Syntheses, Structures, and Reactions of η^6 Complexes of Iridathiabenzene with Chromium, Molybdenum, and Tungsten Carbonyls

Jiabi Chen,[†] Victor G. Young, Jr., and Robert J. Angelici*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011
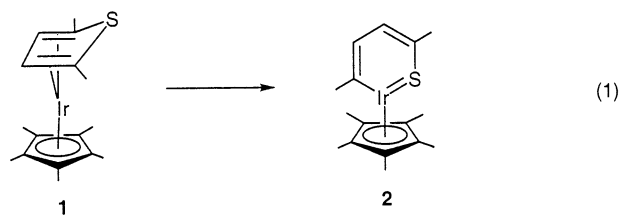
The iridathiabenzene analogues [η^6-Cp*Ir(C,S-2,5-Me₂T)]M(CO)₃, where M = Cr (**3**), Mo (**5**), W (**7**), of (η^6-arene)M(CO)₃ are prepared from M(CO)₃(NCMe)₃ and Cp*Ir(C,S-2,5-Me₂T) (**2**), where C,S-2,5-Me₂T is ring-opened 2,5-dimethylthiophene. The high reactivity and coordination flexibility of the η^6-Cp*Ir(C,S-2,5-Me₂T) ligand leads to a variety of products upon reaction with phosphine ligands. The reaction of **3** with PEt₃ leads to PEt₃ adduct formation at the Ir in the product [η^5-Cp*Ir(PEt₃)(C,S-2,5-Me₂T)][Cr(CO)₃] (**17**). On the other hand, reaction of the analogous tungsten complex **7** with PEt₃ yields the adduct [η^4-Cp*Ir(C,S-2,5-Me₂T)]W(CO)₂(PEt₃)(μ-CO) (**19**), in which PEt₃ adds to the W atom. These and other studies show that the iridathiabenzene ligand is capable of coordination to Cr, Mo, or W through one, four, five, or six of its ring atoms. When **7** is reacted with CF₃SO₃H, protonation occurs at the tungsten, as occurs in the protonation of the analogous arene complex (η^6-C₆Me₆)W(CO)₃. Structures of four of the complexes were established by X-ray studies.

Introduction

Among the many novel compounds generated in reactions of thiophenes with transition-metal complexes[1,2] are those that have been described as metallathiabenzenes **A** (Chart 1). The presence of a delocalized π-system in these complexes, analogous to that in arenes, is supported by experimental[3−5] and theoretical[6] studies. Complexes of this type have been reported for the following L$_x$M fragments: (η^5-C₅Me₅)Ir,[3] [MeC(CH₂-PPh₂)₃]Ir⁺,[7] (Et₃P)₃Ir⁺,[5] and (Et₃P)₂Pt.[8] Some of these complexes have substituents on one or more of the carbon atoms in the six-membered ring. Although not isolated, related (η^5-C₅Me₅)Rh complexes have been detected spectroscopically in solution.[9,10]

Our studies of these types of complexes have focused on Cp*Ir(C,S-2,5-Me₂T) (**2**).[11] It is prepared by reducing Cp*Ir(C,S-2,5-Me₂T)²⁺ to give Cp*Ir(η^4-2,5,Me₂T) (**1**), which rearranges (eq 1) to **2** thermally or more rapidly

$$\text{(1)}$$

in the presence of base or ultraviolet light.[3,11] In an earlier communication,[12] we showed that the iridathiabenzene unit in **2** forms π-complexes when reacted with M(CO)₃(NCMe)₃, where M = Cr, Mo, W. The resulting [η^6-Cp*Ir(C,S-2,5-Me₂T)]M(CO)₃ complexes have structures in which the six-membered ring of **2** is η^6-coordinated to the M(CO)₃ fragment. A similar complex, [η^6-Cp*Ir(C,S-2,5-Me₂T)]FeCp⁺, is formed when **2** reacts with (η^6-ClC₆H₅)FeCp⁺.[12] The only other metallathiabenzene complex reported to give an η^6 complex of type **B** (Chart 1) is (Et₃P)₃Ir(C,S-3,4-Me₂T)⁺.[5,13] Its reaction with (η^6-xylene)Mo(CO)₃ gives [η^6-(Et₃P)₃Ir(C,S-3,4-Me₂T)]Mo(CO)₃⁺.

In principle, metallathiabenzene complexes **A** can coordinate to metals in ways other than η^6. In fact, modes **C**−**E** (Chart 1) are also known. Mode **C** is found in [η^4-(CO)₃Fe(C,S-2-MeT)]Fe(CO)₃,[14] [η^4-(CO)(Et₃P)₂Ir-(C,S-3,4-Me₂T)]Mo(CO)₂(PMe₃)₂⁺,[5] [η^4-Cp*Co(C,S-T)]-

† Permanent address: Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, People's Republic of China.

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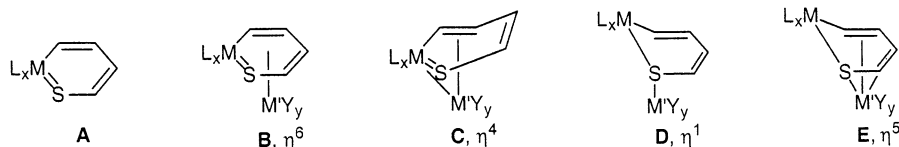(10) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9851.

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Chart 1

CoCp*,[15a] $[\eta^4\text{-Cp*Rh(C,S-Me}_4\text{T)]RhCp*}$,[15b] and $[\eta^4\text{-}$(R$_2$PCH$_2$CH$_2$PR$_2$)Ni(C,S-T)]Ni(R$_2$PCH$_2$CH$_2$PR$_2$).[16] Only one example of a complex of type **D**, Cp*Ir[C,S-2,5-Me$_2$T·W(CO)$_5$](CO), has been reported.[17] Examples of mode **E** are found in $[\eta^5\text{-(CO)}_4\text{M(C,S-2,5-Me}_2\text{T)]M(CO)}_3$, where M = Mn[18,19] Re,[20] and $[\eta^5\text{-(Ph}_3\text{P)}_2\text{Pt(C,S-2,5-Me}_2\text{T)]Mn(CO)}_3{}^+$.[21]

In the present paper, we give full details of the syntheses of the $[\eta^6\text{-Cp*Ir(C,S-2,5-Me}_2\text{T)]M(CO)}_3$ complexes, where M = Cr, Mo, W, and their reactions with a variety of Lewis bases (ligands) and Lewis acids. These reactions give a range of products, including examples of complexes with structural types **B**–**E** (Chart 1).

Experimental Section

General Procedure. All reactions were performed under an N$_2$ atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and were dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N$_2$ prior to use. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were distilled from sodium benzophenone ketyl, while hexanes and CH$_2$Cl$_2$ were distilled from CaH$_2$. The neutral Al$_2$O$_3$ (Brockmann, activity I, 80–100 mesh) used for chromatography was deoxygenated under vacuum at room temperature for 16 h, deactivated with 5% (w/w) N$_2$-saturated water, and stored under N$_2$, while neutral SiO$_2$ (60–200 mesh) was deoxygenated under vacuum at room temperature for 12 h. Columns were 1.5 × 5–15 cm. The compounds PEt$_3$, Me$_2$S, Cp$_2$Fe$^+$BF$_4^-$, maleic anhydride, Me$_3$NO·2H$_2$O, HgCl$_2$, and CF$_3$SO$_3$H were purchased from Aldrich Chemical Co., Eastman Kodak Co., or 3M Industrial Chemical Products Division. The complexes Cp*Ir(η^4-2,5-Me$_2$T) (**1**), Cp*Ir(C,S-2,5-Me$_2$T) (**2**), and [Cp*Ir(η^5-2,5-Me$_2$T)](BF$_4$)$_2$ (**10**) were prepared as previously described.[3] Mo(CO)$_3$(CH$_3$CN)$_3$,[22] W(CO)$_3$-(CH$_3$CN)$_3$,[22] Cr(CO)$_3$(CH$_3$CN)$_3$,[23] (η^6-C$_6$H$_5$CH$_3$)Mo(CO)$_3$,[24] Mo(CO)$_3$(THF)$_3$,[24a] (η^6-C$_6$H$_5$CH$_3$)W(CO)$_3$,[25] Na$_2$[Mo$_2$(CO)$_{10}$],[26] and Cp*Ir(CO)(PMe$_3$)[27] were prepared by literature methods. All elemental analyses were performed by Galbraith Labora-

tory, Inc., or National Chemical Consulting, Inc. The IR spectra were measured on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates. All ^{1}H NMR spectra were recorded at ambient temperature in CDCl$_3$ solution with CHCl$_3$ as an internal reference using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were run on a Finnigan 4500 spectrometer at 70 eV. The melting points were recorded in sealed nitrogen-filled capillaries and are uncorrected.

Reaction of 1 with Cr(CO)$_3$(NCCH$_3$)$_3$ To Give [η^6-Cp*Ir-(C,S-2,5-Me$_2$T)]Cr(CO)$_3$ (3) and Cp*Ir(η^4-2,5-Me$_2$T·Cr(CO)$_3$-(NCCH$_3$)$_2$) (4). To a stirred, light yellow solution of **1** (0.050 g, 0.114 mmol) in THF (30 mL) at approximately −60 °C was added 0.036 g (0.139 mmol) of fresh Cr(CO)$_3$(NCCH$_3$)$_3$. Immediately the solution became gold-yellow. The reaction solution was stirred at −60 to −10 °C for 8 h, during which time the gold-yellow solution turned purple. The solvent was then removed in vacuo to give a dark purple residue. This residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. The purple band which eluted first was collected, and then a yellow band was eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (10:1:1) and collected. After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C. From the first fraction, 0.020 g (31%, based on **1**) of dark purple crystalline **3** was obtained (mp 183–184 °C dec). IR (hexanes): ν(CO) 1950(vs), 1893 (s), 1880 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.86 (d, 1H), 5.46 (d, 1H), 2.72 (s, 3H), 2.52 (s, 3H), 2.07 (s, 15H). MS: m/e 576 (M$^+$). Anal. Calcd for C$_{19}$H$_{23}$O$_3$SIrCr: C, 39.64; H, 4.03. Found: C, 39.00; H, 3.98. From the second fraction, 0.034 g (45%, based on **1**) of bright yellow crystals of **4** was obtained (mp 170–171 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1988 (s), 1875 (vs, br), 1836 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.47 (s, 2H), 1.95 (s, 6H, CH$_3$CN), 1.92 (s, 15H), 1.28 (s, 6H). MS: m/e 576 (M$^+$ − 2CH$_3$CN), 492 (M$^+$ − 2CH$_3$CN − 3CO). Anal. Calcd for C$_{23}$H$_{29}$O$_3$N$_2$SIrCr: C, 41.99; H, 4.44. Found: C, 41.30; H, 4.43.

