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Complexes from Ring Opening of Lawesson's Reagent and Phosphorus−Phosphorus Coupling

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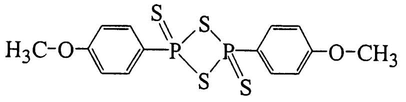
At *ambient temperature* the reaction of $[CpCr(CO)_3]_2$ (**1**; Cp = η^5-C_5H_5) with 1 mol equiv of Lawesson's reagent, $Ar_2P_2S_4$ (**2**; Ar = $C_6H_4OCH_3$), for 3 h led to the isolation of brown crystals of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**), dark red solids of $Cp_2Cr_2(CO)_5(S_2PAr)$ (**4**), deep blue solids of $Cp_2Cr_2(S_2P(O)Ar)_2$ (**5**), greenish yellow solids of $CpCr(CO)_3H$ (**9**), and deep green crystals of $Cp_2Cr_2(CO)_4S$ (**10**) with yields of 5, 11, 20, 7, and 8%, respectively; a similar reaction *at 90 °C* for 2 h gave **5** (36%), $CpCr(CO)_2(SP(H)Ar)$ (**6**) as red crystals (9%), $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**7**) as dark brown crystalline solids (14%), and its isomer *trans*-**7** as dark red crystals (5%), together with **9** (4%) and **10** (11%). The *ambient-temperature* reaction of $[Cp^*Cr(CO)_3]_2$ (**1***; Cp* = η^5-C_5Me_5) yielded the Cp* analogues of **4**, **5**, **9**, and **10**, i.e., **4***, **5***, **9***, and **10*** with yields of 51, 17, 6, and 8%, respectively. The thermolysis of $Cp^*_2Cr_2(CO)_5(S_2PAr)$ (**4***) resulted in the isolation of $Cp^*Cr(CO)_2(SP(H)Ar)$ (**6***), $Cp^*_2Cr_2(CO)_4(SPAr)$ (**8***), and $Cp^*_2Cr_2(S_2P(O)Ar)_2$ (**5***) with yields of 7, 14, and 13%, respectively. A NMR spectral study demonstrated that thermolytic degradation of complex **3** or its reaction with sulfur or Lawesson's reagent (**2**) led to the formation of *cis*-**7**; *cis*- and *trans*-**7** were found to interconvert under elevated temperatures, giving 4:1 equilibrium mixtures at 80 °C; both isomers react with **1** to re-form **3.** The solid-state structures of all the above-mentioned complexes have been characterized by single-crystal X-ray diffraction analysis. Complexes **3** and **8*** contain the phosphinothioylidene ligand in different coordination modes. The analogous structures of complexes **4**/**4*** reveal a bridging dithiophosphorane ligand, being η^2(S,S′) coordinated to a Cp/Cp*Cr$(CO)_2$ moiety and η^1(P) coordinated to a Cp/Cp*Cr$(CO)_3$ moiety. The similar molecular structures of **5** and **5*** contain an eight-membered ring, comprising two CpCr/Cp*Cr units and two $[S_2P(O)Ar]$ moieties. Complexes **6**/**6*** contain a rare η^2-arylthioxophosphane ligand. The complexes *cis*- and *trans*-**7** are conformers of a P−P-bonded dimer.

Introduction

Lawesson's reagent, (p-methoxyphenyl)thionophosphine sulfide (**2**), is an efficient S-donor agent for the conversion of carbonyl to thiocarbonyl compounds.[1]



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Although thionation reactions of Lawesson's reagent toward organic substrates are well-documented, its reactivity with transition-metal compounds has so far been little studied. We found in the literature only a limited number of reactions, viz. those with (i) the carbonyl complexes $Cp_2Mo_2(CO)_4$,[2a] $(Cp)_2Ti(CO)_2$,[2b] and $Fe_2(CO)_9$,[2c] (ii) the group 10 compounds MCl_2,[2d] K_2MCl_4,[2d] and $(PR_3)_2MCl_2$ (M = Ni, Pd, Pt),[2e] $Pt(C_2H_4)(PPH_3)_2$,[2f] and $NiCl_2$ in the presence of 1,3-dialkylimidazolidine-2-thione-4,5-dione,[2g] and (iii) the group 14 complexes $M[N(SiMe_3)_2]_2$, $M(Bu^tNCH_2CH_2NBu^t)$, and $M[(SPAr)_2]_2$ (M = Ge, Sn).[2h] In these reactions, the metal center has coordinated to fragments from Lawesson's reagent as shown in Chart 1.

In the context of our interest in the chemistry of $[CpCr(CO)_3]_2$ (**1**) with S- and/or P-containing compounds, we have chosen to investigate the reactivity of **1** toward the P_2S_4 central ring component of **2**. To date, we have studied **1**-initiated interchalcogen cleavage in a variety of systems, viz. in homopolynuclear inorganic compounds,[3] in organic substrates, e.g. Ph_2E_2 (E = S, Se, Te),[4] in bis(phosphorodithioato)disulfanes, $(R_2P$-

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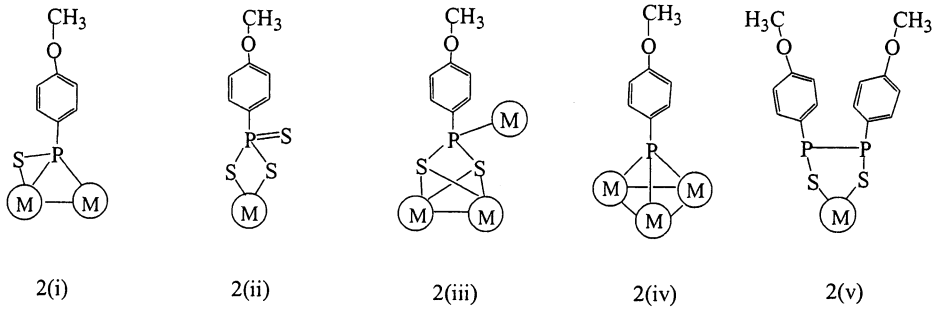
Chart 1. Coordination of Fragments from 2[a]


2(i) 2(ii) 2(iii) 2(iv) 2(v)

[a] Ⓜ = metal fragment.

(S)S−)$_2$ (R = Ph^{5a} and ^{i}PrO,^{5b} respectively), in teraalkylthiuram disulfanes ($R_2NC(S)S-)_2$,^{6} and very recently in dibenzothiazolyl disulfane, ($-SCSN(C_6H_4))_2$.^{7a} For chalcogen−pnicogen bond cleavage, our previous work had dealt with the closo polyhedra P_4E_3 (E = S,^{8a} Se^{8b}) and the polymeric Sb_2S_3.^{8c} In this present study, the four-membered P_2S_2 ring with doubly bonded S substituents on P presents a different class of S- and P-containing substrates that we envisage will possess rich reactivity features with **1**. These are described in this paper.

Experimental Section

General Considerations. 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_6H_6 in C_6D_6 and ^{31}P chemical shifts to external H_3PO_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**) and $[Cp^*Cr(CO)_3]_2$ (**1***) were prepared according to literature procedures.^{9} Lawesson's reagent (98% purity) was used as supplied by Fluka Chemical Co. All solvents were dried over sodium/benzophenone and distilled before use. Silica gel (Merck Kieselgel 60, 230−400 mesh) was dried at 140 °C overnight before chromatographic use.

Reaction of $[CpCr(CO)_3]_2$ (1) with Lawesson's Reagent. (a) At Ambient Temperature. A deep green mixture of $[CpCr(CO)_3]_2$ (**1**; 100 mg, 0.25 mmol) and Lawesson's reagent (**2**; 101 mg, 0.25 mmol) in toluene (8 mL) was stirred at ambient temperature for 4 h. The resultant greenish brown product mixture was concentrated to 4 mL and filtered to remove unreacted **2** (ca. 30 mg). The filtrate was loaded onto a silica gel column (2 × 10 cm) prepared in *n*-hexane. Elution under slight pressure gave five fractions: (i) a dark green eluate in *n*-hexane/toluene (4:1, 10 mL), from which was obtained green solids (ca. 26 mg), the ^{1}H NMR spectra of which indicated the presence of an approximately 1:2 molar mixture of $CpCr(CO)_3H$ (**9**; estimated 7 mg, 0.03 mmol, 7% yield) and unreacted **1** (estimated 19 mg, 0.05 mmol, 19% recovery); (ii) a green eluate in *n*-hexane/toluene (1:1, 4 mL), from which was obtained $[CpCr(CO)_2]_2S$ (**10**) as deep green crystals (8 mg, 0.02 mmol, 8% yield); (iii) a brown eluate in toluene (5 mL), which on concentration gave dark brown crystals of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**; 7 mg, 0.01 mmol, 5% yield); (iv) a red eluate in toluene (8 mL), which yielded the dark red solid $Cp_2Cr_2(CO)_5(S_2PAr)$ (**4**; 15 mg, 0.03 mmol, 11% yield); (v) a blue eluate in toluene/THF (1:1, 15 mL), which yielded a deep blue solid of $Cp_2Cr_2(S_2P(O)Ar)_2$ (**5**; 34 mg, 0.05 mmol, 20%). A deep blue band remained unmoved on the top of the column.

