Organometallics **1996,** *15,* 2727−2734

Reactions of Cp*Ir(2,5-dimethylthiophene) with $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$

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Reactions of the isomers Cp*Ir(η^4-2,5-Me_2T) (**1**) and Cp*Ir(*C,S*-2,5-Me_2T) (**2**), where 2,5-Me_2T is 2,5-dimethylthiophene, with $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ yield a remarkable diversity of products. With $Ru_3(CO)_{12}$, both **1** and **2** give the CO-substituted product Cp*Ir(η^4-2,5-Me_2T·$Ru_3(CO)_{11}$) (**4**), in which the 2,5-Me_2T group is η^4-coordinated to the Ir and S-coordinated to a Ru in the plane of the triangular $Ru_3(CO)_{11}$ cluster. With $Re_2(CO)_{10}$, **1** reacts to give the CO-substituted product Cp*Ir(η^4-2,5-Me_2T·$Re_2(CO)_9$) (**6**), in which **1** is S-coordinated in an equatorial position of the metal−metal dimer $Re_2(CO)_9$. However, another product of this reaction is Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$)[$Re_2(CO)_9$] (**7**), in which the 2,5-Me_2T ligand has been converted to a ring-opened acyl−thiolate unit that is S-coordinated to $Re_2(CO)_9$. Compound **7** is the major product of the reaction of **2** with $Re_2(CO)_{10}$. The reaction of **2** with $Mn_2(CO)_{10}$ gives Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$)[$Mn_2(CO)_9$] (**9**), the Mn analog of **7**. The reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with **1** gives the product Cp*Ir(η^4-2,5-Me_2T·Ru(η^6-C_6H_6)Cl_2) (**10**), which illustrates again the strong S-donor ability of the Cp*Ir(η^4-2,5-Me_2T) (**1**) group. Structures of **4**, **6**, and **7** were established by X-ray diffraction studies.

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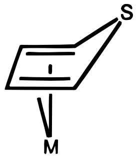
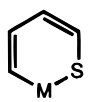
Introduction

In the hydrodesulfurization (HDS) of thiophenes over transition-metal-based catalysts,[1,2] the thiophene is presumably activated to undergo carbon−sulfur bond cleavage by coordination to a metal site on the catalyst surface. Of the several ways that thiophenes are known to coordinate[3−5] in metal complexes, the η^4 (**A**) and ring-opened *C,S* (**B**) modes are among the most reactive.

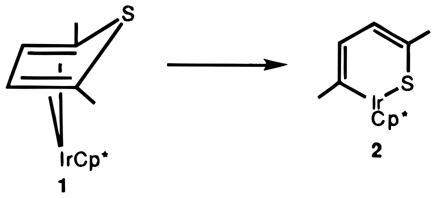
A: η^4



B: *C,S*



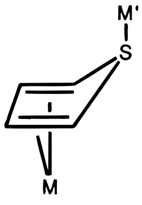
There are now many examples of complexes containing these types of ligands.[1,6−11] The only system which exhibits a thiophene in both of these coordination modes is Cp*Ir(2,5-Me_2T), where Cp* = η^5-C_5Me_5 and 2,5-Me_2T = 2,5-dimethylthiophene.[12,13] The yellow η^4 isomer (**1**) isomerizes (eq 1) to the more stable red C,S isomer (**2**)



(1)

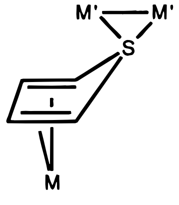
in the presence of base catalysts[13] or ultraviolet light.[14] These isomers react below room temperature with the iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$[15] to form Cp*Ir(η^4,*S*-μ_2-2,5-Me_2T)$Fe(CO)_4$ and Cp*Ir(η^4,*S*-μ_3-2,5-Me_2T)$Fe_2(CO)_7$ with structure types **C** and **D**, respectively. These are complicated reactions giving up to five different products, some in which both C−S bonds of the thiophene ligand have been cleaved. Carbon−sulfur-cleaved products are particularly evident for the reactions of **2**; a mechanism for thiophene HDS on

C:



η^4,S-μ_2

D:



η^4,S-μ_3

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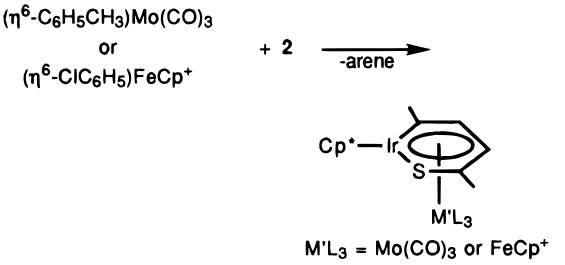
heterogeneous catalysts was proposed on the basis of those studies.[15] Other reported reactions of **1** or **2** with metal carbonyl complexes are those with the unsaturated dimers $Cp(CO)_2M{\equiv}M(CO)_2Cp$, where M = Mo, W,[14,16] which give products $Cp^*Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)Mo_2(CO)_4Cp_2$ of structural type **D**. In the present study, we explore reactions of **1** and **2** with the di- and trinuclear metal carbonyl complexes $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $Ru_3(CO)_{12}$ in order to determine whether or not they follow the same patterns of reactivity as the iron carbonyls.

In addition, we examine the reactions of **1** and **2** with the η^6-arene complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. Previously, we showed[17] that the iridathiabenzene isomer **2** is capable of displacing η^6-toluene and η^6-chlorobenzene ligands to give the η^6-iridathiabenzene complexes shown in eq 2.



(2)

Thus, it seemed possible that the benzene in $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ could be displaced by **2** to give the η^6-iridathiabenzene analog. On the other hand, the sulfur in **1** is known[1,13,14,16,18] to be an excellent donor toward Lewis acid centers; thus, it might react with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ by cleaving the bridging Ru−Cl bonds to give an adduct of the type $(\eta^6\text{-}C_6H_6)Ru(Cl)_2(L)$, where L is the S-coordinated **1** group. Similar cleavage reactions of $[(\eta^6\text{-}arene)RuCl_2]_2$ complexes with a variety of L ligands are well-known.[19,20] Thus, either η^6-benzene displacement or Ru−Cl cleavage are precedented reactions that might occur between $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and **1** or **2**. It would not be surprising if both gave the same products in their reactions with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, since these two isomers usually give the same products in their reactions with Lewis acids,[13,14,16] Lewis bases,[21] and oxidizing agents.[22]

Experimental Section

General Procedures. All reactions were performed under an N_2 atmosphere following standard Schlenk techniques. Solvents were reagent grade and were dried by refluxing over appropriate drying agents and stored over 4-Å molecular sieves under an N_2 atmosphere until used. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from potassium benzophenone ketyl, while hexanes and CH_2Cl_2 were distilled from CaH_2. The neutral Al_2O_3 (Brockman, activity I, 80−100 mesh) used for chromatography was deoxygenated (under high vacuum at room temperature for 16 h), deactivated with 5% (w/w) N_2-saturated water, and stored under N_2; columns were 1.5 × (10−15) cm. $Ru_3(CO)_{12}$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ were purchased from Strem Chemicals, Inc. The complexes $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**1**),[13] $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (**2**),[13,14] and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$[19] were prepared as previously described.

Elemental analyses were performed by Galbraith Laboratories, Inc., and the Shanghai Institute of Organic Chemistry. The IR spectra were measured on a Nicolet 710 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature on samples in $CDCl_3$ solution with $CHCl_3$ as the internal reference using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Melting points were recorded in sealed nitrogen-filled capillaries and are uncorrected.

Reaction of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (1) with $Ru_3(CO)_{12}$ To Give $Cp^*Ir(2,5\text{-}Me_2T)\cdot Ru_2(CO)_8$ (3) and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot Ru_3(CO)_{11})$ (4). Compound **1** (0.050 g, 0.114 mmol) was dissolved in 50 mL of THF at 0 °C. To this solution was added 0.073 g (0.114 mmol) of $Ru_3(CO)_{12}$. The mixture was stirred at 0−20 °C for 0.5 h; the light yellow solution turned brick red. After 24 h of stirring at room temperature, the resulting solution was evaporated under vacuum to dryness. The brick red residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A yellow band eluted first; a red band was then eluted with hexanes/CH_2Cl_2 (10:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.017 g (17%, based on **1**) of **3** as orange crystals was obtained (mp 150−152 °C dec). IR (CH_2Cl_2): ν(CO) 2061 vs, br, 2029 s, br, 2009 m, br cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.22 (d, 1 H), 4.18 (d, 1 H), 2.71 (s, 3 H), 2.39 (s, 3 H), 2.17 (s, 15 H). MS (*m/e*): 738, 720, 680. Anal. Calcd for $C_{24}H_{23}O_8SIrRu_2$: C, 33.29; H, 2.68. Found: C, 33.60; H, 2.97. From the second fraction, 0.054 g (45%, based on **1**) of orange-red crystalline **4** was obtained (mp 137−138 °C dec). IR (CH_2Cl_2): ν(CO) 2088 s, 2059 w, 2035 vs, 2021 m, 2004 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.63 (s, 2 H), 1.94 (s, 15 H), 1.28 (s, 6 H). MS (*m/e*): 914 ($M^+ - 5CO$). Anal. Calcd for $C_{27}H_{23}O_{11}SIrRu_3$: C, 30.86; H, 2.21. Found: C, 30.38; H, 2.23.