Reaction of 2 with Cr(CO)$_3$(NCCH$_3$)$_3$ To Give 3. A solution of **2** (0.030 g, 0.068 mmol) in THF (30 mL) was cooled to −70 °C. Fresh Cr(CO)$_3$(NCCH$_3$)$_3$ (0.023 g, 0.089 mmol) was then added. Immediately the red solution turned purple-red. The mixture was stirred at −70 to −60 °C for 5 h. The resulting dark purple solution was evaporated under vacuum to dryness. Further treatment of the residue as described above gave 0.036 g (92%, based on **2**) of dark purple crystals of **3**, which was identified by its melting point and IR, ^{1}H NMR, and MS spectra.

Reaction of 1 with Mo(CO)$_3$(NCCH$_3$)$_3$ To Give [η^6-Cp*Ir(C,S-2,5-Me$_2$T)]Mo(CO)$_3$ (5) and Cp*Ir(η^4-2,5-Me$_2$T·Mo(CO)$_3$(NCCH$_3$)$_2$) (6). To 0.040 g (0.091 mmol) of **1** dissolved in 30 mL of THF at −50 °C was added 0.035 g (0.115 mmol) of freshly prepared Mo(CO)$_3$(NCCH$_3$)$_3$. The mixture was stirred at −30 to −10 °C for 12 h, during which time the light yellow solution turned gradually from gold-yellow to purple-red. After the solution was evaporated in vacuo to dryness, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. The purple band which eluted first was collected, and then the yellow band was eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C. From the first fraction, 0.027 g (48%, based on **1**) of dark purple crystals of **5** was obtained (mp 188–189 °C dec). IR (hexanes): ν(CO) 1957 (vs), 1894 (s),

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1880 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 6.00 (d, 1H), 5.81 (d, 1H), 2.69 (s, 3H), 2.54 (s, 3H), 2.06 (s, 15H). MS: *m/e* 622 (M⁺, based on ⁹⁸Mo). From the second fraction, 0.026 g (41%, based on **1**) of yellow crystals of **6** was obtained (mp 170−172 °C dec). IR (CH₂Cl₂): ν(CO) 2003 (s), 1890 (vs, br), 1838 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 4.45 (s, 2H), 1.94 (s, 6H, NCCH₃), 1.92 (s, 15H), 1.24 (s, 6H). MS: *m/e* (based on ⁹⁸Mo) 622 (M⁺ − 2CH₃CN), 536 (M⁺ − 2CH₃CN − 3CO). Anal. Calcd for C₂₃H₂₉O₃N₂-SIrMo: C, 39.36; H, 4.17. Found: C, 39.80; H, 4.20.

Reaction of 2 with Mo(CO)₃(NCCH₃)₃ To Give 5. To a solution of 0.030 g (0.068 mmol) of **2** dissolved in 30 mL of THF at −55 °C was added fresh Mo(CO)₃(NCCH₃)₃ (0.024 g, 0.079 mmol). The reaction mixture was stirred at −55 to −40 °C for 3 h, during which time the solution turned from red to purple. After the solution was evaporated in vacuo, subsequent treatment of the resulting residue as described above for the reaction of **1** with Mo(CO)₃(NCCH₃)₃ gave 0.039 g (93%, based on **2**) of **5**, which was identified by its melting point and ¹H NMR spectrum.

Reaction of 1 with W(CO)₃(NCCH₃)₃ To Give [η⁶-Cp*Ir-(C,S-2,5-Me₂T)]W(CO)₃ (7) and Cp*Ir[η⁴-2,5-Me₂T·W(CO)₃-(NCCH₃)₂] (8). In 30 mL of THF at −50 °C was dissolved 0.040 g (0.091 mmol) of **1**. To this solution was added 0.042 g (0.107 mmol) of fresh W(CO)₃(NCCH₃)₃. The reaction solution was stirred at −5 to 15 °C for 16 h, during which time the light yellow solution turned purple-red gradually. After vacuum removal of the solvent, the resulting residue was chromatographed on Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (10:1) as the eluant. The purple band which eluted first was collected; then the yellow band was eluted with hexanes/CH₂Cl₂/Et₂O (10:1:1). After the solvents were evaporated from the above two eluates, the crude products were recrystallized from hexanes/CH₂Cl₂ at −80 °C. From the first fraction, 0.033 g (51%, based on **1**) of dark purple crystals of **7** was obtained (mp 194−195 °C dec). IR (hexanes): ν(CO) 1955 (vs), 1888 (s), 1878 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 5.89 (d, 1H), 5.81 (d, 1H), 2.83 (s, 3H), 2.72 (s, 3H), 2.05 (s, 15H). MS: *m/e* 708 (M⁺, based on ¹⁸⁴W). Anal. Calcd for C₁₉H₂₃O₃SIrW: C, 32.25; H, 3.28. Found: C, 32.68; H, 3.21. From the second fraction, 0.020 g (28%, based on **1**) of **8** as yellow crystals was obtained (mp 195−196 °C dec). IR (CH₂Cl₂): ν(CO) 1998 (s), 1883 (vs, br), 1832 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 4.44 (s, 2H), 1.95 (s, 6H, NCCH₃), 1.93 (s, 15H), 1.25 (s, 6H). MS: *m/e* (based on ¹⁸⁴W) 708 (M⁺ − 2CH₃CN), 624 (M⁺ − 2CH₃CN − 3CO). Anal. Calcd for C₂₃H₂₉O₃N₂SIrW: C, 34.98; H, 3.70. Found: C, 34.49; H, 3.51.

Reaction of 2 with W(CO)₃(NCCH₃)₃ To Give 7. A solution of **2** (0.030 g, 0.068 mmol) in THF (30 mL) was treated with W(CO)₃(NCCH₃)₃ (0.032 g, 0.082 mmol) at −50 to −15 °C for 8 h, during which time the red solution turned purple-red to dark purple. The resulting mixture was evaporated under vacuum to dryness. Further treatment of the resulting residue as described above for the reaction of **1** with W(CO)₃-(NCCH₃)₃ gave 0.044 g (92%, based on **2**) of dark purple crystalline **7**, which was identified by its melting point and IR, ¹H NMR, and MS spectra.

Thermolysis of 6 To Give 2 and 5. A solution of **6** (0.020 g, 0.028 mmol) in 15 mL of THF was refluxed for 4 h, during which time the yellow solution turned gradually purple. After evaporation of the solvent in vacuo, the residue was chromatographed on Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (10:1) as the eluant. A red band eluted first. This was followed by a purple band which eluted with hexanes/CH₂Cl₂/Et₂O (15:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes or hexanes/CH₂Cl₂ at −80 °C. From the first fraction, 0.004 g (33%) of **2** was obtained, which was identified by its melting point and ¹H NMR spectrum. From the second fraction, 0.008 g (44%) of purple crystals of **5** was obtained, which was identified by its melting point and IR and ¹H NMR spectra.

Photolysis of 6 To Give 2 and 5. A solution of **6** (0.020 g, 0.028 mmol) in THF (10 mL) in a quartz photolysis tube was photolyzed with a 450 W, 254 nm mercury lamp over a period of 6 h. During this time the yellow solution gradually turned purple-red. After vacuum removal of the solvent, the residue was worked up as described for the thermolysis of **6** to give 0.004 g (33%) of **2** and 0.010 g (55%) of **5**.

Thermolysis of 8 To Give 2 and 7. Similar to the thermolysis of **6**, a solution of **8** (0.025 g, 0.032 mmol) in THF (15 mL) was refluxed for 4 h. After the solvent was evaporated, further treatment of the residue as described above for the thermolysis of **6** afforded 0.003 g (25%) of **2** and 0.015 g (69%) of **7**, which were identified by their melting points and IR and ¹H NMR spectra.

Photolysis of 8 To Give 2 and 7. As in the photolysis of **6** above, a solution of **8** (0.015 g, 0.019 mmol) in 15 mL of THF was photolyzed for 6 h. The resulting solution was worked up as described for the thermolysis of **6** to give 0.003 g (38%) of **2** and 0.007 g (54%) of **7**.

Reaction of 1 with Mo(CO)₃(THF)₃ To Give 5 and Cp*Ir[η⁴-2,5-Me₂T·Mo(CO)₃(THF)₂] (9). A solution of 0.030 g (0.110 mmol) of (η⁶-C₆H₅CH₃)Mo(CO)₃ in 30 mL of THF at −50 °C was treated with 0.040 g (0.091 mmol) of **1**. While being stirred at −30 °C, the solution turned from light yellow to light gold-yellow. The mixture was stirred at −30 to 5 °C for 15 h, during which time the solution turned gradually purple-red. The solvent was evaporated under vacuum, and the dark purple residue was chromatographed on Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (10:1) as the eluant. A purple band eluted first; then a yellow band was eluted with hexanes/CH₂Cl₂/Et₂O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH₂Cl₂ at −80 °C. From the purple fraction, 0.029 g (52%, based on **1**) of **5** was obtained. From the yellow fraction, 0.023 g (33%, based on **1**) of yellow crystals of **9** were obtained (mp 178−180 °C dec). IR (CH₂Cl₂): ν(CO) 2003 (s), 1890 (vs), 1838 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 4.45 (s, 2H), 3.70 (m, 8H), 1.92 (s, 15H), 1.81 (m, 8H), 1.24 (s, 6H). MS: *m/e* 622 (M⁺ − 2THF).

Reaction of 2 with Mo(CO)₃(THF)₃ To Give 5. Using the same procedure above, a solution of (η⁶-C₆H₅CH₃)Mo(CO)₃ (0.028 g, 0.103 mmol) in 30 mL of THF was treated with **2** (0.035 g, 0.080 mmol) at −60 °C. The mixture was stirred at −60 to −10 °C for 6 h, during which time the red solution turned purple-red to purple. Workup as described above gave 0.045 g (92%, based on **2**) of **5**, which was identified by its melting point and IR and ¹H NMR spectra.

Reaction of 2 with (η⁶-C₆H₅CH₃)Mo(CO)₃ To Give 5. To a stirred, red solution of **2** (0.025 g, 0.057 mmol) in 20 mL of hexanes at room temperature was added 0.018 g (0.066 mmol) of (η⁶-C₆H₅CH₃)Mo(CO)₃. The reaction mixture was stirred at room temperature for 6 h, during which time the solution turned gradually from red to purple. After removal of the solvent in vacuo, the dark purple residue was chromatographed on Al₂O₃ (neutral) with hexanes/CH₂Cl₂ (10:1) as the eluant. The purple band was eluted and collected. The solvent was removed under vacuum, and the dark purple crude product was recrystallized from hexanes/CH₂Cl at −80 °C to give 0.033 g (94%, based on **2**) of **5**.