(b) At 90 °C. A deep green mixture of $[CpCr(CO)_3]_2$ (**1**; 201 mg, 0.50 mmol) and **2** (202 mg, 0.50 mmol) in toluene (10 mL) was stirred at 90 °C for 2 h. The resultant dark brown product mixture was filtered to remove an uncharacterizable insoluble dark green compound (ca. 20 mg). The filtrate was concentrated to ca. 3 mL and loaded onto a silica gel column (2 × 15 cm) prepared in *n*-hexane. Elution gave six fractions: (i) a yellow eluate in *n*-hexane/toluene (5:1, 8 mL), from which was obtained greenish yellow solids of $CpCr(CO)_3H$ (**9**; 9 mg, 0.04 mmol, 4%); (ii) a green eluate in *n*-hexane/toluene (2:1, 8 mL), from which was obtained $[CpCr(CO)_2]_2S$ (**10**; 21 mg, 0.06 mmol, 11% yield); (iii) a red eluate in toluene (10 mL), which gave red crystals of $CpCr(CO)_2(SP(H)Ar)$ (**6**; 31 mg, 0.09 mmol, 9% yield); (iv) a reddish brown eluate in toluene (15 mL), which yielded a dark brown crystalline solid of $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**7**; 48 mg, 0.07 mmol, 14% yield); (v) a red eluate in toluene (10 mL), which on concentration yielded a dark red solid of $[CpCr(CO)_2(SPAr)]_2$ (*trans*-**7**; 18 mg, 0.026 mmol, 5% yield); (vi) a deep blue eluate in toluene/THF (4:1, 10 mL), which yielded a deep blue solid of $Cp_2Cr_2(S_2P(O)Ar)_2$ (**5**; 121 mg, 0.18 mmol, 36% yield). A deep blue band remained unmoved on the top of the column.

Reaction of $[Cp^*Cr(CO)_3]_2$ (1*) with Lawesson's Reagent at Ambient Temperature. A deep purple mixture of $[Cp^*Cr(CO)_3]_2$ (**1***; 135 mg, 0.25 mmol) and **2** (101 mg, 0.25 mmol) in toluene (8 mL) was stirred at ambient temperature for 3 h. The resultant reddish brown product mixture was filtered to remove an uncharacterizable blue compound (7 mg). The filtrate was concentrated to 3 mL and loaded onto a silica gel column (2 × 8 cm) prepared in *n*-hexane. Elution gave four fractions: (i) a yellow eluate in *n*-hexane/toluene (4:1, 5 mL), from which was obtained greenish yellow crystals of $Cp^*Cr(CO)_3H^{10}$ (**9***; 8 mg, 0.03 mmol, 6% yield); (ii) a green eluate in *n*-hexane/toluene (2:1, 4 mL), from which was obtained dark green crystals of $Cp^*_2Cr_2(CO)_4S$ (**10***; 10 mg, 0.02 mmol, 8% yield); (iii) a reddish brown eluate in toluene (10 mL), which

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yielded a brown solid of $Cp^*_2Cr_2(CO)_5(S_2PAr)$ (**4***; 92 mg, 0.13 mmol, 51% yield); (iv) a blue eluate in toluene/THF (1:1, 15 mL), which yielded a deep blue solid of $Cp^*_2Cr_2(S_2P(O)Ar)_2$ (**5***; 34 mg, 0.04 mmol, 17% yield).

Thermolysis of $Cp^*_2Cr_2(CO)_5(S_2PAr)$ (4*). A reddish brown solution of $Cp^*_2Cr_2(CO)_5(S_2PAr)$ (**4***; 120 mg, 0.17 mmol) in toluene (5 mL) was stirred at 90 °C for 10 min. The resultant greenish brown product mixture was loaded onto a silica gel column (2 × 8 cm) prepared in *n*-hexane. Elution gave four fractions. (i) This fraction was a yellow eluate in *n*-hexane/toluene (4:1, 5 mL), from which was obtained **9*** (4 mg, 0.02 mmol, 4% yield). (ii) A green eluate in *n*-hexane/toluene (1:1, 8 mL) was the second fraction from the column, from which was obtained **10*** (20 mg, 0.04 mmol, 23% yield). (iii) A reddish brown eluate in toluene (10 mL) was obtained, which gave brown solids (24 mg), the ^1H NMR spectra of which indicated the presence of a 1:3 molar mixture of **6*** and **8***. This mixture was extracted with *n*-hexane/toluene (1:2, 2 × 3 mL), leaving behind on the walls of the flask a dark red solid of $Cp^*_2Cr_2(CO)_4(SPAr)$ (**8***; ca. 16 mg, 0.03 mmol, 14% yield). The combined extracts were concentrated to dryness, yielding red crystalline solids of $Cp^*Cr(CO)_2(SP(H)Ar)$ (**6***; ca. 5 mg, 0.01 mmol, 7% yield). (iv) A blue eluate in toluene/THF (1:1, 15 mL) was obtained, which yielded a deep blue solid of $Cp^*_2Cr_2(S_2P(O)Ar)_2$ (**5***; 18 mg, 0.02 mmol, 13% yield). A deep blue band remained unmoved on the top of the column.

Data for 3. IR (KBr, $\nu(CO)/cm^{-1}$): 2015 s, 1958 s, 1942 s, 1921 s, 1848 s. ^1H NMR (C_6D_6): δ 4.29 (s, 5H, C_5H_5), 4.21 (s, 5H, C_5H_5), 6.54 (dd, $J = 8$ Hz, 2H, C_6H_4), 7.78 (t, $J = 9$ Hz, 2H, C_6H_4), 3.15 (s, 3H, OCH_3). ^{13}C NMR (C_6D_6): δ 94.1, 91.4 (C_5H_5), 160.9 (C_6H_4), 142.3 (C_6H_4), 132.0 (d, $J = 12$ Hz, C_6H_4), 114.2 (d, $J = 10$ Hz, C_6H_4), 55.3 (OCH_3), 264.2 (CO), 255.0 (d, $J = 8$ Hz, CO), 243.3 (d, $J = 13$ Hz, CO), 238.2 (d, $J = 36$ Hz, CO). ^{31}P NMR (C_6D_6): δ 74.7. Anal. Calcd for $C_{22}H_{17}Cr_2O_6PS$: C, 48.5; H, 3.2. Found: C, 48.8; H, 3.2. MS FAB$^+$ (m/z): 544 $[M]^+$, 460 $[M - 3CO]^+$, 404 $[M - 5CO]^+$. HR-MS FAB$^+$ (m/z): for $[M]^+$ 543.9296 (found), 543.9294 (calcd).

Data for 4. IR (toluene, $\nu(CO)/cm^{-1}$): 2017 s, 1947 br, 1880 br. ^1H NMR (C_6D_6): δ 4.60 (s, 5H, C_5H_5), 4.53 (br, $\nu_{1/2} = 36$ Hz, 5H, C_5H_5), 8.31 (br, 2H, C_6H_4), 6.84 (br, 2H, C_6H_4), 3.22 (s, 3H, OCH_3). ^{13}C NMR (C_6D_6): δ 95.5, 95.0 (C_5H_5), 132.7 (C_6H_4), 130.8 (C_6H_4), 114.0 (d, $J = 11$ Hz, C_6H_4), 55.3 (OCH_3). ^{31}P NMR (C_6D_6): δ 169.1. Anal. Calcd for $C_{22}H_{17}Cr_2O_6PS_2 \cdot {}^1/_4C_7H_8$: C, 47.6; H, 3.2. Found: C, 47.1; H, 3.2. MS FAB$^+$ (m/z): 576 $[M]^+$, 520 $[M - 2CO]^+$, 436 $[M - 5CO]^+$.

Data for 4*. IR (KBr, $\nu(CO)/cm^{-1}$): 2001 s, 1947 s, 1928 s, 1919 s, 1854 s. ^1H NMR (C_6D_6): δ 1.78 (s, 15H, $C_5(CH_3)_5$), 1.52 (s, 15H, $C_5(CH_3)_5$), 6.77 (d, $J = 8$ Hz, 2H, C_6H_4), 8.20 (m, 2H, C_6H_4), 3.21 (s, 3H, OCH_3). ^{13}C NMR (C_6D_6): δ 105.4 ($C_5(CH_3)_5$), 103.9 ($C_5(CH_3)_5$), 161.2 (C_6H_4), 146.7 (d, $J = 26$ Hz, C_6H_4), 130.7 (d, $J = 11$ Hz, C_6H_4), 113.1 (d, $J = 11$ Hz, C_6H_4), 55.3 (OCH_3), 11.2 ($C_5(CH_3)_5$), 10.2 ($C_5(CH_3)_5$), 274.5 (CO), 245.5 (CO), 245.3 (CO), 239.9 (CO), 239.3 (CO). ^{31}P NMR (C_6D_6): δ 184.7. Anal. Calcd for $C_{32}H_{37}Cr_2O_6PS_2 \cdot {}^1/_2C_7H_8$: C, 55.9; H, 5.4; S, 8.4. Found: C, 55.4; H, 5.8; S, 8.6. MS FAB$^+$ (m/z): 716 $[M]^+$, 660 $[M - 2CO]^+$, 576 $[M - 5CO]^+$.

Data for 5. ^1H NMR (C_6D_6): δ 4.31 (s, C_5H_5), 17.6 (br, C_6H_4), 10.02 (br, C_6H_4), 3.33 (br, OCH_3). Anal. Calcd for $C_{24}H_{24}Cr_2O_4P_2S_4 \cdot {}^1/_4C_7H_8$: C, 44.6; H, 3.8. Found: C, 44.3; H, 3.7. MS FAB$^+$ (m/z): 672 $[M + 2H]^+$.

Data for 5*. ^1H NMR (C_6D_6): δ 1.59 (s, $C_5(CH_3)_5$), 16.7 (br, C_6H_4), 10.0 (br, C_6H_4), 3.32 (br, OCH_3). Anal. Calcd for $C_{34}H_{44}Cr_2O_4P_2S_4 \cdot {}^1/_2C_7H_8$: C, 52.5; H, 5.6. Found: C, 52.1; H, 5.6. MS FAB$^+$ (m/z): 812 $[M + 2H]^+$.