Reaction of $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (2) with $Ru_3(CO)_{12}$ To Give 3, 4, and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (5). To a solution of **2** (0.050 g, 0.114 mmol) in THF (50 mL) was added $Ru_3(CO)_{12}$ (0.073 g, 0.114 mmol) at 0 °C with stirring. The solution was stirred at room temperature for 24 h, during which time the red solution gradually turned brick red. After the solution was evaporated *in vacuo*, the brick red residue was chromatographed on Al_2O_3 (neutral) with hexanes as eluant. A yellow band eluted first; a red band was then eluted with hexanes/CH_2Cl_2 (10:1). A third band (brick red) was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). After removal of the solvents from the above three eluates under vacuum, the crude products were recrystallized from hexanes/CH_2Cl_2 solution at −80 °C. From the first fraction was isolated 0.028 g (29%, based on **2**) of orange crystalline **3** (mp 151−152 °C dec). IR (CH_2Cl_2): ν(CO) 2060 vs, br, 2028 s, br, 2009 m, br cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.23 (d, 1 H), 4.17 (d, 1 H), 2.71 (s, 3 H), 2.39 (s, 3 H), 2.17 (s, 15 H). From the second fraction, 0.038 g (32%, based on **2**) of **4** as orange-red crystals was obtained (mp 137−138 °C dec). IR (CH_2Cl_2): ν(CO) 2088 s, 2059 w, 2035 vs, 2020 m, 2004 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.63 (s, 2 H), 1.94 (s, 15 H), 1.28 (s, 6 H). From the third fraction, 0.026 g (27%, based on **2**) of orange crystals of **5**[21] (mp 121−122 °C dec) were obtained. IR (CH_2Cl_2): ν(CO) 2020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.78 (d, 1 H), 5.44 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 15 H). MS (*m/e*): 468 (M^+), 440 ($M^+ - CO$). Anal. Calcd for $C_{17}H_{23}OSIr$: C, 43.66; H, 4.96. Found: C, 43.21; H, 5.20.

Reaction of 1 with $Re_2(CO)_{10}$ To Give 2, $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot Re_2(CO)_9)$ (6), and $Cp^*Ir(\eta^4\text{-}SC_3H_2MeC({=}O)Me)[Re_2(CO)_9]$ (7). In 30 mL of THF at room temperature was dissolved 0.060 g (0.136 mmol) of **1**. To this solution was added 0.090 g (0.138 mmol) of $Re_2(CO)_{10}$. The reaction solution was stirred at room temperature for 40 h, during which time the

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Table 1. Crystal and Data Collection Parameters for Cp*Ir(η^4-2,5-$Me_2T\cdot Ru_3(CO)_{11}$) (4), Cp*Ir(η^4-2,5-$Me_2T\cdot Re_2(CO)_9$) (6), and Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$)[$Re_2(CO)_9$] (7)