Reaction of 2 with (η⁶-C₆H₅CH₃)W(CO)₃ To Give 7. A solution of 0.010 g (0.023 mmol) of **2** and 0.010 g (0.028 mmol) of (η⁶-C₆H₅CH₃)W(CO)₃ dissolved in 20 mL of hexanes in a quartz photolysis tube was photolyzed with a 450 W, 254 nm lamp for 12 h, during which time the red solution gradually turned purple. The solvent was removed under vacuum. Further treatment of the resulting residue as described in the reaction of **2** with (η⁶-C₆H₅CH₃)Mo(CO)₃ gave 0.010 g (62%, based on **2**) of **7**.

Reaction of [Cp*Ir(η⁵-2,5-Me₂T)](BF₄)₂ (10) with Na₂[Mo₂(CO)₁₀] To Give Cp*[η⁴-2,5-Me₂T·Mo(CO)₅] (11) and 5. To compound **10** (0.390 g, 0.630 mmol) dissolved in 30 mL of THF at 0 °C was added Na₂[Mo₂(CO)₁₀] (0.330 g, 0.637 mmol). While being stirred at 0−15 °C, the solution gradually turned from light yellow to dark yellow. After 48 h, the solvent

was evaporated under vacuum, and the dark residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. The yellow band which eluted first was collected; then the purple band was eluted with hexanes/CH$_2$Cl$_2$ (5:1). After removal of the solvents in vacuo from the above eluates, the residues were recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C. From the first fraction, 0.295 g (69%, based on **10**) of **11** as light yellow crystals was obtained (mp 134−136 °C dec). IR (hexanes): ν(CO) 2065 (m), 1941 (vs), 1929 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.51 (s, 2H), 1.94 (s, 15H), 1.25 (s, 6H). MS: *m/e* 678 (M$^+$, based on ^{98}Mo). Anal. Calcd for C$_{21}$H$_{23}$O$_5$-SIrMo: C, 37.33; H, 3.43. Found: C, 37.20; H, 3.50. From the second fraction, 0.082 g (21%, based on **10**) of **5** was obtained.

Photolysis of 11 To Give Cp*Ir[(CO)(C,S-2,5-Me$_2$T)(Mo-(CO)$_5$)] (12), 5, and Cp*Ir(CO)(C,S-2,5-Me$_2$T) (13). (A) Photolysis of 11 for 6 h. A solution of 0.030 g (0.044 mmol) of **3** dissolved in 20 mL of THF in a quartz photolysis tube was photolyzed with a 450 W, 245 nm lamp for 6 h, during which time the light yellow solution gradually turned from red to purple-red. The solvent was removed under vacuum, and the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (15:1) as the eluant. The yellow band which eluted first was collected; then the purple band was eluted with hexanes/CH$_2$Cl$_2$ (10:1). After vacuum removal of the solvent from the above two eluates, the residues were recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C. From the yellow fraction, 0.008 g (25%) of yellow crystals of **12** was obtained (mp 116−118 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 2089 (m), 2011 (s), 1935 (vs, br), 1888 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.78 (d, 1H), 5.68 (d, 1H), 2.34 (s, 3H), 1.89 (s, 3H), 1.87 (s, 15H). MS: *m/e* (based on ^{98}Mo) 706 (M$^+$), 622 (M$^+$ − 3CO), 538 (M$^+$ − 6CO). Anal. Calcd for C$_{22}$H$_{23}$O$_6$SIrMo: C, 37.55; H, 3.29. Found: C, 37.0; H, 3.32. From the purple fraction, 0.019 g (68%) of **5** was obtained.

(B) Photolysis of 11 for 12 h. A solution of 0.080 g (0.118 mmol) of **11** was photolyzed for 12 h. After the solvent was removed under vacuum, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (15:1) as the eluant. The yellow band which eluted first contained 0.012 g (14%) of **12**; then a purple band that eluted with hexanes/CH$_2$Cl$_2$ (10:1) contained 0.026 g (36%) of **5**. Finally, a dark orange band was eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (10:1:1) and gave 0.010 g (18%) of orange crystals of previously reported **13**[4] (mp 121−122 °C dec). IR (hexanes): ν(CO) 2020 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.79 (d, 1H), 5.45 (d, 1H), 2.29 (s, 3H), 1.97 (s, 3H), 1.88 (s, 15H). MS: *m/e* 468 (M$^+$), 440 (M$^+$ − CO).

Thermolysis of 11 To Give 2 and 5. A solution of **11** (0.080 g, 0.118 mmol) in THF (20 mL) was refluxed for 5 h, during which time the light yellow solution gradually turned purple. After evaporation of the solvent in vacuo, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes, which eluted 0.005 g (10%) of **2**. This was followed by a purple band containing 0.061 g (84%) of **5** that eluted with hexanes/CH$_2$Cl$_2$ (10:1).

Photolysis of 5 To Give 2. A solution of 0.015 g (0.024 mmol) of **5** dissolved in 20 mL of THF in a quartz photolysis tube was photolyzed with a 450 W, 254 nm lamp for 10 h. Chromatography of the reaction mixture on Al$_2$O$_3$ (neutral) with hexanes and recrystallization at −80 °C gave 0.004 g (36%) of **2**.

The analogous photolysis of **7** (0.015 g, 0.021 mmol) in 15 mL of THF for 12 h gave 0.005 g (56%) of **2**.

Reaction of 2 with PEt$_3$ To Give Cp*Ir(PEt$_3$)(C,S-2,5-Me$_2$T) (18). To a solution of **2** (0.100 g, 0.22 mmol) in hexanes (30 mL) was added PEt$_3$ (0.27 g, 2.28 mmol) at −50 °C with stirring. The mixture was stirred at −50 to −20 °C for 3 h, during which time the red solution turned orange-yellow. The solvent was evaporated under vacuum, and the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes first and then hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. The eluted yellow band was evaporated under vacuum, and the residue was

recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C to yield 0.105 g (83%, based on **2**) of orange-yellow crystals of **18** (mp 163−165 °C dec). ^{1}H NMR (CDCl$_3$): δ 5.78 (d, 1H), 5.36 (d, 1H), 2.18 (s, 3H), 1.87 (s, 3H), 1.72 (s, 15H), 2.09−1.77 (m, 6H), 1.06−0.93 (m, 9H). MS: *m/e* 558 (M$^+$). Anal. Calcd for C$_{22}$H$_{38}$-SPIr: C, 47.37; H, 6.87. Found: C, 47.25; H, 6.60.

Reaction of 18 with Mo(CO)$_3$(NCMe)$_3$ To Give [η^5-Cp*Ir(PEt$_3$)(C,S-2,5-Me$_2$T)][Mo(CO)$_3$] (20). To a stirred, yellow solution of **18** (0.030 g, 0.054 mmol) dissolved in THF (20 mL) at −50 °C was added 0.035 g (0.11 mmol) of Mo(CO)$_3$-(NCMe)$_3$. The reaction mixture was stirred at −50 to −20 °C for 4 h, during which time the yellow solution turned bright red. After vacuum removal of the solvent, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. The red band was collected. The solvent was evaporated in vacuo, and the residue was recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C to afford 0.031 g (78%, based on **18**) of light red crystals of **20** (mp 143−145 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1915 (vs), 1820 (s), 1806 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.04 (d, 1H), 4.07 (d, 1H), 2.43 (m, 3H), 2.29 (s, 3H), 2.02 (m, 3H), 1.80 (s, 3H), 1.65 (s, 15H), 1.06 (m, 9H). MS: *m/e* 738 (M$^+$). Anal. Calcd for C$_{25}$H$_{28}$O$_3$SPIrMo: C, 40.70; H, 3.83. Found: C, 39.94; H, 3.89.

Reaction of 18 with W(CO)$_3$(NCMe)$_3$ To Give [η^5-Cp*Ir-(PEt$_3$)(C,S-2,5-Me$_2$T)][W(CO)$_3$] (21). As described for the reaction of **18** with Mo(CO)$_3$(NCMe)$_3$, **18** (0.023 g, 0.041 mmol) reacted with W(CO)$_3$(NCMe)$_3$ (0.032 g, 0.082 mmol) at −20 to −10 °C for 4 h, during which time the yellow solution turned bright red. After vacuum removal of the solvent, further treatment of the residue as described above for **20** gave 0.022 g (65%, based on **18**) of **21** as bright red crystals (mp 122−124 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1917 (vs), 1826 (s), 1805 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.84 (d, 1H), 4.34 (d, 1H), 2.46 (s, 3H), 2.44−2.31 (m, 3H), 2.05−1.94 (m, 3H), 1.83 (s, 3H), 1.68 (s, 15H), 1.13−0.98 (m, 9H). MS: *m/e* 558 (M$^+$ − W(CO)$_3$). Anal. Calcd for C$_{25}$H$_{28}$O$_3$SPIrW: C, 36.37; H, 4.64. Found: C, 36.52; H, 4.32.

Reaction of 3 with PEt$_3$ To Give 18 and [η^5-Cp*Ir-(PEt$_3$)(C,S-2,5-Me$_2$T)][Cr(CO)$_3$] (17). To a stirred, purple solution of **3** (0.025 g, 0.043 mmol) in THF (20 mL) at −30 °C was added 0.020 g (0.169 mmol) of PEt$_3$. The reaction solution was stirred at −10 to 10 °C for 12 h, during which time the purple solution turned gradually purple-red. After evaporation of the solvent under vacuum, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (15:1) as the eluant. The orange band which eluted first was collected; then the purple-red band was eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (15:1:1). After vacuum removal of the solvent from the above two eluates, the residues were recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C. From the first fraction was obtained 0.008 g (33%, based on **3**) of orange-yellow crystals of **18**, which was identified by its melting point and ^{1}H NMR and MS spectra. From the second fraction, 0.010 g (33%, based on **3**) of purple-red crystals of **17** was obtained (mp 122−124 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1935 (m), 1915 (vs), 1820 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.46 (d, 1H), 4.04 (d, 1H), 2.72 (s, 3H), 2.52 (s, 3H), 2.07 (s, 15H), 1.92−1.80 (m, 6H), 1.11−0.81 (m, 9H). MS: *m/e* 576 (M$^+$ − PEt$_3$), 520 (M$^+$ − PEt$_3$ − 2CO), 492 (M$^+$ − PEt$_3$ − 3CO). Anal. Calcd for C$_{25}$H$_{38}$O$_3$SPIrCr: C, 43.28; H, 5.52. Found: C, 42.84; H, 6.00.

Reaction of 7 with PEt$_3$ To Give [η^4-Cp*Ir(C,S-2,5-Me$_2$T)][W(CO)$_2$(PEt$_3$)](μ-CO) (19). Similar to the reaction of **3** with PEt$_3$, 0.015 g (0.021 mmol) of **7** and 0.015 g (0.127 mmol) of PEt$_3$ were allowed to react with stirring at −5 to 10 °C for 6 h, during which time the purple solution turned gradually to bright red. After removal of the solvent in vacuo, the red residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (15:1) as the eluant. The red band was collected. The solvent was removed, and the crude product was recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C to yield 0.014 g (82%, based on **7**) of bright red crystals of **19** (mp 131−132 °C

dec). IR (hexanes): ν(CO) 1953 (vs), 1861 (s), 1838 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.36 (d, 1H), 4.60 (d, 1H), 2.60 (s, 3H), 2.18 (s, 3H), 1.99 (s, 15H), 1.88−1.78 (m, 6H), 1.19−0.96 (m, 9H). MS: m/e 826 (M$^+$), 742 (M$^+$ − 3CO). Anal. Calcd for C$_{25}$H$_{38}$O$_3$SPIrW: C, 36.37; H, 4.64. Found: C, 36.81; H, 4.88.