Data for 6. IR (toluene, $\nu(CO)/cm^{-1}$) 1958 s, 1886 s. ^1H NMR (C_6D_6): δ 4.33 (s, 5H, C_5H_5), 6.56 (d, $J = 8$ Hz, 2H, C_6H_4), 7.24 (m, 2H, C_6H_4), 3.12 (s, 3H, OCH_3), 5.89 (d, $J = 403$ Hz, 1H, PH). ^{13}C NMR (C_6D_6): δ 90.2 (C_5H_5), 163.4 (C_6H_4), 134.4 (d, $J = 14$ Hz, C_6H_4), 120.8 (C_6H_4), 115.7 (d, $J = 12$ Hz, C_6H_4), 55.4 (OCH_3), 255.6 (d, $J = 45$ Hz, CO), 250.7 (d, $J = 10$ Hz, CO). ^{31}P NMR (C_6D_6; proton coupled): δ 38.7 (d, $J = 403$ Hz). Anal. Calcd for $C_{14}H_{12}CrO_3PS$: C, 48.9; H, 3.8; S, 9.3. Found: C, 49.4; H, 3.7; S, 9.2. MS FAB$^+$ (m/z): 344 $[M]^+$, 288 $[M - 2CO]^+$. HR-MS ESI$^+$ (m/z): for $[M]^+$ 343.9731 (found), 343.9728 (calcd).

Data for 6*. IR (KBr, $\nu(CO)/cm^{-1}$): 1942 s, 1870 s. ^1H NMR (C_6D_6): δ 1.58 (d, $J = 1$ Hz, 15H, $C_5(CH_3)_5$), 6.55 (dd, $J = 8$ Hz, 2H, C_6H_4), 7.31 (m, 2H, C_6H_4), 3.11 (s, 3H, OCH_3), 5.40 (d, $J = 384$ Hz, 1H, PH). ^{13}C NMR (C_6D_6): δ 101.6 ($C_5(CH_3)_5$), 163.1 (C_6H_4), 134.4 (d, $J = 14$ Hz, C_6H_4), 123.1 (d, $J = 58$ Hz, C_6H_4), 115.6 (d, $J = 14$ Hz, C_6H_4), 55.4 (OCH_3), 10.8 ($C_5(CH_3)_5$), 257.9 (d, $J = 46$ Hz, CO), 252.5 (d, $J = 8$ Hz, CO). ^{31}P NMR (C_6D_6; proton-coupled): δ 50.4 (d, $J = 384$ Hz). Anal. Calcd for $C_{19}H_{23}CrO_3PS$: C, 55.1; H, 5.6. Found: C, 55.2; H, 5.6. MS FAB$^+$ (m/z): 414 $[M]^+$, 358 $[M - 2CO]^+$. HR-MS ESI$^+$ (m/z): for $[M]^+$ 414.0513 (found), 414.0511 (calcd).

Data for *cis*-7. IR (KBr, $\nu(CO)/cm^{-1}$): 1944 s, 1883 s. ^1H NMR (C_6D_6): δ 4.12 (s, 10H, C_5H_5), 6.79 (d, $J = 8$ Hz, 4H, C_6H_4), 8.03 (m, 4H, C_6H_4), 3.22 (s, 6H, OCH_3). ^{13}C NMR (C_6D_6): δ 91.0 (C_5H_5), 163.4 (C_6H_4), 136.1 (C_6H_4), 122.9 (C_6H_4), 114.6 (t, $J = 6$ Hz, C_6H_4), 55.5 (OCH_3), 257.5 (CO), 249.1 (CO). ^{31}P NMR (C_6D_6): δ 80.3. Anal. Calcd for $C_{28}H_{24}Cr_2O_6P_2S_2 \cdot {}^1/_2C_4H_8O$: C, 49.9; H, 3.9. Found: C, 49.8; H, 3.8. MS FAB$^+$ (m/z): 686 $[M]^+$, 630 $[M - 2CO]^+$, 574 $[M - 4CO]^+$.

Data for *trans*-7. IR (KBr, $\nu(CO)/cm^{-1}$): 1952 s, 1886 s. ^1H NMR (C_6D_6): δ 4.31 (s, 10H, C_5H_5), 6.75 (d, $J = 8$ Hz, 4H, C_6H_4), 7.95 (m, 4H, C_6H_4), 3.21 (s, 6H, OCH_3). ^{13}C NMR (C_6D_6): δ 91.0 (C_5H_5), 163.3 (d, $J = 16$ Hz, C_6H_4), 137.4 (t, $J = 8$ Hz, C_6H_4), 135.3 (t, $J = 10$ Hz, C_6H_4), 115.9 (t, $J = 6$ Hz, C_6H_4), 114.4 (t, $J = 6$ Hz, C_6H_4), 55.5 (OCH_3), 259.8 (CO), 248.8 (CO). ^{31}P NMR (C_6D_6): δ 85.2. Anal. Calcd for $C_{28}H_{24}Cr_2O_6P_2S_2$: C, 49.0; H, 3.5. Found: C, 49.5; H, 3.5. MS FAB$^+$ (m/z): 686 $[M]^+$, 630 $[M - 2CO]^+$, 574 $[M - 4CO]^+$.

Data for 8*. IR (KBr, $\nu(CO)/cm^{-1}$): 1959 s, 1888 s. ^1H NMR (C_6D_6): δ 1.32 (s, 30H, $C_5(CH_3)_5$), 6.83 (d, $J = 8$ Hz, 2H, C_6H_4), 7.92 (m, 2H, C_6H_4), 3.29 (s, 3H, OCH_3). ^{13}C NMR (C_6D_6): δ 102.3 ($C_5(CH_3)_5$), 163.7 (C_6H_4), 137.6 (C_6H_4), 130.8 (C_6H_4), 114.1 (C_6H_4), 55.5 (OCH_3), 10.8 ($C_5(CH_3)_5$), 260.4 (t, $J = 24$ Hz, CO), 250.2 (CO). ^{31}P NMR (C_6D_6): δ 85.2. Anal. Calcd for $C_{31}H_{37}Cr_2O_5PS$: C, 56.7; H, 5.7. Found: C, 56.0; H, 5.5. MS FAB$^+$ (m/z): 656 $[M]^+$, 600 $[M - 2CO]^+$, 544 $[M - 4CO]^+$.

Data for 9 and 9*. ^1H NMR (C_6D_6): **9**, δ 4.02 (s, C_5H_5), −5.58 (s, CrH); **9***, δ 1.57 (s, $C_5(CH_3)_5$), −5.58 (s, CrH).

Data for 10 and 10*. ^1H NMR (C_6D_6): **10**, δ 4.36 (s, C_5H_5); **10***, δ 1.63 (s, $C_5(CH_3)_5$).

NMR-Tube Reactions. The following reactions were carried out in C_6D_6 (0.5 mL) in septum-capped 5 mm tubes under argon at ca. 80 °C for 40 min (unless otherwise specified), followed by ^1H NMR spectral scans.

(i) Reaction of $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ with **2**: a deep green mixture of $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ (4 mg, 0.01 mmol) and **2** (4 mg, 0.01 mmol).

(ii) Reaction of $[CpCr(CO)_3]_2$ (**1**) with **2**: a deep green mixture of **1** (4 mg, ca. 0.01 mmol) and **2** (4 mg, 0.01 mmol).

(iii) Cothermolysis of $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**7**) with **1**: a brown mixture of *cis*-**7** (7 mg, 0.01 mmol) and **1** (4 mg, 0.01 mmol).

(iv) Cothermolysis of $[CpCr(CO)_2(SPAr)]_2$ (*trans*-**7**) with **1**: a brown mixture of *trans*-**7** (7 mg, 0.01 mmol) and **1** (4 mg, 0.01 mmol).

(v) Thermolysis of $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**7**): a red-brown solution of *cis*-**7** (7 mg, 0.01 mmol).

(vi) Thermolysis of $[CpCr(CO)_2(SPAr)]_2$ (*trans*-**7**): a red solution of *trans*-**7** (7 mg, 0.01 mmol).

(vii) Thermolysis of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**): a reddish brown solution of **3** (6 mg, 0.01 mmol).