	4	6	7
formula	$C_{27}H_{23}IrO_{11}Ru_3S$	$C_{25}H_{23}O_9SIrRe_2$	$C_{25}H_{23}IrO_{10}Re_2S$
fw	1050.9	1064.15	1080.1
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	8.997(1)	9.433(3)	18.046(2)
b, Å	13.691(4)	19.622(3)	19.340(2)
c, Å	13.704(3)	16.054(3)	19.575(3)
α, deg	76.40(2)	90.0	90.0
β, deg	82.14(2)	97.89(2)	98.26(2)
γ, deg	87.00(2)	90.0	90.0
V, Å^3	1624.9(7)	2943(1)	6761(2)
Z	2	4	8
d_{calc}, Mg/m^3	2.148	2.401	2.116
cryst size (mm)	0.50 × 0.19 × 0.08	0.30 × 0.20 × 0.20	0.30 × 0.25 × 0.25
μ, mm^{-1}	19.897	12.85	11.14
diffractometer	Siemens P4RA	Rigaku AFC7R	Enraf-Nonius
radiation	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 73 Å)
temp, K	293	293	293
scan method	$\theta-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data collection range, 2θ, deg	5.0−115.0	4.0−45.0	4.0−50.0
no. of data collected	4706	4272	5959
no. of unique data (R_{int})	4373 (0.023)	3992 (0.042)	5382 (0.021)
no. of data obs	3135, $F_o > 4\sigma(F)$	2596, $F_o > 6\sigma(F)$	4101. $F_o > 4\sigma(F)$
no. of params refined	398	344	414
transmissn factors: min, max	0.28−1.00	0.59−1.00	0.62−1.00
refinement program	SHELXTL-PLUS V4.2	TEXSAN	SHELXTL-PLUS V5.0
R^a	0.0414	0.032	0.035
$R_w{}^b$ (wR2)^c	0.0475	0.031	(0.105)
goodness of fit	0.94	1.16	1.08
largest peak, e/Å^3	0.90	0.81	1.35
largest shift, final cycle	0.00	0.00	0.00

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_0^4]]^{1/2}$. [d] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

light yellow solution gradually turned orange. After vacuum removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A red band eluted first; then a yellow band was eluted with hexanes/CH_2Cl_2 (5:1). A third band (yellow) was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:2). After the solvents were evaporated from the above three eluates in vacuo, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.011 g (18%, based on **1**) of dark red crystals of **2** were obtained (mp 147−148 °C dec). ^1H NMR ($CDCl_3$): δ 7.46 (s, 2 H), 3.10 (s, 3 H), 2.79 (s, 3 H), 1.93 (s, 15 H). From the second fraction, 0.048 g (34%, based on **1**) of orange-yellow crystalline **6** was obtained (mp 156−157 °C dec). IR (CH_2Cl_2): ν(CO) 2096 s, 2030 s, 1986 vs, br, 1952 m, 1914 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.59 (s, 2 H), 1.91 (s, 15 H), 1.26 (s, 6 H). MS (*m*/*e*): 922 (M^+ − 5CO). Anal. Calcd for $C_{25}H_{23}O_9SIrRe_2$: C, 28.22; H, 2.18. Found: C, 28.20; H, 2.41. From the third fraction, 0.045 g (31%, based on **1**) of **7** as light yellow crystals was obtained (mp 108−110 °C dec). IR (CH_2Cl_2): ν(CO) 2097 w, 2034 s, 1988 vs, 1952 m, 1912 s, 1723 s, 1653 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.67 (d, 1 H), 2.63 (d, 1 H), 2.27 (s, 3 H), 2.03 (s, 3 H), 1.86 (s, 15 H). MS (*m*/*e*): 938 (M^+ − 5CO), 826 (M^+ − 9CO). Anal. Calcd for $C_{25}H_{23}O_{10}SIrRe_2$: C, 27.80; H, 2.15. Found: C, 27.51; H, 2.30.

Reaction of 2 with $Re_2(CO)_{10}$ in THF To Give 7. As described for the reaction of **1** with $Re_2(CO)_{10}$, 0.025 g (0.057 mmol) of **2** in THF (30 mL) was treated with $Re_2(CO)_{10}$ (0.037 g, 0.057 mmol) at room temperature for 30 h. Workup of the resulting solution as described above for the reaction of **1** with $Re_2(CO)_{10}$ gave 0.040 g (66%, based on **2**) of **7** as light yellow crystals (mp 109−110 °C dec). IR (CH_2Cl_2): ν(CO) 2097 w, 2034 s, 1988 vs, 1952 m, 1912 s, 1723 s, 1653 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.67 (d, 1 H), 2.63 (d, 1 H), 2.27 (s, 3 H), 2.03 (s, 3 H), 1.86 (s, 15 H).

