	75.23(2)
Cr(1)–S(1)–Cr(2)	75.73(2)	Cr(2)–S(1)–Cr(3)	78.38(2)
Cr(2)–P(1)–Cr(3)	74.89(2)	P(1)–Cr(2)–Cr(3)	52.400(18)
P(1)–Cr(3)–Cr(2)	52.707(19)	Cr(1)–C(1)–Cr(2)	81.63(9)
Cr(1)–C(2)–Cr(3)	81.39(9)		

been characterized, possessing Cr–Cr distances in the ranges 2.920(6)–2.956(6) and 2.544(1)–2.565(1) Å, respectively.<sup>26</sup> All three Cr–S distances are in the range of Cr– $\mu_3$ -S single bonds found in Cp<sub>4</sub>Cr<sub>4</sub>S<sub>m</sub>(CO)<sub>n</sub> ( $m = 4$ ,  $n = 0$ ;  $m = 2$ ,  $n = 2$ ) cubanes (2.226(2)–2.267(5) Å);<sup>2a,27</sup> Cr(1), which is bonded to both  $\mu$ -CO ligands, is further from S(1) (2.2948(7) Å) than the other two Cr atoms (2.2283(6), 2.2292(6) Å).

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**Supporting Information Available:** Text giving complete details for the synthesis of all compounds, spectral characteristics, and X-ray crystallographic data for **2a**, **b**, **3a**, **b**, **4a**, and **5a**, ORTEP diagrams for these compounds, and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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