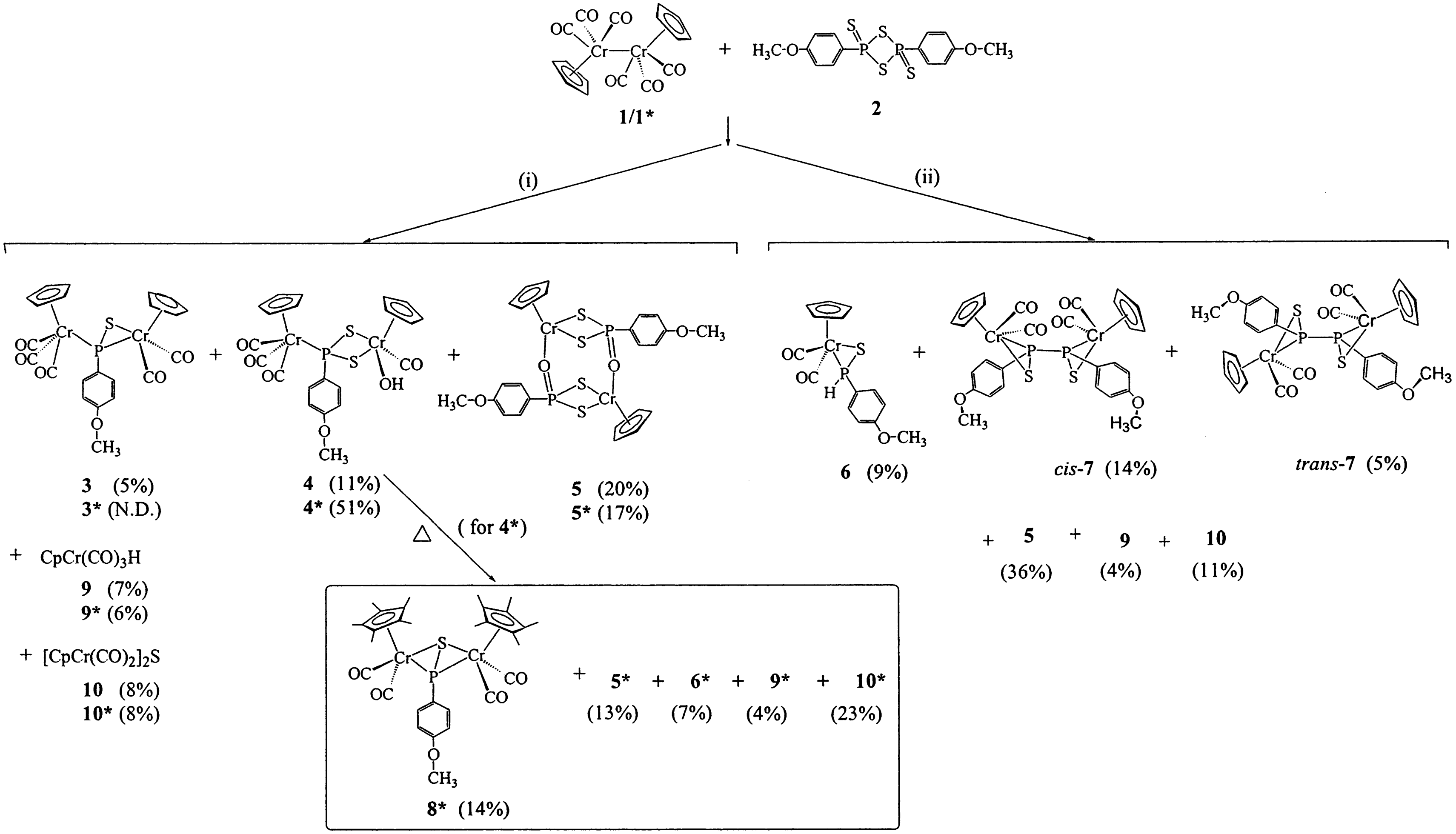
(viii) Reaction of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**) with S_8: a reddish brown solution of **3** and S_8 (3 mg, 0.01 mmol) in C_6D_6 (0.5 mL) was shaken up for 10 min and kept at ambient temperature for 1 h.

Table 1. Data Collection and Processing Parameters

	3	**4**	**4***	**5**	**5***	**6**	**6***	*cis*-**7**	*trans*-**7**	**8***
formula	$C_{22}H_{17}Cr_2$-O_6PS	$C_{22}H_{17}Cr_2$-O_6PS_2	$C_{32}H_{37}Cr_2$-O_6PS_2	$C_{24}H_{24}Cr_2$-$O_4P_2S_4$	$C_{34}H_{44}Cr_2$-$O_4P_2S_4$	$C_{14}H_{13}Cr$-O_3PS	$C_{19}H_{22}Cr$-O_3PS	$C_{28}H_{24}Cr_2$-$O_6P_2S_2\cdot$ C_7H_8O	$C_{28}H_{24}Cr_2$-$O_6P_2S_2\cdot$ C_7H_8	$C_{31}H_{37}Cr_2$-$O_5PS\cdot$ $^1/_2C_7H_8$
M_r	544.39	576.45	716.71	670.61	810.87	344.27	414.40	758.64	778.67	702.70
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$Pbca$	$C2/c$	$C2/c$	$P2_1/n$
a, Å	19.6999(17)	18.9679(7)	8.8030(3)	7.9144(3)	9.5684(2)	8.08730(10)	8.4131(8)	19.8474(15)	19.369(7)	11.8590(3)
b, Å	9.6164(9)	16.0998(6)	35.2875(14)	7.8690(2)	12.6743(3)	9.3009(2)	14.7195(14)	8.3393(6)	19.308(6)	14.4615(5)
c, Å	11.5827(10)	17.1099(6)	11.0952(4)	22.8610(8)	15.6861(4)	10.6840(3)	31.680(3)	21.5466(17)	10.922(4)	21.3366(7)
α, deg	90	90	90	90	90	79.1080(10)	90	90	90	90
β, deg	90	117.3370(10)	97.922(2)	98.387(2)	94.6100(10)	82.6220(10)	90	109.003(1)	122.243(7)	98.197(2)
γ, deg	90	90	90	90	90	69.4390(10)	90	90	90	90
V, Å^3	2194.3(3)	4641.5(3)	3413.7(2)	1408.52(8)	1896.14(8)	737.21(3)	3923.2(7)	3371.9(4)	3455(2)	3621.8(2)
Z	4	8	4	2	2	2	8	4	4	4
density, g cm^{-3}	1.648	1.650	1.395	1.581	1.420	1.551	1.403	1.494	1.497	1.289
abs coeff, mm^{-1}	1.196	1.222	0.846	1.211	0.913	1.028	0.786	0.909	0.887	0.739
F(000)	1104	2336	1488	684	844	352	1728	1560	1600	1468
θ range for data collecn, deg	2.07−25.00	2.42−26.37	2.18−26.37	2.60−26.37	2.07−30.50	1.95−29.28	2.57− 30.80	2.00−30.02	2.11−24.99	2.10−24.71
index ranges										
h	−20 to +23	−23 to +21	−11 to +10	−9 to +9	−13 to + 13	−10 to +10	0 to +11	−26 to +27	−23 to +13	−13 to +13
k	−11 to +11	0 to +20	0 to +44	0 to +9	0 to +17	−10 to +12	0 to +20	−6 to +11	−22 to +22	0 to +17
l	−13 to +13	0 to + 21	0 to +13	0 to +28	0 to +21	−7 to +14	0 to +43	−29 to +25	−12 to +12	0 to +25
no. of rflns collected	11 907	30 473	27 171	11 842	16 256	4790	30 520	13 294	9901	26 733
no. of indep rflns	3784	4758	6970	2861	5463	3401	5731	4791	3050	6155
no. of data/ restraints/ params	3784/1/290	4758/0/290	6970/0/399	2861/0/164	5463/0/208	3401/0/183	5731/0/236	4791/0/204	3050/1/192	6155/0/401
final R indices ($I > 2\sigma(I)$)^{a,b}										
R1	0.0508	0.1159	0.0506	0.0692	0.0746	0.0438	0.0687	0.0512	0.0530	0.0804
wR2	0.1122	0.2406	0.0853	0.1478	0.2110	0.1170	0.1462	0.1088	0.1415	0.2218
R indices (all data)										
R1	0.0653	0.1300	0.1434	0.0752	0.0907	0.0586	0.1246	0.0776	0.0684	0.1008
wR2	0.1165	0.2471	0.0996	0.1505	0.2415	0.1255	0.1619	0.1164	0.1496	0.2351
goodness of fit on $F^{2\,c}$	0.994	1.332	0.676	1.300	1.105	1.022	0.966	1.038	1.005	1.118
large diff peak, hole, e Å^{-3}	1.665, −0.361	1.419, −0.712	0.664, −0.373	0.780, −0.470	1.546, −1.309	0.444, −0.632	1.284, −0.386	0.512, −0.320	1.268, −0.730	1.678, −0.342

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

Scheme 1. Reaction Products and Their Isolated Yields[a]



[a] In this scheme, the pentagonal ring with the inner circle is Cp/Cp*. Reaction conditions: (i) 4 h at ambient temperature; (ii) 2 h at 90 °C. N.D. = not detected.

Table 2. Yields (%) of Products[a]

reaction	products 3	 4	 5	 6	 *cis*-7	 *trans*-7	 8*	 9	 10
1 + **2** at room temp/3 h	5	11	20	0	0	0	0	7	8
1 + **2** at 90 °C/2 h	0	0	36	9	14	5	0	4	11
1* + **2** at room temp/3 h	N.D.	(51)	(17)	N.D.	(0)	(0)	(0)	(6)	(8)
thermolysis of **4*** at 90 °C/10 min	N.D.	N.D.	(13)	(7)	*b*	*b*	(14)	(4)	(23)

[a] Values in parentheses are the products from Cp* analogues. N.D. = not detected. [b] A trace was observed in the NMR spectrum of the product mixture but was lost in the chromatographic separation.

(ix) Reaction of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**) with **2**: a reddish brown solution of **3** and **2** (3 mg, 0.01 mmol) in C_6D_6 (0.5 mL) was shaken up for 10 min and kept at ambient temperature for 2 h.

(x) Thermolysis of $CpCr(CO)_2(SP(H)Ar)$ (**6**): a dark red solution of **6** (8 mg, 0.02 mmol) in toluene-d_8 (0.5 mL) was maintained at ca. 110 °C, and its proton NMR spectrum was scanned at intervals up to 2 h.

Crystal Structure Analyses. Diffraction-quality single crystals were obtained at −29 °C as follows: from solutions in toluene layered with hexane, **3** as dark brown irregular polyhedra, **4** and **4*** as dark red needles, **8*** as red rhombuses after 2−4 days, and *trans*-**7** as dark red needles after 5 days; from solutions in THF layered with hexane, **5** and **5*** as deep blue prisms after 4 and 7 days, respectively, **6** and **6*** as red rhombuses after 3 days, and *cis*-**7** as dark brown prisms after 5 days. 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[11] and for absorption effects with SADABS.[12] Structure solution and refinement were carried out with the SHELXTL suite of programs.[13] 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. The data collection and processing parameters are given in Table 1.