Reaction of 3 with Cp*Ir(CO)(PMe$_3$) To Give [Cp*Ir-(C,S-2,5-Me$_2$T)][Cp*Ir(CO)]Cr(CO)$_3$ (23). To a stirred solution of **3** (0.030 g, 0.052 mmol) in THF (20 mL) was added 0.030 g (0.070 mmol) of Cp*Ir(CO)(PMe$_3$). After the mixture was stirred for 48 h at room temperature, the solvent was removed under vacuum and the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. After unreacted **3** was eluted (purple band), a black band was eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (1:2:1) and collected. The solvent was removed, and the residue was recrystallized from CH$_2$Cl$_2$/hexanes at −80 °C to yield 0.012 g (25%, based on **3**) of black crystalline **23** (mp 183−185 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 2028 (s), 1947 (vs), 1885 (s), 1818 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.52 (d, 1H), 3.32 (d, 1H), 2.83 (s, 3H), 1.84 (s, 15H), 1.75 (s, 15H), 1.73 (s, 3H). MS: m/e 902 (M$^+$ − CO), 846 (M$^+$ − 3CO), 818 (M$^+$ − 4CO). Anal. Calcd for C$_{30}$H$_{38}$O$_4$SIr$_2$Cr: C, 38.70; H, 4.11. Found: C, 38.89; H, 4.46.

Reaction of 3 with Me$_2$S To Give 2 and Cp*Ir[η^4-SC-(Me)CHCHC(=O)Me] (22). To 0.040 g (0.069 mmol) of **3** dissolved in 30 mL of THF was added 0.040 g (0.050 mL, 0.64 mmol) of Me$_2$S. The solution was stirred at room temperature for 4 days. After vacuum removal of the solvent, the residue was chromatographed on Al$_2$O$_3$ (neutral) with hexanes/CH$_2$Cl$_2$ (10:1) as the eluant. After an orange-red band was eluted and collected, a purple band containing **3** was eluted with hexanes/CH$_2$Cl$_2$ (5:1). A yellow band was then eluted with hexanes/CH$_2$Cl$_2$/Et$_2$O (5:1:1). The first and third eluates were evaporated to dryness, and the residues were recrystallized from hexanes or hexanes/CH$_2$Cl$_2$ solution at −80 °C. From the first fraction, 0.006 g (20%, based on **3**) of **2** was obtained. From the yellow fraction, 0.010 g (32%, based on **3**) of yellow crystalline **22**[28] was obtained (mp 131−132 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1655 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.67 (d, 1H), 2.63 (d, 1H), 2.27 (s, 3H), 2.03 (s, 3H), 1.86 (s, 15H). MS: m/e 456 (M$^+$).

Reaction of 3 with 1 To Give 2 and 22. Compound **3** (0.040 g, 0.069 mmol) in 20 mL of THF reacted with 0.032 g (0.073 mmol) of **1** as described in the reaction of **3** with Me$_2$S for 3 days to yield 0.008 g (26%, based on **3**) of **2** and 0.009 g (28%, based on **3**) of **22**.

Reaction of 3 with HgCl$_2$ To Give Cp*Ir(C,S-2,5-Me$_2$T)-[Cr(CO)$_3$](HgCl$_2$) (25). To compound **3** (0.030 g, 0.052 mmol) dissolved in 20 mL of THF at −40 °C was added 0.020 g (0.074 mmol) of HgCl$_2$. The reaction mixture was stirred at −40 to 0 °C for 12 h, during which time the purple solution turned gradually light purple. After evaporation of the solution in vacuo, the purple-red residue was recrystallized from THF/hexanes or acetone/hexanes solution at −80 °C to give 0.035 g (80%, based on **3**) of **25** as brick red crystals (mp 188−189 °C dec). IR (acetone): ν(CO) 2144 (m), 1950 (m), 1915 (vs) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.34 (d, 1H), 5.88 (d, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.96 (s, 15H). MS: m/e 820 (M$^+$ − CO), 722 (M$^+$ − 2CO −2Cl). Anal. Calcd for C$_{19}$H$_{23}$O$_3$Cl$_2$SIrCrHg: C, 26.94; H, 2.74. Found: C, 27.33; H, 2.60.

Reaction of 7 with HgCl$_2$ To Give Cp*Ir(C,S-2,5-Me$_2$T)-[W(CO)$_3$](HgCl$_2$) (26). Compound **7** (0.030 g, 0.042 mmol) reacted with HgCl$_2$ (0.015 g, 0.055 mmol) at −40 to −30 °C for 4 h. Subsequent treatment as described for **25** gave 0.028 g (68%, based on **7**) of brick red crystals of **26** (mp 163−165 °C dec). IR (acetone): ν(CO) 2144 (vs, br), 1999 (m), 1978 (m) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): 6.86 (d, 1H), 4.70 (d, 1H), 2.64 (s, 3H), 2.59 (s, 3H), 2.23 (s, 15H). MS: m/e 954 (M$^+$ − 2CO − 2Cl), 752 (M$^+$ −2CO− HgCl$_2$). Anal. Calcd for C$_{19}$H$_{23}$O$_3$Cl$_2$-SIrWHg: C, 23.31; H, 2.37. Found: C, 22.92; H, 2.45.

(28) Chen, J.; Su, Y.-Z.; Angelici, R. J. *J. Organomet. Chem.* **1996**, *512*, 149.

Reaction of 7 with CF$_3$SO$_3$H To Give [{η^6-Cp*Ir(C,S-2,5-Me$_2$T}W(CO)$_3$H](CF$_3$SO$_3$) (24). To a solution of **7** (0.025 g, 0.035 mmol) in CH$_2$Cl$_2$ (15 mL) at −30 °C was added 0.006 g (0.004 mL, 0.040 mmol) of CF$_3$SO$_3$H. The purple solution immediately turned dark green. After the mixture was stirred at −30 to −20 °C for 1 h, the solvent was evaporated under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/hexanes at −80 °C to give 0.020 g (67%, based on **7**) of orange-red crystals of **24** (mp 82−84 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 2062 (m), 2033 (vs), 1935 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.47 (d, 1H), 5.34 (d, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 1.96 (s, 15H), −11.08 (s, 1H). MS: m/e 857 (M$^+$ − H), 706 (M$^+$ − H − CF$_3$SO$_3$). Anal. Calcd for C$_{20}$H$_{24}$O$_6$S$_2$F$_3$IrW: C, 28.01; H, 2.82. Found: C, 27.85; H, 2.94.

Reaction of 7 with Cp$_2$Fe$^+$BF$_4^-$ To Give [{η^6-Cp*Ir(C,S-2,5-Me$_2$T}W(CO)$_3$]$_2$(BF$_4$)$_2$ (27). To a stirred, purple solution of **7** (0.030 g, 0.042 mmol) in CH$_2$Cl$_2$ (30 mL) at −35 °C was added 0.015 g (0.055 mmol) of Cp$_2$Fe$^+$BF$_4^-$. The mixture was stirred at −35 to −5 °C for 4 h, during which time the purple solution turned gradually purple-red. After evaporation of the solvent in vacuo, the residue was washed with Et$_2$O (15 mL) and then hexanes (15 mL) and recrystallized from hexanes/CH$_2$Cl$_2$ at −80 °C to give 0.023 g (72%, based on **7**) of black crystals of **27** (mp 96−98 °C dec). IR (CH$_2$Cl$_2$): ν(CO) 1997 (vs, br), 1936 (vs), 1856 (s, br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.28 (d, 2H), 3.73 (d, 2H), 2.84 (s, 6H), 2.72 (s, 6H), 2.12 (s, 30H). MS: m/e 707 (M$^+$ − 2BF$_4$ − Cp*Ir(C,S-2,5-Me$_2$T)W(CO)$_3$]. Anal. Calcd for C$_{38}$H$_{46}$O$_6$S$_2$B$_2$F$_8$IrW$_2$: C, 30.39; H, 3.09. Found: C, 30.63; H, 2.97.

X-ray Crystal Structure Determinations of Complexes 11, 12, 17, and 19. Single crystals of complexes **11**, **12**, **17**, and **19** suitable for X-ray diffraction study were obtained by recrystallization from hexanes or hexanes/CH$_2$Cl$_2$ solution at −80 °C. The single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for **11**, **12**, **17**, and **19** were collected with a Siemens P4RA or an Enraf-Nonius CAD4 diffractometer.

The structures of **11**, **12**, **17**, and **19** were solved by direct methods. For the four complexes, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined as riding atoms with C−H distances of 0.96 Å with individual (arene and methylene) or group (methyl) isotropic displacement parameters. All the calculations were performed on Digital Equipment Corp. Micro VAX3100 computer using the SHELXTL-Plus programs.

Details of the crystallographic data and the procedures used for data collection and reduction for complexes **11, 12, 17,** and **19** are given in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structures for the complexes are presented in Figures 1−4, respectively.