Reaction of 1 with $Mn_2(CO)_{10}$ To Give Cp*Ir$(CO)_2$ (8) and Cp*Ir(C,S-2,5-Me_2T)(CO) (5). To a stirred, light yellow solution of **1** (0.030 g, 0.068 mmol) in THF (30 mL) at −10 °C was added 0.027 g (0.069 mmol) of $Mn_2(CO)_{10}$. The mixture was stirred at room temperature for 24 h, during which time the light yellow solution gradually turned orange. After vacuum removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A yellow band eluted first; then an orange band was eluted with hexanes/CH_2Cl_2 (10:1). The solvents were removed from the above two eluates in vacuo, and the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.011 g (42%, based on **1**) of light yellow crystalline **8**[15] was obtained (mp 110−111 °C). IR (hexanes): ν(CO) 2019 vs, 1959 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s). From the second fraction, 0.017 g (53%, based on **1**) of **5** as orange-red crystals (mp 121−122 °C dec) was obtained. IR (CH_2Cl_2): ν(CO) 2020 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.78 (d, 1 H), 5.45 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 15 H). MS (*m*/*e*): 468 (M^+), 440 (M^+ − CO). Anal. Calcd for $C_{17}H_{23}OSIr$: C, 43.66; H, 4.96. Found: C, 43.80; H, 4.82.

Reaction of 2 with $Mn_2(CO)_{10}$ To Give 8, 5, and Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$)[$Mn_2(CO)_9$] (9). The reaction of **2** (0.030 g, 0.068 mmol) with $Mn_2(CO)_{10}$ (0.027 g, 0.069 mmol) was allowed to proceed, as described for the reaction of **1** with $Mn_2(CO)_{10}$, for 24 h at room temperature, during which time the red solution gradually turned orange-yellow. After the resulting solution was evaporated to dryness *in vacuo*, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A yellow band was eluted first, then an orange band was eluted with hexanes/CH_2Cl_2 (10:1), and finally a third band (yellow) was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). After vacuum removal of the solvents from the above three eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction was isolated 0.008 g (31%, based on **2**) of **8** as light yellow crystals (mp 110−111 °C). IR (hexanes): ν(CO) 2019 vs, 1959 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s). From the second-fraction, 0.014 g (44%, based on **2**) of orange-red crystalline **5** was obtained (mp 138−139 °C dec). IR (CH_2Cl_2): ν(CO) 2020 s cm^{-1}. MS (*m*/*e*): 468

Table 2. Selected Bond Distances (Å) and Angles (deg) with Esd's for Cp*Ir(η^4-2,5-$Me_2T\cdot Ru_3(CO)_{11}$) (4)

Distances			
Ir−C(2)	2.14(1)	Ir−C(3)	2.11(2)
Ir−C(4)	2.11(2)	Ir−C(5)	2.11(1)
Ir−C(11)	2.21(1)	Ir−C(12)	2.20(2)
Ir−C(13)	2.20(1)	Ir−C(14)	2.22(1)
Ir−C(15)	2.27(1)	S−C(2)	1.78(1)
S−C(5)	1.77(1)	S−Ru(1)	2.394(3)
C(1)−C(2)	1.49(2)	C(2)−C(3)	1.42(2)
C(3)−C(4)	1.43(2)	C(4)−C(5)	1.46(2)
C(5)−C(6)	1.50(2)	Ru(1)−C(101)	1.91(1)
Ru(1)−C(102)	1.87(2)	Ru(1)−C(103)	1.90(2)
Ru(1)−Ru(2)	2.865(2)	Ru(1)−Ru(3)	2.842(2)
Ru(2)−Ru(3)	2.868(2)	Ru(2)−C(201)	1.91(2)
Ru(2)−C(202)	1.94(2)	Ru(2)−C(203)	1.94(2)
Ru(2)−C(204)	1.93(2)	Ru(3)−C(302)	1.90(2)
Ru(3)−C(301)	1.97(2)	Ru(3)−C(304)	1.93(2)
Ru(3)−C(303)	1.90(2)		
Angles			
C(2)−S−C(5)	83.6(6)	C(2)−S−Ru(1)	117.2(5)
C(5)−S−Ru(1)	112.4(4)	S−C(2)−C(1)	118.2(9)
C(1)−C(2)−C(3)	126.7(1)	S−C(2)−C(3)	109.4(9)
C(2)−C(3)−C(4)	110.8(1)	S−C(5)−C(4)	109(1)
C(3)−C(4)−C(5)	108(1)	S−C(5)−C(6)	120(1)
C(4)−C(5)−C(6)	122(1)	S−Ru(1)−C(101)	85.6(4)
C(202)−Ru(2)−C(204)	175.1(6)	C(101)−Ru(1)−C(102)	92.7(6)
Ru(1)−Ru(2)−Ru(3)	59.4(1)	C(101)−Ru(1)−C(103)	176.0(6)
Ru(1)−Ru(3)−Ru(2)	60.2(1)	S−Ru(1)−Ru(2)	101.0(1)
Ru(2)−Ru(1)−Ru(3)	60.3(1)	C(102)−Ru(1)−Ru(2)	157.7(4)
S−Ru(1)−C(102)	100.9(5)	S−Ru(1)−Ru(3)	161.2(1)
Ru(1)−Ru(2)−C(203)	153.3(5)	Ru(2)−Ru(3)−C(302)	156.9(5)
C(201)−Ru(2)−Ru(3)	157.7(5)	Ru(1)−Ru(3)−C(303)	158.9(5)
C(201)−Ru(2)−C(203)	106.5(7)	C(301)−Ru(3)−C(304)	175.4(6)