Results and Discussion

Products and Reaction Pathways. The product mixture from the reaction of $[CpCr(CO)_3]_2$ (**1**) with 1 mol equiv of Lawesson's reagent (**2**) in toluene varied with reaction conditions, as shown in Scheme 1. Thus, from a reaction at ambient temperature for 4 h were isolated dark brown crystals of $Cp_2Cr_2(CO)_5(SPAr)$ (**3**), dark red solids of $Cp_2Cr_2(CO)_5(S_2PAr)$ (**4**), deep blue solids of $Cp_2Cr_2(S_2P(O)Ar)_2$ (**5**), yellowish green solids of $CpCr(CO)_3H$ (**9**), and deep green crystals of $Cp_2Cr_2(CO)_4S$ (**10**) in yields shown in the scheme. From a similar reaction of $[Cp^*Cr(CO)_3]_2$ (**1***), the analogue of **3** was not detected. The same reaction performed at 90 °C for 2 h gave **5**, **9,** and **10**, together with new products, viz., red crystals of $CpCr(CO)_2(SP(H)Ar)$ (**6**) and dark brown crystalline solids of $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**7**) and its isomer *trans*-**7** as dark red crystals, but the ambient-temperature products **3** and **4** were not detected. However, an NMR-tube reaction in C_6D_6 for 60 min at 80 °C did show the presence of **3**, in admixture with **5**−**7**, **9** and **10**, in an approximate molar ratio of 9:2:4:3:2:5, respectively. Indeed, it was found that **4*** (and by inference **4** also) was thermally labile. The thermolysis of $Cp^*_2Cr_2(CO)_5(S_2PAr)$ (**4***) at 90 °C for 10 min yielded **5***, cherry red $Cp^*Cr(CO)_2(SP(H)Ar)$ (**6***), and dark red solids of $Cp^*_2Cr_2(CO)_4(SPAr)$ (**8***) (14%), together with **9*** and **10***. A small amount of **7*** (ca. 6%) was seen (^{1}H NMR δ 1.53 (Cp*), 3.26 (OMe); ^{31}P NMR δ 88.9) in the crude product solution but was lost in the chromatographic process. The data depicted in Scheme 1 are also tabulated in Table 2 for a clearer comparison.

The molecular structures of **3** and **4** suggest that they both originate from a common intermediate, the radical species **2A**, shown in Scheme 2, formed via interaction of $CpCr(CO)_3^{\bullet}$ (**1A**), the incumbent monomer of **1**, and the "monomer" of **2**. Rauchfuss had demonstrated that the mechanism for the thiation of organic carbonyls by Lawesson's reagent involves monomeric $ArPS_2$ intermediates into which **2** reversibly cleaves (route i).[14] In the situation here the radical **1A** is likely to play a dominant role in cleaving the P_2S_4 central unit of **2**, forming directly the moiety **2A** (route ii). Further reaction of **2A** with **1A** then generates **3** and **10** (route iii) and compound **4** (route iv), as well as compound **5** by dimerization with elimination of CO (route v), as illustrated. In the absence of oxygen or water, we surmise that the O atom in the eight-membered ring in **5**/**5*** originates from a CO ligand. Unfortunately, evidence for this is difficult to obtain and we have not been successful in identifying any compound with a CS ligand. The formation of hydride **9** has been observed in many reactions of **1** with various substrates, and experimental evidence has ruled out the solvent as the source of the hydridic H.[4c,8a,b,15] It is probable that the source is coordinated Cp, considering that we have observed in crude product solutions, as well as in some of the chromatographed fractions, several low-intensity unassignable peaks between δ 4.17 and 5.37. These fall in the same Cp region where resonances have been reported for the crystallographically characterized trinuclear $Cp_2M_2M'(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(CO)_6$ (M = Mo and M′ = W) complexes, which were obtained from photolytic C−H cleavage of $Cp_2M_2(CO)_6$, along with the hydrides $CpM(H)(CO)_3$ and $Cp_2M_2(\mu\text{-}H)_2(CO)_4$.[16]

The thermolytic products of **4*** are in agreement with the occurrence of homolytic cleavage, followed by coupling reactions, as proposed in Scheme 3; thus a Cr−P bond scission (route a) will give the P-centered radical **4A*** and the Cr-centered radical $Cp^*Cr(CO)_3^{\bullet}$ (**1A***), while P−S bond cleavage (route b) together with Cr−S bond scission (route c) will yield the P-centered radical **3A*** and the S-centered radical $Cp^*Cr(CO)_2S^{\bullet}$. It is

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[11] SMART, version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 2000.

[12] Sheldrick, G. M. SADABS, a Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 2000.

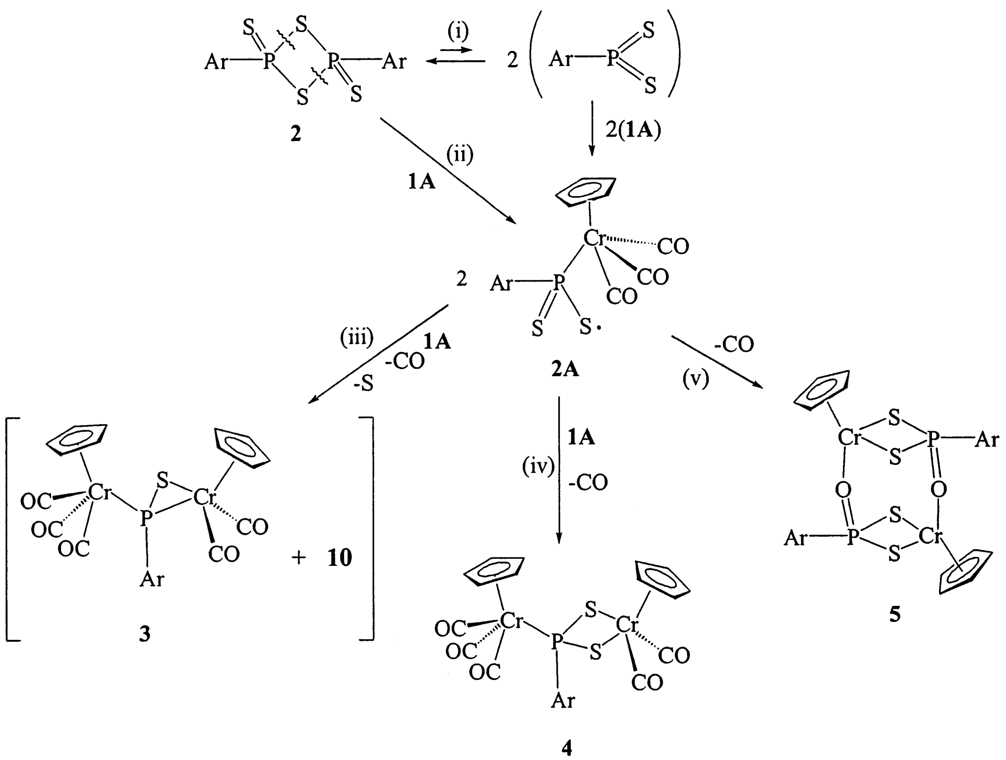
[13] SHELXTL, version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

[14] Rauchfuss, T. B.; Zank, G. A. *Tetrahedron Lett.* **1986**, *27*, 3445.

[15] Goh, L. Y.; Tay, M. S. Unpublished observations, 1992.

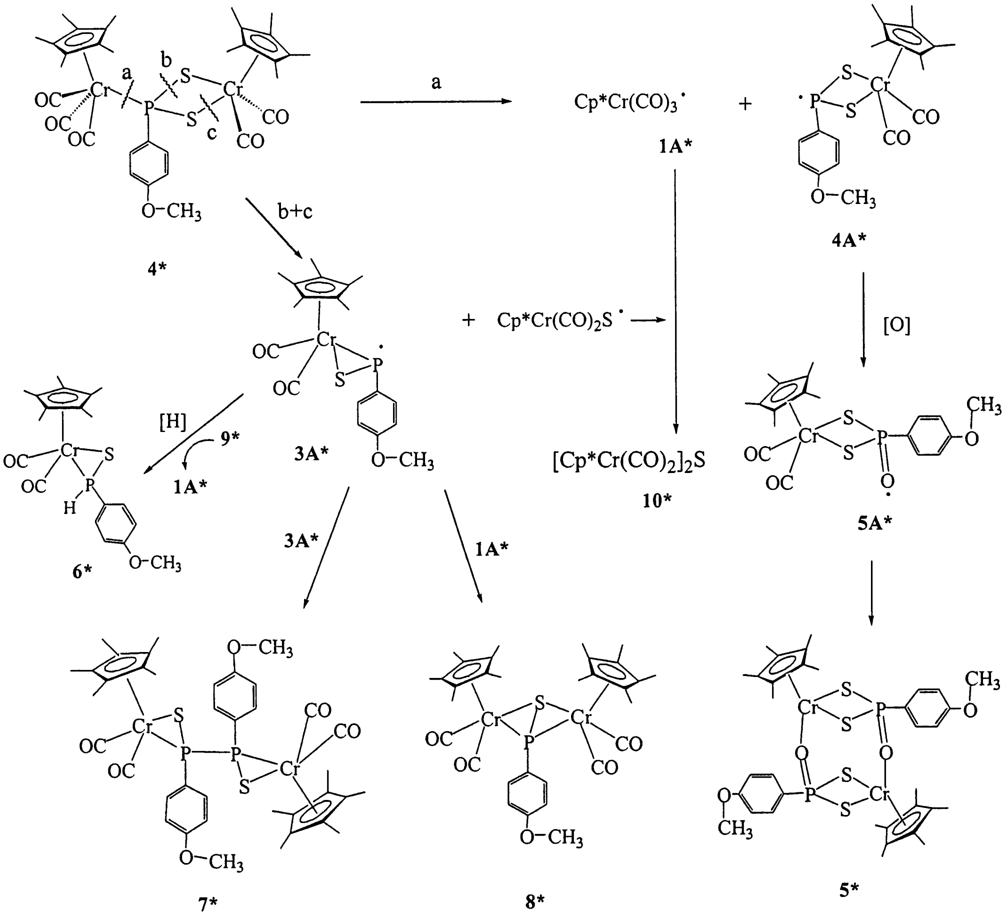
[16] Alvarez, M. A.; Garcia, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1324.