Results and Discussion

Synthetic Routes to [η^6-Cp*Ir(C,S-2,5-Me$_2$T)]M-(CO)$_3$, Where M = Cr (3), Mo (5), W (7). The highest-yield route (>90%) to these complexes is the previously communicated[12] reaction (eq 2) of the ring-opened **2** with M(CO)$_3$(NCMe)$_3$ below room temperature. The X-ray-
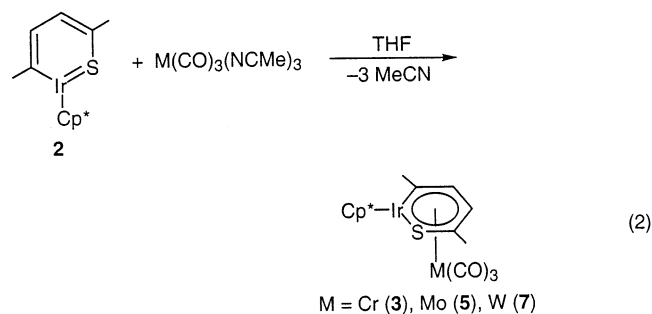

$$M = Cr\ (3),\ Mo\ (5),\ W\ (7) \tag{2}$$

Table 1. Crystal Data and Experimental Details for Complexes 11, 12, 17, and 19

	11[a]	12[a]	17[b]	19[a]
formula	$C_{21}H_{23}O_5SIrMo$	$C_{22}H_{23}O_6SIrMo$	$C_{25}H_{38}O_3PSIrCr$	$C_{25}H_{38}O_3PSIrW$
fw	675.6	703.6	693.78	825.6
space group	$C2/c$	$P2/n$	$P2_1/n$	$P2_1/n$
a (Å)	27.477(2)	23.864(4)	11.029(2)	9.2018(8)
b (Å)	9.747(1)	8.837(2)	13.686(2)	21.749(4)
c (Å)	20.205(2)	23.934(2)	18.143(3)	13.470(2)
β (deg)	116.61(1)	93.18(1)	104.47(1)	91.642(9)
V (Å³)	4836.5(9)	5039.6(10)	2651.7(8)	2694.6(6)
Z	8	8	4	4
d_{calcd} (g/cm³)	1.854	1.855	1.738	2.035
cryst size (mm)	$0.20 \times 0.14 \times 0.10$	$0.55 \times 0.07 \times 0.07$	$0.22 \times 0.18 \times 0.05$	$0.225 \times 0.03 \times 0.023$
abs coeff (mm⁻¹)	6.122	15.205	14.441	18.665
$F(000)$	2592	2704	1376	1576
radiation (monochromated in incident beam)	Mo Kα ($\lambda = 0.710\ 73$ Å)	Cu Kα ($\lambda = 1.541\ 78$ Å)	Cu Kα ($\lambda = 1.541\ 78$ Å)	Cu Kα ($\lambda = 1.541\ 78$ Å)
diffractometer	Enraf-Nonius CAD4	Siemens P4RA	Siemens P4RA	Siemens P4RA
temp (°C)	25	25	−60	−60
scan method	$\omega - 2\theta$	$2\theta - \theta$	$2\theta - \theta$	$2\theta - \theta$
data collecn range, 2θ (deg)	2.0−25.0	4.0−115.0	8.18−113.6	4.0−115.0
no. of unique data, total	4255	6763	3549	3595
no. of data with $F \geq 4.0\sigma(F)$	2803	5155	3117	3001
no. of params refined	271	578	320	308
correction factors: max−min	0.7153−0.9079	0.2781−0.8463	0.316−1.000	0.5159−0.9105
R^c	0.045	0.0312	0.0392	0.0308
$R_w{}^d$ (wR2)^e	0.056	0.0337	(0.0975)	0.0338
quality-of-fit indicator^f	0.94	0.95	1.035	1.11
largest shift/esd final cycle	0.002	0.002	0.001	0.001
max peak, e/Å³	2.01	0.57	2.260	1.49
min peak, e/Å³	−0.97	−0.85	−2.059	−1.26

^{a} Refined using SHELXL-Plus V4.0 (VMS), Siemens Analytical X-ray, Inc., 1990. ^{b} Refined using SHELXL-93. $^c R = \sum ||F_o| - |F_c||/ \sum |F_o|$. $^d R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{e} wR2 $= [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp + d + e(\sin \theta)]$. ^{f} Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

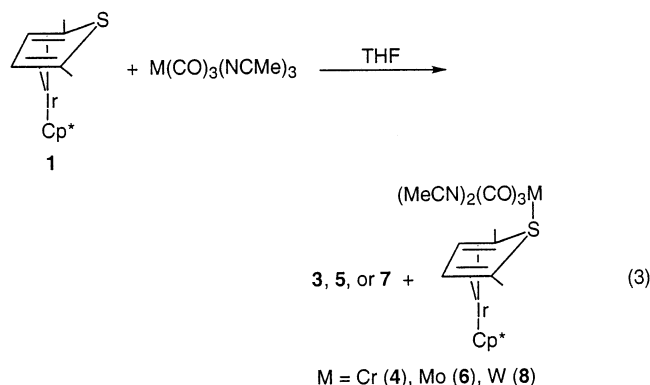## Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 11, 12, 17, and 19

	11 M = Mo	12 M = Mo	17 M = Cr	19 M = W		11 M = Mo	12 M = Mo	17 M = Cr	19 M = W
Ir−M				2.847(1)	C(2)−C(3)	1.43(2)	1.32(1)	1.37(1)	1.33(1)
Ir−S		2.369(2)	2.333(2)	2.342(2)	C(3)−C(4)	1.38(2)	1.45(1)	1.444(9)	1.46(1)
S−M	2.543(4)	2.582(2)	2.424(2)	2.530(2)	C(4)−C(5)	1.43(2)	1.33(2)	1.374(9)	1.41(1)
Ir−C(2)	2.10(1)				C(5)−C(6)	1.53(2)	1.51(1)	1.524(10)	1.53(1)
Ir−C(3)	2.09(1)				C(2)−M			2.167(6)	
Ir−C(4)	2.14(1)				C(3)−M			2.168(7)	
Ir−C(5)	2.13(1)	2.08(1)	2.075(6)	2.01(2)	C(4)−M			2.291(6)	2.475(8)
Ir−C(7)		1.84(1)			C(5)−M				2.405(8)
Ir−C(8)				2.590(8)	C(8)−M				1.998(9)
C(1)−C(2)	1.48(2)	1.50(1)	1.520(9)	1.51(1)	Ir−C(Cp*) (av)	2.199	2.247	2.264	2.215
S−Ir−M				57.4(1)	M−C(CO) (av)	2.026	2.001	1.823	1.978
S−Ir−C(5)		88.0(2)	84.0(2)	87.8(2)	Ir−C(5)−C(6)	127(1)	115.9(8)	117.1(6)	119.9(6)
M−Ir−C(5)				56.3(2)	S−C(2)−C(1)	118.7(16)	114.3(6)	116.5(5)	116.9(6)
Ir−S−M		119.9(1)	100.37(7)	71.4(1)	C(2)−S−M	113.2(4)	103.3(3)	60.0(2)	101.2(3)
Ir−S−C(2)		106.7(3)	114.9(2)	106.2(3)	C(5)−S−M	115.0(4)			
Ir−C(2)−C(1)	126(1)				S−Ir−C(7)		95.7(3)		
S−C(2)−C(3)	107(1)	121.6(7)	121.6(5)	118.5(7)	S−Ir−C(8)				91.8(2)
C(2)−C(3)−C(4)	111(2)	129(1)	124.1(7)	122.7(8)	C(5)−Ir−C(7)		89.9(4)		
C(3)−C(4)−C(5)	109(1)	130(1)	130.4(6)	126.3(8)	C(5)−Ir−C(8)				77.5(3)
C(4)−C(5)−Ir	70.5(9)	124.1(7)	129.5(5)	124.8(6)	Ir−M−P				140.8(1)
C(1)−C(2)−C(3)	126(2)	124.1(9)	121.8(6)	124.5(8)	Ir−M−C(8)				61.7(2)
C(4)−C(5)−C(6)	122(1)	120.0(9)	113.1(6)	115.2(7)	Ir−C(8)−M				75.5(3)
C(2)−S−C(5)	81.8(7)				M−Ir−C(8)				42.8(2)
S−C(5)−C(4)	109(1)								
S−C(5)−C(6)	119(1)								

^{a} Estimated standard deviations in the least significant figure are given in parentheses.

determined structure[12] of **5** shows all six atoms of the iridathiabenzene ring to lie in a plane bonded to the Mo atom. Bond distances within the six-membered ring of **5** are the same, within experimental error, as those in **2**. The ν(CO) values (in hexanes) of **5** (1957 vs, 1894 s, 1880 s cm⁻¹) are lower than those in (η^6-toluene)Mo-(CO)₃ (1985 vs, 1914 vs cm⁻¹), which indicates that the [η^6-Cp*Ir(C,S-2,5-Me₂T)] ligand is a stronger donor than η^6-toluene. The Cr (**3**) and W (**7**) complexes have the

same structure as **5**, as indicated by the similarity of their ¹H NMR spectra and ν(CO) bands in their IR spectra.

For a range of reactions,[11] both isomers, **1** and **2**, often react to give the same products because of the facile interconversion between **1** and **2**. When isomer **1** reacts (eq 3) with the M(CO)₃(NCMe)₃ complexes, two types of products are formed in significant amounts. One is the [η^6-Cp*Ir(C,S-2,5-Me₂T)] series of complexes, **3**, **5**,

$$\text{1} + M(CO)_3(NCMe)_3 \xrightarrow{\text{THF}}$$

$$\text{3, 5, or 7} + \quad \text{(MeCN)}_2\text{(CO)}_3\text{M} \qquad (3)$$

M = Cr (**4**), Mo (**6**), W (**8**)

and **7**, which are isolated as dark purple crystals in yields (31−51%) that are lower than those obtained from **2** (eq 2). These complexes obviously form as a result of the isomerization of **1** to **2**. The other type of product (**4**, **6**, and **8**), which was obtained as a yellow solid in 28 to 45% yield, results from the simple displacement of a MeCN ligand from the $M(CO)_3(NCMe)_3$ reactant. Although X-ray-quality crystals of these complexes were not obtained, their ^1H NMR spectra are typical of related S-adducts of **1**, including **1**·Fe(CO)$_4$, **1**·Re$_2$(CO)$_9$, and **1**·Ru$_3$(CO)$_{11}$.[11] For example, the equivalent methyl groups (δ 1.24 ppm) and ring hydrogens (δ 4.45 ppm) occur as singlets with chemical shifts that are very similar to those of other S-adducts.[11] The observation that all three of the ν(CO) bands for **4**, **6**, and **8** are of strong or very strong intensity, e.g., 2003 s, 1890 vs, and 1838 s cm^{-1} for **6**, indicates that the three CO ligands are mutually cis, rather than any pair of them being trans to each other. The singlet absorption for the MeCN ligands in the ^1H NMR spectra of the complexes is consistent with the facial arrangement of the CO ligands around the octahedral Cr, Mo, or W atom.

Although the formation of complexes **3**, **5**, and **7** in reaction 3 could occur by several pathways, one possibility is the rearrangement of **4**, **6**, and **8** with loss of two MeCN ligands. That this is not involved is established by the absence of this conversion under the below-room-temperature conditions of reaction 3. However, when **6** and **8** are refluxed in THF for 4 h, the η^6-Cp*(C,S-2,5-Me$_2$T) complexes, **5** and **7**, are obtained in 44−69% yield; the other product, **2**, is isolated in 25−33% yield. When **6** and **8** are photolyzed for 6 h in THF, **5** and **7** are obtained in 33−54% yield, while **2** is isolated in 33−38% yield.

Another high-yield (92%) route to **5**, similar to that (eq 2) using Mo(CO)$_3$(NCMe)$_3$, is the reaction of Mo(CO)$_3$(THF)$_3$ with **2** below room temperature. As for Mo(CO)$_3$(NCMe)$_3$, Mo(CO)$_3$(THF)$_3$ reacts with isomer **1** to give **5** (52% yield) and another product, **9**, whose IR and ^1H NMR spectra are fully consistent with the formulation Cp*Ir[η^4-2,5-Me$_2$T·Mo(CO)$_3$(THF)$_2$], the THF analogue of **6**; however, the instability of yellow **9** prevented a successful elemental analysis.