(M^+), 440 ($M^+ - CO$). ^1H NMR ($CDCl_3$): δ 5.78 (d, 1 H), 5.45 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 15 H). From the third fraction, 0.013 g (23%, based on **2**) of **9** as light yellow crystals was obtained (mp 100−101 °C dec). IR (CH_2Cl_2): ν(CO) 2056 s, 2001 vs, 1971 m, 1920 s, 1722 s, 1656 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.68 (d, 1 H), 2.65 (d, 1 H), 2.27 (s, 3 H), 2.03 (s, 3 H), 1.86 (s, 15 H). MS (*m/e*): 958, 840, 718. Anal. Calcd for $C_{25}H_{23}O_{10}SIrMn_2$: C, 36.72; H, 2.84. Found: C, 37.06; H, 3.01.

Reaction of 1 with [(η^6-C_6H_6)$RuCl_2$]$_2$ To Give Cp*Ir(η^4-2,5-$Me_2T\cdot Ru$(η^6-C_6H_6)Cl_2) (10). A mixture of **1** (0.035 g, 0.080 mmol) and [(η^6-C_6H_6)$RuCl_2$]$_2$ (0.045 g, 0.090 mmol) in 10 mL of benzene was heated at 35 °C for 4 h, during which time the color turned from brown to red. After removal of the solvent under vacuum, the residue was redissolved in CH_2Cl_2. The CH_2Cl_2 solution was filtered, and the filtrate was reduced to a volume of about 5 mL under vacuum. To this solution was added 30 mL of hexanes to precipitate the product, which was recrystallized from hexanes/CH_2Cl_2 solution at −80 °C to give orange needle crystals of **10** (0.044 g, 80% yield based on **1**, mp 160 °C dec). ^1H NMR ($CDCl_3$): δ 5.55 (s, 6 H, C_6H_6), 4.79 (s, 2 H), 1.93 (s, 15 H), 1.46 (s, 6 H). MS (*m/e*): 690 (M^+). Anal. Calcd for $C_{22}H_{29}Cl_2SIrRu$: C, 38.31; H, 4.24. Found: C, 37.85; H, 4.11.

Reaction of 2 with [(η^2-C_6H_6)$RuCl_2$]$_2$ To Give Cp*Ir(2,5-Me_2T)[(η^6-C_6H_6)$RuCl_2$] (11). As described in the procedure for the reaction of **1** with [(η^6-C_6H_6)$RuCl_2$]$_2$, **2** (0.025 g, 0.057 mmol) was reacted with [(η^6-C_6H_6)$RuCl_2$]$_2$ (0.029 g, 0.058 mmol) at 35 °C for 6 h. Workup of the reaction mixture as described above gave 0.027 g (69%, based on **2**) of **11** as dark red crystals (mp 150 °C dec). ^1H NMR ($CDCl_3$): δ 5.73 (s, 6 H, C_6H_6), 5.37 (d, 1 H), 5.28 (d, 1 H), 2.28 (s, 3 H), 1.98 (s, 3 H), 1.92 (s, 15 H). MS (*m/e*): 692, 690 (M^+). Anal. Calcd for $C_{22}H_{29}Cl_2SIrRu$: C, 38.31; H, 4.24. Found: C, 38.15; H, 3.98.

X-ray Crystal Structure Determinations of 4, 6, and 7. All three structure determinations were conducted on different diffractometers using vendor-supplied refinement packages (Table 1).[23] Data collections were all carried out at room temperature, and Lorentz and polarization corrections were applied. Data for all three crystals were corrected for radiation damage effects by monitoring three standard reflections throughout the data collections. All were corrected for absorption effects by the empirical method from a series of azimuthal scans.