Scheme 2[a]



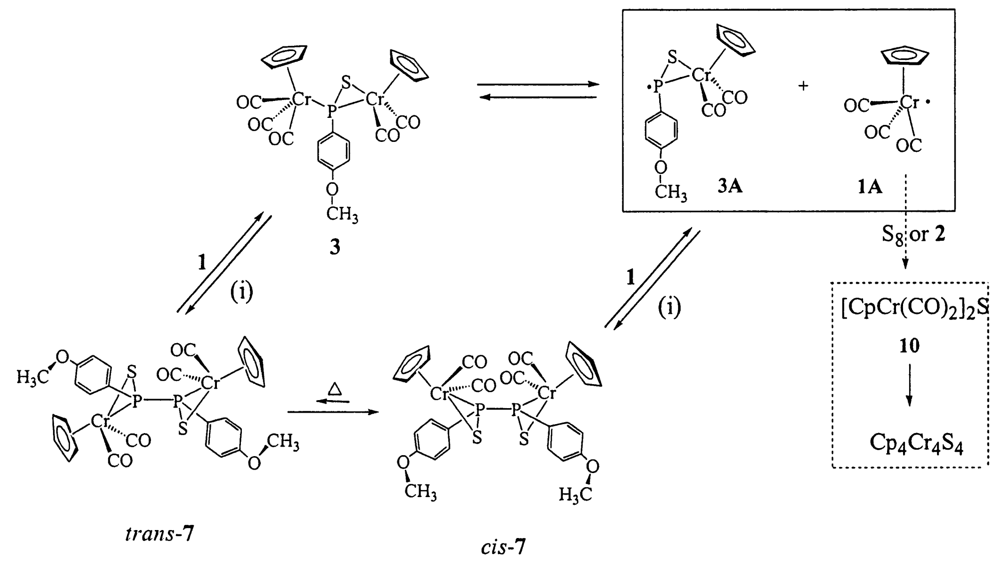
[a] Legend: Ar = $C_6H_4OCH_3$; [\] = bond cleavage.

Scheme 3[a]



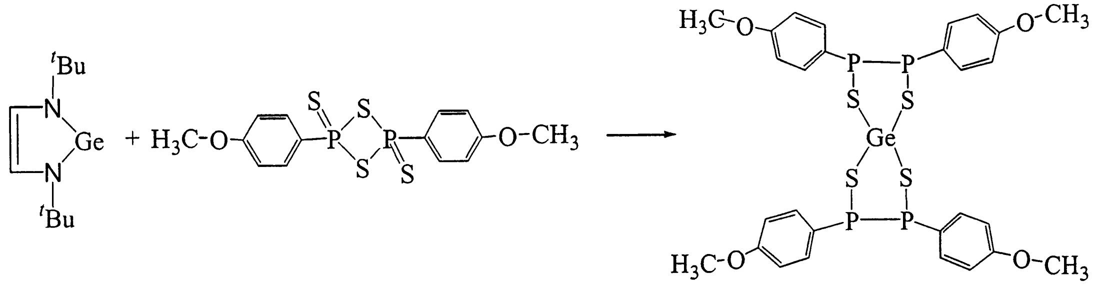
[a] Routes a–c are bond scissions.

Scheme 4[a]



[a] Legend: (i) Δ, S_8 or **2**.

Scheme 5



envisaged that coupling of the latter with **1A*** accompanied by loss of a CO ligand will yield **10***, while it is possible for **3A*** to generate **7***, **8***, and **6*** by dimerization via P−P coupling, coupling with **1A***, and abstraction of H from a hydrogen source, respectively. This source is likely to be $Cp^*Cr(CO)_3H$ (**9***), which is also one of the products in this reaction, considering that it was demonstrated experimentally that a deuteride analogue of **6*** was not formed from a thermolytic reaction in benzene-d_6 or toluene-d_8, thus ruling out abstraction of D (or H) from solvent. As mentioned above, in the absence of oxygen or water, the most probable source of O in the O-containing eight-membered metallacyclic complex **5*** seems to be a carbonyl ligand of the P-centered radical **4A***.

The low yield of **3** from the ambient-temperature reaction, together with its noticeable absence among the products from the reaction at 90 °C, and also from the ambient-temperature reaction of $[Cp^*Cr(CO)_3]_2$, points to its thermal lability. Indeed, this was confirmed by NMR-tube reactions in C_6D_6, which showed that **3** thermally degraded or reacted with S_8 or Lawesson's reagent at ambient temperature, giving *cis*-**7** (12−15%), **10** (ca. 8%), and a trace amount of $Cp_4Cr_4S_4$; it was also demonstrated that *cis*- or *trans*-**7** can be transformed back to **3** with 80% conversion by interaction with **1** for 40 min at 80 °C. In addition, it was observed that *cis*- or *trans*-**7** in solution reached a 4:1 equilibrium mixture after 40 min at 80 °C. These interconversions, as presented in Scheme 4, explain the variation of products with reaction temperatures and the preponderance of isolated *cis*-**7** over *trans*-**7**.

Although **7** may be considered as a dimer of **6** with H_2 elimination, an NMR-tube reaction showed that heating **6** for 2 h in refluxing toluene-d_8 gave only $Cp_4Cr_4S_4$ (ca. 13% yield) and other insoluble noncharacterizable compounds. It is probable that the formation of **7** is initiated by a homolytic cleavage of a Cr−P bond in **3**, generating $CpCr(CO)_3^\bullet$ (**1A**) and the phosphinothioylidene radical **3A**, which then undergoes P−P bond coupling to give **7**. This proposition is supported by (i) the reversal of the transformation by addition of **1**, and (ii) the *ambient-temperature* facilitation of the process by elemental sulfur or Lawesson's reagent, which as effective scavengers for **1A** drives the reaction toward formation of **7**. We noted that Cowley et al. had recently reported the only other case of P−P coupling in a reaction involving **2**, as illustrated in Scheme 5.[2h]

Under such thermolytic conditions, **1** will also undergo decarbonylation to $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$.[17] The reactivity of the latter complex with **2** was therefore investigated; an NMR tube reaction in benzene-d_6 demonstrated that reaction was complete after 30 min at 80 °C, producing mainly **5**, **6**, and **9**.

Properties and Spectral Characteristics. In the solid state, **3**, **4***, **5**−**7**, and **8*** are stable in air for a few hours, while **4** is unstable in air or argon. In solution,

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[17] Hackett, P.; O'Neill, P. S.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1625.

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

	3	**4**	**4***	**5**	**5***
		Bond Lengths (Å)			
Cr(1)−P(1)	2.3391(17)				
Cr(2)−P(1)	2.4722(17)	2.451(2)	2.4400(15)		
Cr(1)−S(1)	2.466(2)	2.472(3)	2.4901(14)	2.3723(15)	2.3862(10)
Cr(1)−S(2)		2.477(3)	2.4882(13)	2.3758(15)	2.3951(10)
Cr(1)−O(11A)				1.959(3)	1.989(3)
P(1)−S(1)	2.025(2)	2.034(3)	2.0441(15)	2.0338(18)	2.0346(12)
P(1)−S(2)		2.029(3)	2.0403(16)	2.0288(18)	2.0343(12)
P(1)−O(11)				1.509(4)	1.523(3)
P(1)−C(31)	1.848(6)	1.824(9)	1.828(4)	1.795(5)	1.789(4)
C(34)−O(34)	1.362(7)	1.387(11)	1.373(5)	1.361(6)	1.353(4)
C(37)−O(34)	1.414(10)	1.409(14)	1.407(5)	1.425(7)	1.427(5)
		Bond Angles (deg)			
S(1)−Cr(1)−S(2)		78.80(8)	77.57(4)	83.99(5)	83.47(3)
P(1)−S(1)−Cr(1)	61.85(6)	87.56(10)	85.99(6)	85.03(6)	85.37(4)
P(1)−S(2)−Cr(1)		87.54(10)	86.12(5)	85.05(6)	85.14(4)
Cr(1)−P(1)−Cr(2)	131.64(7)				
C(31)−P(1)−S(2)		107.9(3)	106.26(16)	109.39(17)	109.65(12)
C(31)−P(1)−S(1)	108.5(2)	108.6(3)	106.68(15)	109.40(17)	108.21(12)
S(2)−P(1)−S(1)		101.28(13)	99.54(7)	102.88(7)	102.94(5)
C(31)−P(1)−Cr(2)	108.13(18)	111.2(3)	107.46(14)		
S(1)−P(1)−Cr(2)	116.06(8)	113.93(11)	117.83(7)		
S(2)−P(1)−Cr(2)		113.29(12)	118.03(6)		
O(1A)−Cr(1)−S(1)				100.10(11)	97.70(8)
O(1A)−Cr(1)−S(2)				98.27(12)	98.88(8)
O(1)−P(1)−C(31)				105.7(2)	105.26(15)
O(1)−P(1)−S(1)				114.27(16)	115.12(11)
O(1)−P(1)−S(2)				115.11(16)	115.51(11)
P(1)−O(1)−Cr(1A)				144.9(2)	145.05(16)
C(34)−O(34)−C(37)	120.2(6)	118.4(9)	117.7(4)	118.9(4)	118.0(3)

3, **5**, **6/6***, and **7** remain unchanged for 30 min in air, but **4/4*** and **8*** are very air-sensitive.