Although Mo(CO)$_3$(THF)$_3$ is prepared by simply dissolving (η^6-toluene)Mo(CO)$_3$ in THF,[24a] (η^6-toluene)Mo(CO)$_3$ itself reacts with **2** at room temperature over the course of 4 h to give a 94% yield of **5**. The analogous reaction of (η^6-toluene)W(CO)$_3$ with **2** does not occur under the same conditions. However, ultraviolet photolysis of this reaction mixture in hexanes solvent gives a 62% isolated yield of **7**.
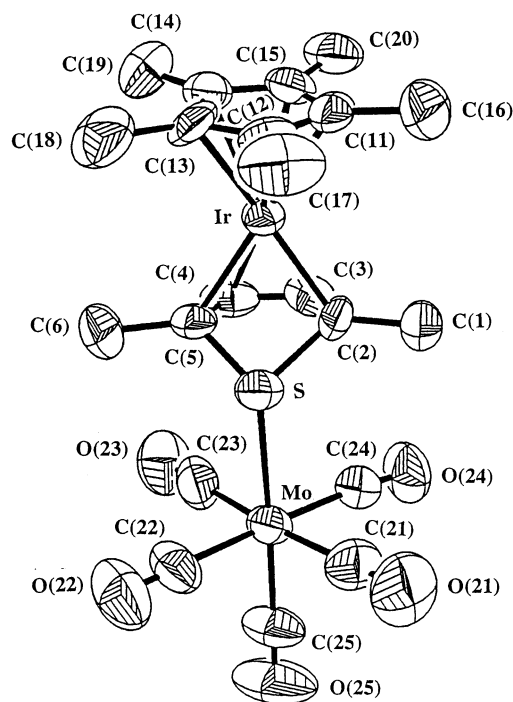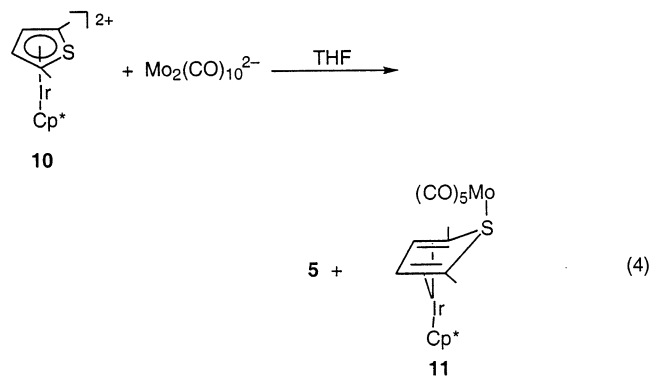

Figure 1. Molecular structure of Cp*[η^4-2,5-Me$_2$T·Mo(CO)$_5$] (**11**), showing the atom-numbering scheme.

In a totally different approach to the synthesis of **5**, [Cp*Ir(η^5-2,5-Me$_2$T)](BF$_4$)$_2$ (**10**) was reacted (eq 4) with Mo$_2$(CO)$_{10}{}^{2-}$ to give a relatively low yield of **5** (21%) but a much higher yield of light yellow **11** (69%). Both

$$\text{10} + Mo_2(CO)_{10}{}^{2-} \xrightarrow{\text{THF}}$$

$$\text{5} + \quad \text{(CO)}_5\text{Mo} \qquad (4)$$

products presumably form by initial Mo$_2$(CO)$_{10}{}^{2-}$ reduction of the dication in **10** to give predominately **1**. Then, **1** reacts with the Mo(CO)$_5$ fragment formed in the reduction step to give **11**. The formation of **5** in reaction 4 probably occurs from **2**, which is always formed in lower amounts when **10** is reduced by other reducing agents such as Na[H$_2$Al(OCH$_2$CH$_2$OMe)$_2$].[3]

The structure of **11** (Figure 1) determined by X-ray diffraction studies shows the Mo(CO)$_5$ unit to be coordinated to the sulfur atom of **1**. The C−C distances (1.43(2), 1.38(2), 1.43(2) Å) in the η^4-2,5-Me$_2$T ring are all very similar and suggest little localized double bonding between carbons. The C(2)−S (1.84(1) Å) and C(5)−S (1.77(1) Å) bond lengths are approximately the same as those (1.76(2), 1.79(2) Å) in **2**.[29] The dihedral angle between the four-carbon plane of the η^4-2,5-Me$_2$T ligand and the plane defined by C(2)−S−C(5) is 40.7°.

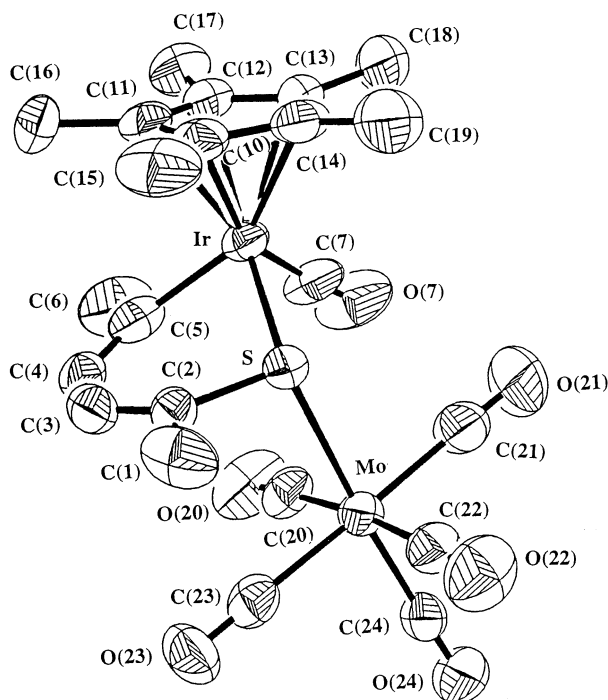(29) Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

Figure 2. Molecular structure of Cp*Ir[(CO)(C,S-2,5-Me₂T)(Mo(CO)₅)] (**12**) and the atom-numbering scheme, showing only one of the two independent molecules.

This angle is very similar to those of other S-adducts of **1**: **1·BH₃** (39.7°), **1·Fe(CO)₄** (37.9°), **1·Ru₃(CO)₁₁** (39.3°).[11]

Although **11** is not converted to **5** under the conditions (15 °C) of reaction 4, it gives an 84% yield of **5** and **2** (10%) when refluxed in THF for 5 h. When photolyzed with ultraviolet light for 6 h in THF solvent, **11** gives **5** (68%) and the new product **12** in 25% yield (eq 5). When
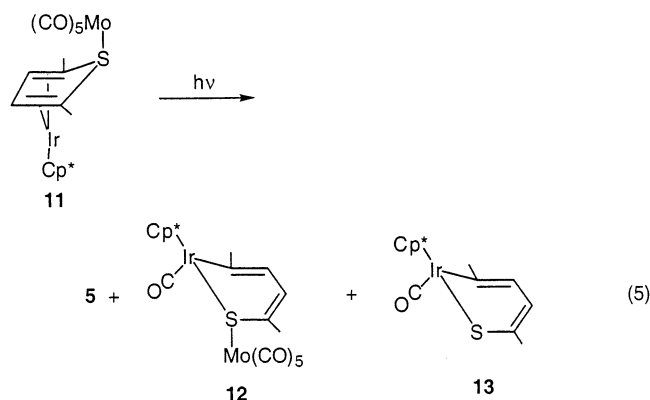
the photolysis is extended to 12 h, the yields of **5** (36%) and **12** (14%) are lower, but another product, **13** (18%),[4] appears. The formation of **13** occurs, at least in part, as a result of the conversion of **5**, because we observed that the photolysis of **5** in THF for 10 h gives a 36% yield of **2**. The photolysis of the tungsten analogue of **5**, namely **7**, in THF for 12 h also gives a significant yield (56%) of **2**. Thus, photolysis of **5** and **7** leads to the removal of ligand **2** from the M(CO)₃ unit.

The structure of **12** (Figure 2) consists of a Cp*Ir(CO)-(C,S-2,5-Me₂T) ligand that is coordinated through the sulfur to Mo(CO)₅. The Mo–S distance (2.582(2) Å) is slightly longer than that in **11** (2.543(4) Å), suggesting that Cp*Ir(CO)(C,S-2,5-Me₂T) is less strongly coordinated than Cp*Ir(η⁴-2,5-Me₂T) to Mo(CO)₅. The shape

and bond distances within the Cp*Ir(CO)(C,S-2,5-Me₂T) unit of **12** are nearly identical with those of free Cp*Ir-(CO)(C,S-2,5-Me₂T) (**13**).[30] As in **13**, the short–long–short C–C bond distances (C(2)–C(3), 1.32(1) Å; C(3)–C(4), 1.45(1) Å; C(4)–C(5), 1.33(2) Å) in the six-membered ring of **12** indicate relatively localized double bonds as in a diene. The only significant difference between the structures is the Ir–S distance in **12** (2.369(2) Å) being slightly longer than in **13** (2.349(3)).

Reactions of [η⁶-Cp*Ir(C,S-2,5-Me₂T)]M(CO)₃, Where M = Cr (3), Mo (5), W (7), with Nucleophiles/Lewis Bases/Ligands. In principle, nucleophiles/Lewis bases/ligands could react with **3**, **5**, or **7** by adding to the Ir, the metal M, or to a site on the six-membered ring. Recently, Bleeke and co-workers[5] described the reaction of the η⁶-iridathiabenzene complex **14** with PMe₃ (eq 6). While there is the substitution of a PEt₃
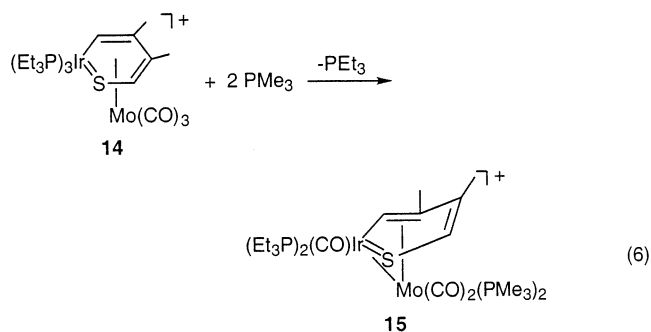
ligand and migration of a CO ligand, this reaction also involves the addition of an extra PMe₃ ligand to the Mo center. This results in decomplexation of one carbon–carbon double bond in the six-membered ring to give a complex of type **C** (Chart 1). On the other hand, we recently observed[17] that CO adds to the Ir center in **3** (eq 7), instead of Cr, to give bright red **16**, whose
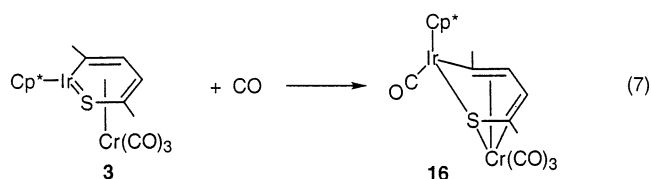
structure was established by X-ray studies. We now find that PEt₃ also adds to **3** (eq 8) to give purple-red **17**,
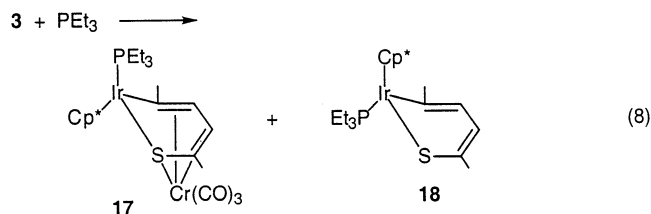
but the structure differs from that of **16** by the position of the PEt₃ ligand, which is on the opposite side of the six-membered ring from the Cr(CO)₃ unit, whereas the CO ligand is on the same side of the ring as the Cr(CO)₃ moiety in **16**. Perhaps it is the larger size of the PEt₃ ligand compared with that of CO which forces the PEt₃ group to be opposite the Cr(CO)₃ group. Steric interac-