Except for the paramagnetic 32-electron Cr(III) compounds **5** and **5***, all the others are diamagnetic 18-electron (mononuclear) or 36-electron (dinuclear) Cr(II) compounds. The NMR spectra of complex **3** show Cp proton resonances at δ 4.29 and 4.21 and ^{13}C resonances at δ 94.1 and 91.4, consistent with the molecular structure, which possesses Cp rings in different molecular environments. The ^{31}P signal is seen at δ 74.7. Likewise, **4/4*** each possess two Cp resonances in the ^{1}H NMR spectrum (**4**, δ 4.60 and 4.53; **4***, δ 1.78 and 1.52) and in the ^{13}C NMR spectrum (**4**, δ 95.5 and 95.0; **4***, δ 11.2 and 10.2 (Me), δ 105.4 and 103.9 for the ring C's). A single ^{31}P signal is seen at δ 169.1. The arylthioxophosphane complexes **6/6*** possess the Cp/Cp*-(Me) resonances at δ 4.33 and 1.58, respectively, in the ^{1}H NMR spectrum and at δ 90.2, and 10.8, 101.6, respectively, in the ^{13}C NMR spectrum. The PH proton resonances are found at δ 5.89 for **6** and δ 5.40 for **6***, with strong coupling to the P atom (J = 403 Hz for **6**; J = 384 Hz for **6***). The complexes *cis*-**7** and *trans*-**7** both display equivalent Cp resonances which are observed at δ 4.12 and 4.31, respectively, in the ^{1}H NMR spectrum and δ 91.0 for both in the ^{13}C NMR spectrum. The ^{31}P signal is observed at δ 80.3 for *cis*-**7** and δ 85.2 for *trans*-**7**.

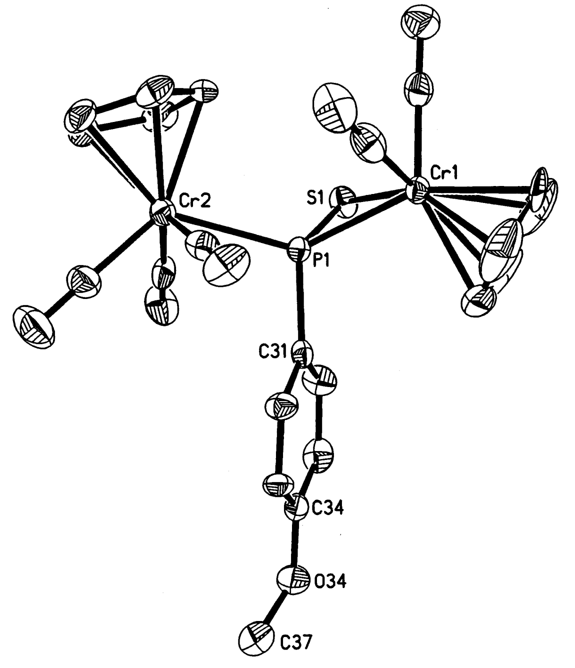

Figure 1. Molecular structure of **3** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

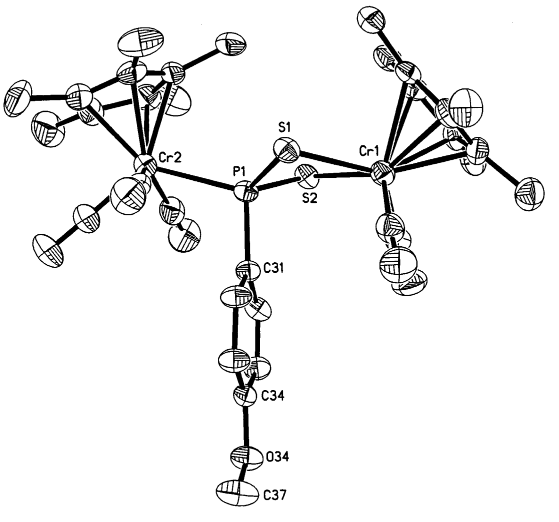

Figure 2. Molecular structure of **4*** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

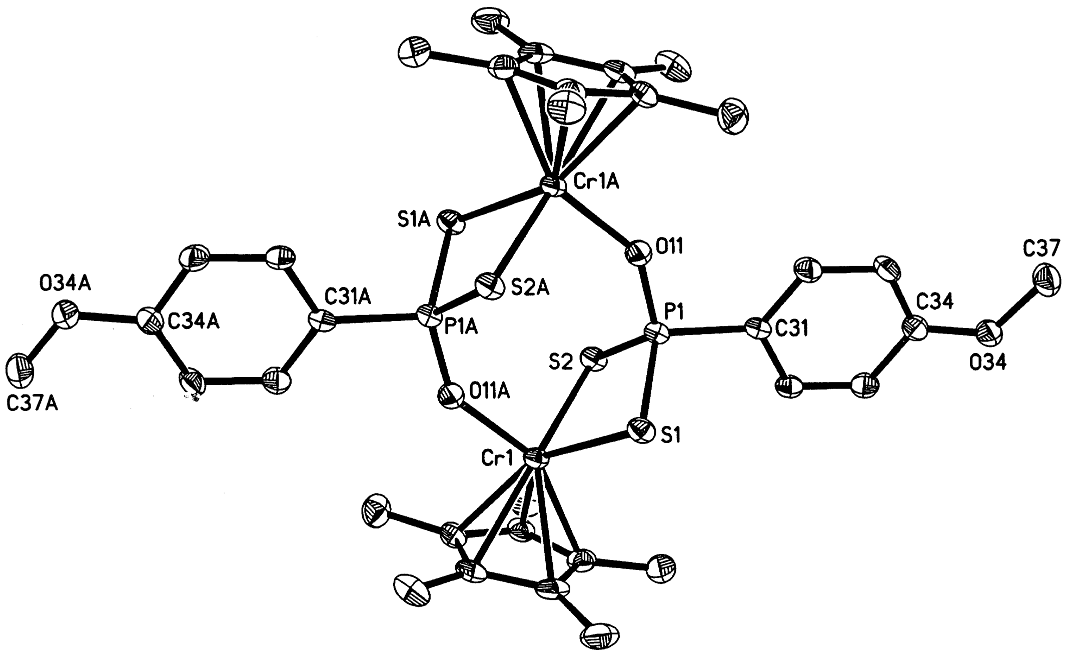

Figure 3. Molecular structure of **5*** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6−8*

	6	6*	*cis*-7	*trans*-7	8*
			Bond Lengths (Å)		
Cr(1)−P(1)	2.2607(8)	2.2704(11)	2.2699(8)	2.2730(13)	2.3681(18)
Cr(2)−P(1)					2.3753(19)
Cr(1)−S(1)	2.5116(8)	2.5079(12)	2.5207(8)	2.4962(15)	2.5001(18)
Cr(2)−S(1)					2.4900(17)
P(1)−S(1)	2.0093(11)	2.0021(14)	2.0024(9)	2.0003(15)	2.031(2)
P(1)−P(1A)			2.2097(13)	2.219(2)	
P(1)−C(8)	1.794(3)	1.805(4)	1.803(2)	1.809(4)	1.814(6)
C(11)−O(3)	1.361(4)	1.364(5)	1.365(3)	1.369(5)	1.369(8)
C(14)−O(3)	1.420(5)	1.422(5)	1.423(3)	1.423(6)	1.421(8)
			Bond Angles (deg)		
P(1)−Cr(1)−S(1)	49.46(3)	49.24(4)	49.07(2)	49.32(4)	49.23(5)
P(1)−Cr(2)−S(1)					49.28(5)
Cr(1)−S(1)−Cr(2)					104.44(6)
P(1)−S(1)−Cr(1)	58.76(3)	59.19(4)	58.92(3)	59.52(5)	62.00(6)
P(1)−S(1)−Cr(2)					62.42(6)
S(1)−P(1)−Cr(1)	71.78(3)	71.57(5)	72.01(3)	71.16(5)	68.77(7)
S(1)−P(1)−Cr(2)					68.30(7)
Cr(1)−P(1)−Cr(2)					112.50(7)
C(8)−P(1)−S(1)	116.18(10)	115.21(14)	116.25(8)	114.71(14)	111.4(2)
C(8)−P(1)−Cr(1)	130.32(9)	126.16(13)	123.84(8)	128.91(13)	122.1(2)
C(8)−P(1)−Cr(2)					121.0(2)
C(8)−P(1)−P(1A)			104.77(8)	104.20(14)	
S(1)−P(1)−P(1A)			108.22(5)	110.65(6)	
P(1A)−P(1)−Cr(1)			126.05(5)	121.50(6)	
C(11)−O(3)−C(14)	118.5(3)	118.1(3)	117.8(2)	118.0(4)	116.6(5)

The carbonyl stretching frequencies in the infrared spectrum in complexes **3**, **4**, **4***, **6**, **6***, *cis*-**7**, *trans*-**7**, and **8*** are observed in the range for terminal carbonyls.

Crystal Structures. The molecular structures of all the isolated complexes have been determined. The ORTEP diagrams for **3**, **4***, **5**, **6**, *cis*-**7** and *trans*-**7**, and **8*** are shown in Figures 1−6, respectively. Selected bond parameters of the complexes **3**−**5** and **6**−**8*** are given in Tables 3 and 4, respectively.

The structure of the molecule of **3** (Figure 1) contains a phosphinothioylidene ligand bridging two $CpCr(CO)_n$ ($n = 2$, 3) moieties. Except for the absence of a Cr−Cr bond, the structure resembles closely that of the Mo complex $Cp_2Mo_2(CO)_4(SPAr)$.[2a] The two Cr−P bond distances (2.3391(17) and 2.4722(17) Å) are significantly different, the shorter being for Cr(1)−P(1), which are also bridged by a S ligand. The Cr−S bond (2.466(2) Å) is slightly shorter than that (2.5155(7) Å) in the complex $CpCr(CO)_2(SPMe_2)$.[7b] The P−S bond distance (2.025(2) Å) shows some double-bond character (P=S = 1.926(1)−1.966(2) Å; P−S = 2.122(1) Å).[18]

The structures of the molecules of **4** and **4*** are similar; the ORTEP diagram of **4*** is shown in Figure 2. The molecule contains a bridging dithiophosphorane ligand, being η^2(S,S′) coordinated to a $Cp^*Cr(CO)_2$ moiety and η^1(P) coordinated to a $Cp^*Cr(CO)_3$ moiety. The Cr−P bond length (2.4400(15) Å) falls between

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(18) (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 Roode, J. H. G. *Can. J. Chem.* **1977**, *55*, 3081.

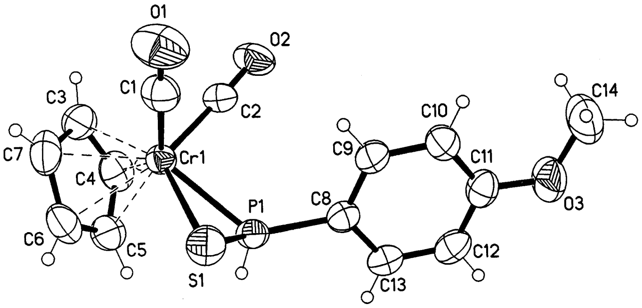

Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level.

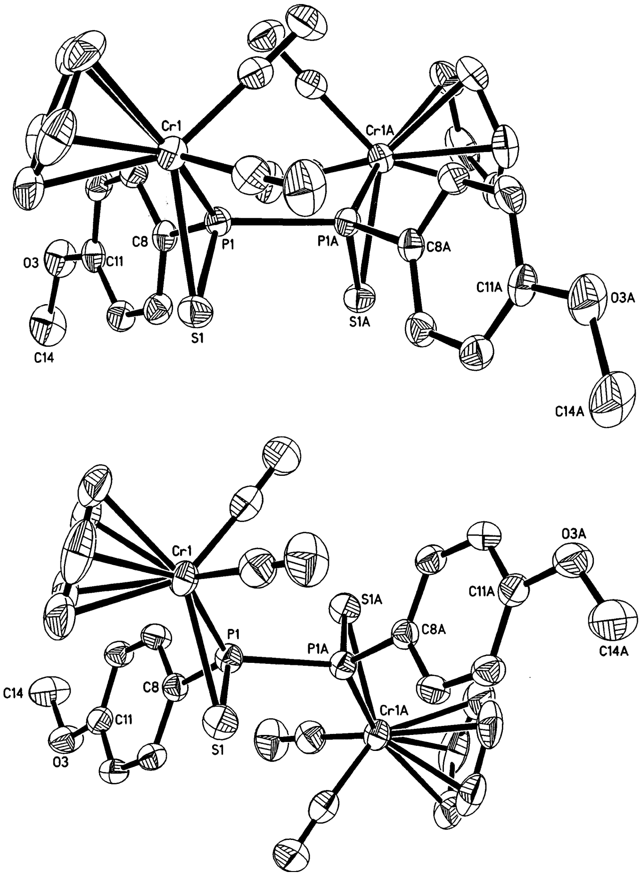

Figure 5. Molecular structures of *cis*- and *trans*-**7** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

those of the corresponding bonds in **3**. The two Cr−S bond distances (2.4901(14) and 2.4882(13) Å) are very close but longer than that in **3**. The two P−S bond distances (2.0441(15) and 2.0403(16) Å) are also very similar.

The molecular structures of **5** and **5*** (Figure 3) are analogous, containing an eight-membered ring, comprised of two Cp/Cp*Cr and two [$S_2P(O)Ar$] moieties, with a center of symmetry in the center of the ring. The two Cr(1)−S(1) and Cr(1)−S(2) bond lengths (2.3862(10) and 2.3951(10) Å, respectively) are almost equivalent, as are the two P(1)−S(1) and P(1)−S(2) bond lengths (2.0346(12) and 2.0343(12) Å, respectively). The P−O bond possesses double-bond character, its bond length (1.523(3) Å) being comparable with the P═O distance (1.56 Å) found in PO_4^{3-}.[19] The Cr(1)−O(11A) bond length (1.989(3) Å) is comparable with those found in the double-cubane complex $Cp_6Cr_8S_4(OH)(SN(C_6H_4))_2(SNC_2(C_6H_4))_2$ (2.085(5) and 2.079(4) Å).[7a]

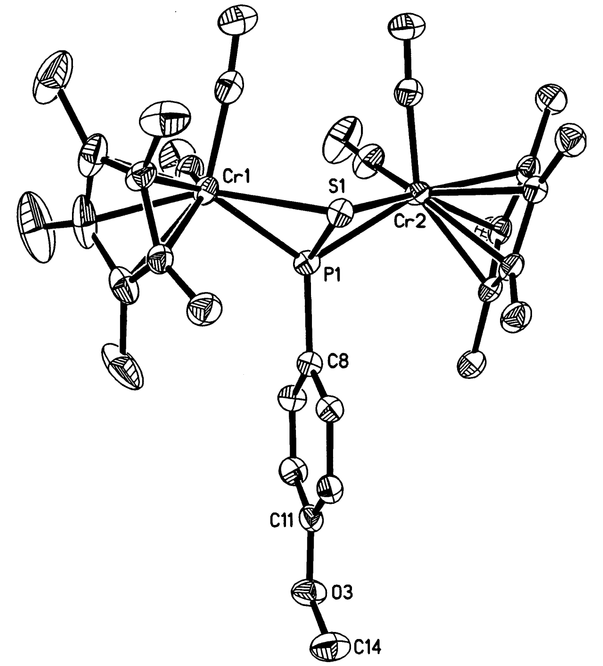

Figure 6. Molecular structure of **8*** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

The analogous structures of **6** (Figure 4) and **6*** each contain a Cp/Cp*Cr moiety bonded to two CO groups and a η^2-arylthioxophosphane ligand, which is rarely encountered; the only example that we found in the literature is in the complex $[Os(\eta^2\text{-}SP(H)Me)(CO)_2(PPh_3)_2]^+$, obtained by methylation of $[Os(\eta^2\text{-}SPH)(CO)_2(PPh_3)_2]$ by Roper et al.[20] The Cr−P bond (2.2607(8) Å in **6** and 2.2704(11) Å in **6***) is comparable to those of η^2-thiophosphinito complexes $CpCr(CO)_2(SPR_2)$ (R = Me, 2.2704(6) Å; R = Et, 2.2738(18) Å) that we have previously reported.[7b] However, it is significantly shorter than those of **3** (2.3391(17) and 2.4722(17) Å). The Cr−S bond distances (2.5116(8) Å in **6** and 2.5079(12) Å in **6***) are indicative of a single Cr−S bond. The P−S bond distance (2.0093(11) Å in **6** and 2.0021(14) Å in **6***) lies between that of a P−S and a P═S bond.[18]

The molecular structures of **7** (Figure 5) reveal a bridging P−P bond, with cis and trans orientations of the $CpCr(CO)_2$ moieties and different conformations of the bridging [$-SPAr]_2$ ligand. The P−P bond (2.2097(13) Å in *cis*-**7** and 2.219(2) Å in *trans*-**7**) is comparable to that of $[(SPAr)_2]_2Ge$ (2.220(2) Å),[2h] the only other known compound possessing a similar P−P-bonded component from Lawesson's reagent. The Cr−S bond (2.5207(8) Å in *cis*-**7** and 2.4962(15) Å in *trans*-**7**), Cr−P bond (2.2699(8) Å in *cis*-**7** and 2.2730(13) Å in *trans*-**7**), and P−S bond (2.0024(9) Å in *cis*-**7** and 2.0003(15) Å in *trans*-**7**) are similar to those found in **6**, indicating that the P−P bond in the SPAr ligand does not have any significant effect on the corresponding bond parameters of these complexes.

In the molecular structure of **8*** (Figure 6), a η^4-phosphinothioylidene ligand bridges two $Cp^*Cr(CO)_2$

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

[20] Bohle, D. S.; Rickard, C. E. F.; Roper, W. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 302.

units. The two Cr−P bond distances (2.3681(18) and 2.3753(19) Å) are significantly longer than those found in **6** and **7**, while the Cr−S bond distances (2.5001(18) and 2.4900(17) Å) are comparable. The P−S bond distance (2.031(2) Å) shows no significant difference from those found in **6** and **7**.

Conclusion

The 17-electron Cp/Cp*Cr(CO)$_3^\bullet$ species has reacted with Lawesson's reagent or its monomer unit to generate the primary products **3** and **4**. A diverse mixture of complexes was obtained from secondary thermolytic and/or Cp/Cp*Cr(CO)$_3^\bullet$-initiated homolytic cleavage of P−S, Cr−P, and Cr−S bonds, followed by radical coupling and hydrogen and oxygen abstraction reactions.

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Supporting Information Available: For structures of **3**, **4**, **4***, **5**, **5***, **6**, **6***, *cis*-**7**, *trans*-**7**, and **8***, complete listings of bond lengths and angles, ORTEP diagrams, and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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