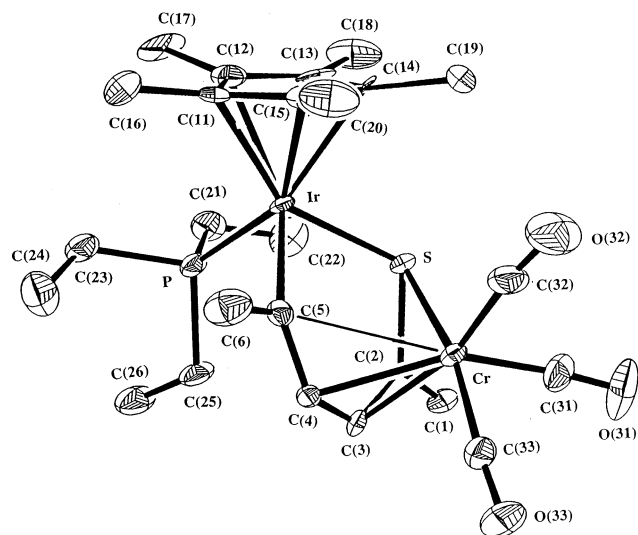(30) Chen, J.; Daniels, L. M.; Angelici, R. J. *Acta Crystallogr.* **1992**, *C48*, 2120.

Figure 3. Molecular structure of [η^5-Cp*Ir(PEt$_3$)(C,S-2,5-Me$_2$T)][Cr(CO)$_3$] (**17**), showing the atom-numbering scheme.

tions also lead to other distortions in **17** that are discussed in the next paragraph. Besides **17**, which is isolated in 33% yield, reaction 8 also gives a 33% yield of **18**. A more efficient route (83%) to **18** is the reaction of **2** with PEt$_3$; several other phosphines were previously shown to react with **2** to give analogous Cp*Ir(PR$_3$)(C,S-2,5-Me$_2$T) complexes.[4]

The structure of **17** (Figure 3) is fundamentally the same as that of **16**,[17] except the Cr(CO)$_3$ and Cp* groups are on the same side of the six-membered ring rather than on opposite sides as in **16**. There are also some differences in bond distances involving the six-membered ring (distances are given in Å for **17** followed by those for **16**[17]): Cr–C(5), 2.73(1), 2.45(1); Cr–C(4), 2.291(6), 2.22(1); Cr–C(3), 2.168(7), 2.19(1); Cr–C(2), 2.167(6), 2.20(1); Cr–S, 2.424(2), 2.420(3); Ir–C(5), 2.075(6), 2.055(11); Ir–S, 2.333(2), 2.353(3); C(4)–C(5), 1.374(9), 1.38(2). The notable difference between these structures is in Cr–C(5), which is 2.73(1) Å in **17** but 2.45(1) Å in **16**. Also, Cr–C(4) is longer in **17** (2.291(6) Å) than in **16** (2.22(1) Å). However, Cr–C(3) and Cr–C(2) are slightly shorter in **17** (2.168(7), 2.167(6) Å) than in **16** (2.19(1), 2.20(1) Å). Thus, the Cr in **17** has moved farther away from C(5) and C(4) toward C(3) and C(2). The reduced bonding between Cr and C(5) seems not to have greatly altered bonding of C(5) to Ir or C(4). The geometry around C(5) is essentially planar in both **17** and **16**, as indicated by the sums (359.7, 355.8°) of the Ir–C(5)–C(4) (129.5(5), 123.7(8)°), Ir–C(5)–C(6) (117.1(5), 116.5(8)°), and C(4)–C(5)–C(6) (113.1(6), 115.6(11)°) angles. Thus, the long Cr–C(5) distance in **17** appears not to be accompanied by other unusual structural features as compared with **16**.

In contrast to the reaction of **3** with PEt$_3$ (eq 8), the tungsten analogue **7** reacts (eq 9) with PEt$_3$ at –5 to –10 °C to give, in 82% isolated yield, bright red **19** in which the PEt$_3$ has added to the W. Thus, unlike the Cr complex **3**, which reacts with both PEt$_3$ (eq 8) and CO (eq 7) by adding to Ir, the corresponding tungsten complex adds PEt$_3$ at the tungsten. Perhaps the larger size of W favors PEt$_3$ attack at this metal. Reaction 9 is similar to reaction 6, in which PMe$_3$ adds to Mo rather than Ir.[5]
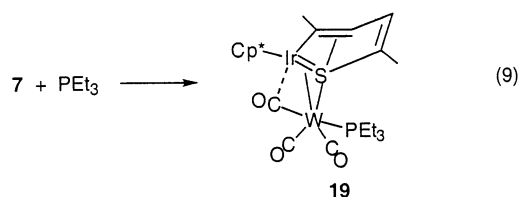
The structure of **19** (Figure 4) shows the tungsten to be η^4-coordinated to the six-membered ring in a manner which is similar to that in **15** (eq 6). As in η^4-coordinated arenes,[31,32] the six-membered ring in **19** is no longer planar and bond distances within the iridathiabenzene ring are changed from those in **2**. In **19**, the Ir–C(5) distance (2.008(8) Å) is longer than the corresponding distance in **2** (1.986(6) Å),[3] Ir–S (2.342(2) Å) is longer in **19** than in **2** (2.203(2) Å), the uncoordinated C(2)–C(3) bond in **19** (1.33(1) Å) is slightly shorter than in **2** (1.375(9) Å), and the uncoordinated S–C(2) and C(3)–C(4) bonds in **19** (1.776(9), 1.46(1) Å) are longer than these bonds in **2** (1.713(6), 1.41(1) Å). All of these bond distance changes are consistent with η^4 coordination of an arene ligand to a metal. In **19**, there is also a semibridging CO ligand, which is strongly coordinated to tungsten (W–C(8), 1.998(9) Å) but weakly interacting with iridium (Ir–C(8), 2.590(8) Å); the W–C(8)–O(8) angle (164.0(7)°) bends O(8) away from the Ir, which is characteristic of semibridging CO ligands.

Considering the ability of Cp*Ir(L)(C,S-2,5-Me$_2$T), where L = PEt$_3$, CO, to coordinate to M(CO)$_x$ fragments in **12**, **16**, and **17**, we reacted Cp*Ir(PEt$_3$)(C,S-2,5-Me$_2$T) (**18**) with M(CO)$_3$(NCMe)$_3$, where M = Mo, W (eq 10).
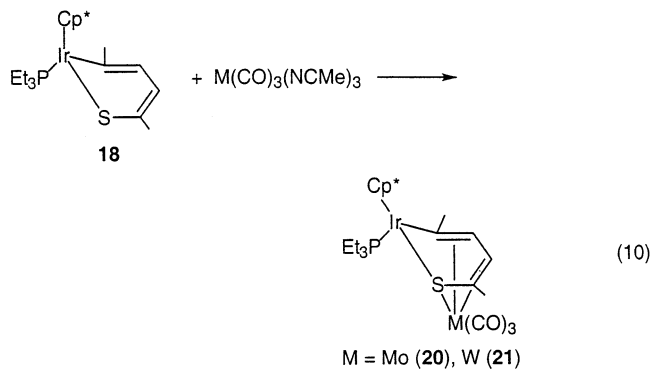
The reaction occurs at –20 to –10 °C to give 78 and 65% yields of red **20** and **21**, which were characterized by their elemental analyses, mass spectra, and ^{1}H NMR and IR spectra. While **21** and **19** have the same composition, it is obvious from their IR and ^{1}H NMR spectra that they are isomers. In fact, when **21** is refluxed in THF for 3 h and the mixture is partially separated by chromatography, **19** is identified as one of the products, along with **7** and other species. We assign the structure of **21** (and its Mo analogue **20**) to that shown in eq 10, on the basis of comparisons of its spectra with those of **16**, whose structure was established by X-ray crystallography.[17] The ν(CO) bands for **20** (1915 vs, 1820 s, 1806 s cm^{-1}) and **21** (1917 vs, 1826 s, 1805 s cm^{-1}) are similar to those of **16** (1933 vs, 1859

(31) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. *Chem. Rev.* **1982**, *82*, 499.
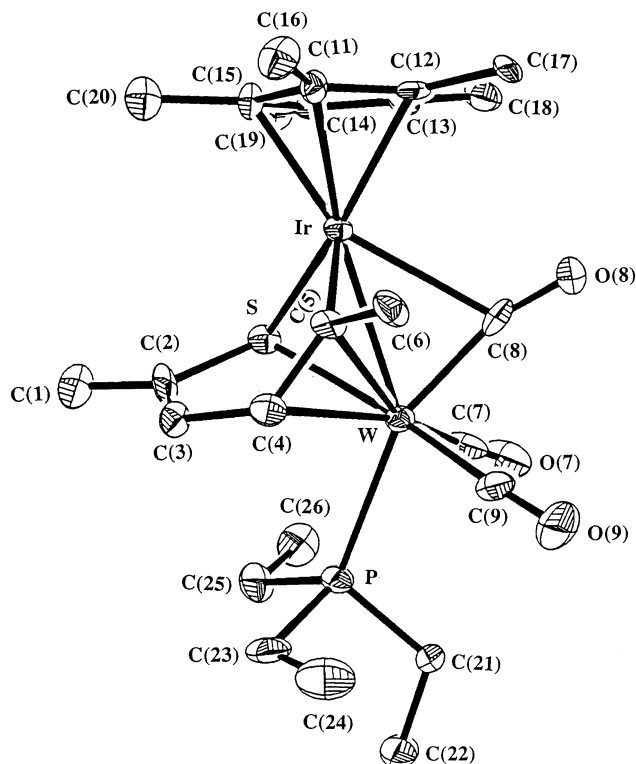(32) LeBozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163.

Figure 4. Molecular structure of $[\eta^4\text{-Cp*Ir(C,S-2,5-Me}_2\text{T)}]$-$[\text{W(CO)}_2(\text{PEt}_3)](\mu\text{-CO})$ (**19**), showing the atom-numbering scheme.

s, 1821 s cm^{-1}; there is also a band at 2023 s cm^{-1} for Ir–CO), which is expected to have higher ν(CO) values because of the greater electron-withdrawing ability of CO as compared to PEt$_3$. Also, the six-membered-ring protons in the ^{1}H NMR spectra of **20** (δ 4.07, 6.04 ppm) and **21** (δ 4.34, 5.84 ppm) are upfield of those in **16** (δ 4.38, 6.06 ppm) because of the stronger electron-donating ability of PEt$_3$ as compared with that of CO. Similarly, the methyl resonances for **20** (δ 1.80, 2.29 ppm) and **21** (δ 1.83, 2.46 ppm) are mostly upfield of those in **16** (δ 2.08, 2.28 ppm).

In addition to reactions of PEt$_3$ and CO (eqs 7–9) with the $[(\eta^6\text{-Cp*})\text{Ir(C,S-2,5-Me}_2\text{T)}]\text{M(CO)}_3$ complexes (**3**, **5**, **7**), we have also examined other nucleophiles/ligands. There was no reaction of **3** with Me$_2$S at room temperature in THF, except after 4 days when **2** (20%) and Cp*Ir[η^4-SC(Me)CHCHC(=O)Me] (**22**; 32%) were isolated; the formation of the acyl thiolate **22** was previously[28] observed in reactions with THF. A stronger donor sulfur ligand than Me$_2$S is **1**.[11] However, even **1** does not react with **3** at room temperature; after the mixture was stirred for 3 days in THF, only **2** (26%) and **22** (28%) were isolated.

The Ir in Cp*Ir(CO)(PMe$_3$) is known to be strongly basic toward protonic acids.[27] It does react slowly (48 h) with **3** at room temperature to give (eq 11) black

(11)

23
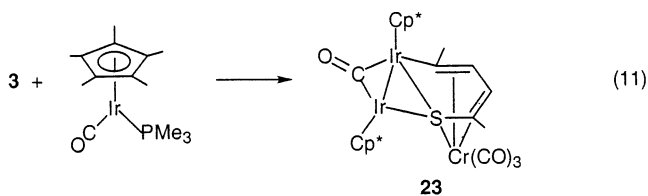
crystalline **23** in 25% yield. Since X-ray-quality crystals

of **23** could not be obtained, its tentatively proposed structure is based on elemental analysis and mass, IR, and ^{1}H NMR spectral data. The presence of the ring-opened 2,5-Me$_2$T is indicated in the ^{1}H NMR spectrum by signals for the inequivalent methyl groups at δ 1.73 and 2.83 ppm and ring protons as doublets at δ 3.32 and 5.52 ppm. The 1818 cm^{-1} ν(CO) band in the infrared spectrum (2028 s, 1947 vs, 1885 s, 1818 s cm^{-1}) is consistent with the presence of a bridging CO ligand. It should be noted, however, that the iridathiabenzene ring is known to coordinate to metals, in a variety of ways; therefore, the structural assignment of **23** in eq 11 must be regarded as tentative.

Reactions of $[\eta^6\text{-Cp*Ir(C,S-2,5-Me}_2\text{T)}]\text{M(CO)}_3$, Where M = Cr (3), Mo (5), W (7), with Electrophiles/Acids and an Oxidizing Agent. As $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3$ is protonated (CF$_3$SO$_3$H in CH$_2$Cl$_2$)[25] at the tungsten to give $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3(\text{H})^+$, so is **7** protonated rapidly under the same conditions to give orange-red **24** (eq 12) in 67% isolated yield. The ^{1}H NMR spectrum of **24**

7 + CF$_3$SO$_3$H ⟶ (12)

24
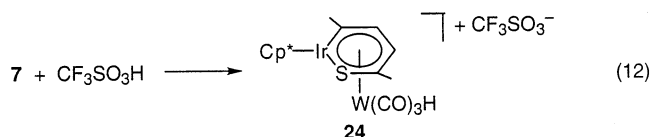
shows a peak at δ −11.08 ppm, which may be attributed to a metal hydride ligand; the W–H resonance in $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3(\text{H})^+$ is at −6.55 ppm. Upon protonation, the ν(CO) bands of **7** (1955 vs, 1888 s, 1878 s cm^{-1}) move to higher wavenumbers in **24** (2062 m, 2033 vs, 1935 s cm^{-1}) by an average of 103 cm^{-1}. The corresponding bands in $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3$ (1942 s, 1854 s, br cm^{-1}) move to 2067 s and 1982 s, br cm^{-1} in $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3(\text{H})^+$, an average increase of 126 cm^{-1}. The similar large increases of ν(CO) values upon protonation of **7** and $(\eta^6\text{-C}_6\text{Me}_6)\text{W(CO)}_3$ suggest that the W atom is protonated in **24**.

The $(\eta^6\text{-arene})\text{M(CO)}_3$ complexes (M = Cr, Mo, W) react with mercuric halides to give 1:1 and 1:2 adducts.[34,35] The X-ray-determined structure[36] of $[[(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)\text{Mo(CO)}_3\cdot2\text{HgCl}_2]_2$ shows that it is a dimer linked through Hg–Cl–Hg bonds; each Mo is directly bonded to a Hg atom. The 1:1 adduct $(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)$-Mo(CO)$_3\cdot$HgCl$_2$ has been proposed to have a structure in which the Mo donates to the Hg of the HgCl$_2$ unit. The ν(CO) bands in $(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)\text{Mo(CO)}_3$ (1979 s, 1905 cm^{-1}) increase by approximately 40 cm^{-1} upon forming the 1:1 adduct (2003 s, 1952 s, 1930 s cm^{-1}; Nujol). Both **3** and **7** react slowly with HgCl$_2$ at −40 to −30 °C to give the brick red 1:1 adducts **25** and **26** (eq 13). The average ν(CO) value for **3** increases by 95 cm^{-1}

3 or **7** + HgCl$_2$ ⟶

Cp*Ir(C,S-2,5-Me$_2$T)[M(CO)$_3$](HgCl$_2$) (13)

M = Cr (**25**), W (**26**)
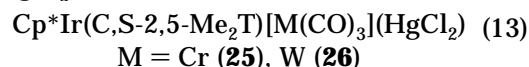
upon formation of **25**, while the average ν(CO) value of

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7 increases by 133 cm^{-1}. The much larger increases in ν(CO) values than observed ($\sim$40 cm^{-1}) for 1:1 HgCl$_2$ adduct formation with (η^6-1,3,5-Me$_3$C$_6$H$_3$)Mo(CO)$_3$ suggest that oxidation is occurring at Cr and W in **3** and **7**. Such an oxidation is observed in the conversion of (η^6-C$_6$Me$_6$)W(CO)$_3$ to (η^6-C$_6$Me$_6$)W(CO)$_3$X$^+$, for X = Cl,[37] I,[38] where the increase in average ν(CO) values is about 145 cm^{-1}. Although we were not able to obtain X-ray-quality crystals for **25** or **26**, possible structures of these compounds include those resulting from oxidative addition and cleavage of the Ir–M bond by addition of the HgCl and Cl units to the Ir and M centers. It is also possible that both HgCl and Cl units add to the Cr or W with partial loss of iridathiabenzene bonding to the M(CO)$_3$ moiety, so as to preserve 18 electrons at both metal centers.

When it is reacted with Cp$_2$Fe$^+$BF$_4^-$, **7** is oxidized to give the black product **27** with the composition [{η^6-Cp*Ir(C,S-2,5-Me$_2$T)}W(CO)$_3$]$_2$(BF$_4$)$_2$. The ^{1}H NMR spectrum of **27** gives absorbances characteristic of ring-opened 2,5-Me$_2$T; the observation of an NMR spectrum also means that **27** is diamagnetic, which suggests that **27** is a dimer. The link between the halves of the dimer could be through either the tungsten (**F**) or the iridium (**G**) atoms.

F

G
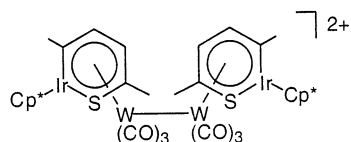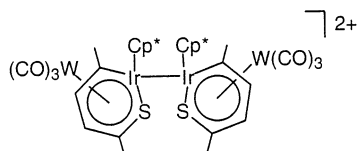
The two highest ν(CO) bands in **27** (1997 vs, 1936 vs, 1856 s, br cm^{-1}) are $\sim$45 cm^{-1} higher than those in **7** (1955 vs, 1888 s, 1878 s cm^{-1}). This increase, however, is substantially smaller than the 84 cm^{-1} average increase when CpW(CO)$_3^-$ (1896 s, 1786 s, 1746 s

cm^{-1})[39,40] is oxidized to [CpW(CO)$_3$]$_2$ (1954 m, 1892 s, 1833 s cm^{-1}) with a W–W bond. Thus, structure **F** is unlikely for **27**. One would expect structure **G** to give a smaller increase in ν(CO), which is consistent with the observations. Because suitable crystals for an X-ray study could not be obtained, it was not possible to establish definitely the structure of **27**.

Conclusions

While the [η^6-Cp*Ir(C,S-Me$_2$T)]M(CO)$_3$ complexes, where M = Cr (**3**), Mo (**5**), W (**7**), are structurally similar to (η^6-arene)M(CO)$_3$ complexes, their reactivities are often very different. Thus, (η^6-arene)M(CO)$_3$ complexes react with phosphines (PR$_3$) by displacement of the arene to give (R$_3$P)$_3$M(CO)$_3$,[41] whereas the chromium complex **3** reacts below room temperature with PEt$_3$ to give **18** (eq 8), a product in which PEt$_3$ has added to the iridium of **3** and the bond between Ir and Cr is cleaved. On the other hand, the analogous tungsten complex **7** reacts with PEt$_3$, also at low temperature, to give **19** (eq 9), a product in which PEt$_3$ has added to the tungsten of **7** by displacing part of the iridathiabenzene ring from the tungsten. It is the ability of the iridathiabenzene ligand to coordinate in a variety of different ways to metal centers (Chart 1) that allows the formation of these different products. Despite these differences in reactivities of the η^6-arene and η^6-iridathiabenzene complexes with donor ligands (PEt$_3$), both (η^6-C$_6$Me$_6$)W(CO)$_3$ and [(η^6-Cp*)Ir(C,S-Me$_2$T)]W(CO)$_3$ are protonated (eq 12) at the tungsten to give cationic hydride complexes, suggesting that the tungsten is the most basic site in both of these complexes.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes, and torsion angles for complexes **11, 12, 17**, and **18**. This information is available free of charge via the Internet at http://pubs.acs.org.

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