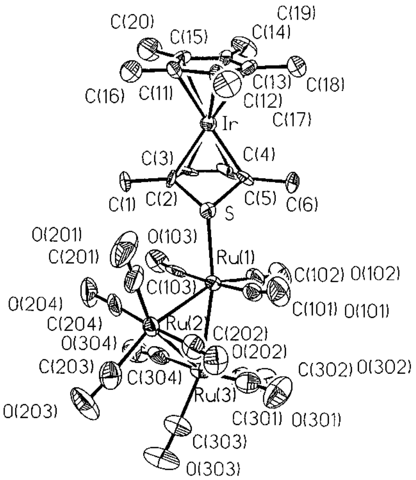

Figure 1. Thermal ellipsoid drawing of Cp*Ir(η^4-2,5-$Me_2T\cdot Ru_3(CO)_{11}$) (**4**).

Table 3. Selected Bond Distances (Å) and Angles (deg) with Esd's for Cp*Ir(η^4-2,5-$Me_2T\cdot Re_2(CO)_9$) (6)

Distances			
Ir−C(11)	2.13(1)	Ir−C(12)	2.07(2)
Ir−C(13)	2.07(2)	Ir−C(14)	2.12(1)
C(10)−C(11)	1.50(2)	C(11)−C(12)	1.41(2)
C(12)−C(13)	1.37(2)	C(13)−C(14)	1.45(2)
C(14)−C(15)	1.47(2)	Re(1)−Re(2)	3.051(1)
Re(1)−C(1)	1.99(2)	Re(1)−C(2)	2.00(2)
Re(1)−C(3)	1.93(2)	Re(1)−C(4)	1.97(2)
Re(1)−C(5)	1.97(2)	Re(2)−S	2.514(4)
Re(2)−C(6)	2.02(2)	Re(2)−C(7)	1.91(2)
Re(2)−C(8)	2.00(2)	Re(2)−C(9)	1.92(1)
S−C(11)	1.84(1)	S−C(14)	1.82(1)
Angles			
Re(2)−Re(1)−C(1)	85.5(5)	Re(2)−Re(1)−C(2)	84.6(4)
Re(2)−Re(1)−C(3)	179.1(5)	Re(2)−Re(1)−C(4)	84.6(4)
Re(2)−Re(1)−C(5)	83.8(4)	Re(2)−S−C(14)	111.7(5)
Re(1)−Re(2)−C(6)	86.1(4)	Re(2)−S−C(11)	114.0(5)
Re(1)−Re(2)−C(8)	85.6(4)	C(11)−S−C(14)	81.7(7)
C(3)−Re(1)−C(5)	95.5(7)	C(6)−Re(2)−C(9)	95.5(6)
Re(1)−Re(2)−S	90.21(8)	C(1)−Re(1)−C(4)	170.1(6)
Re(1)−Re(2)−C(7)	86.0(4)	C(2)−Re(1)−C(3)	96.1(6)
Re(1)−Re(2)−C(9)	176.8(4)	C(2)−Re(1)−C(5)	168.5(6)
S−Re(2)−C(7)	176.0(4)	C(3)−Re(1)−C(4)	94.8(7)
C(6)−Re(2)−C(8)	171.4(6)	S−C(14)−C(15)	119(1)
S−C(14)−C(13)	108(1)	S−C(11)−C(12)	107(1)
C(13)−C(14)−C(15)	126(1)	S−C(11)−C(10)	116(1)
C(11)−C(12)−C(13)	112(1)	C(10)−C(11)−C(12)	127(1)
C(12)−C(13)−C(14)	109(1)		

Selected bond distances and angles for **4**, **6**, and **7** are presented in Tables 2−4, respectively. Thermal ellipsoid drawings of all three complexes are presented in Figures 1−3.

Results and Discussion

Reactions of 1 and 2 with $Ru_3(CO)_{12}$. From the reaction of $Ru_3(CO)_{12}$ with **1** at room temperature for 24 h were isolated two ruthenium-containing products,

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[23] (a) SHELXTL-Plus V4.2: Siemens Analytical X-ray Instruments, Inc., Madison, WI (1989). (b) TEXSAN: Molecular Structure Corp., The Woodlands, TX (1985, 1992). (c) SHELXTL-Plus V5.0: Siemens Industrial Automation, Inc., Madison, WI (1994).

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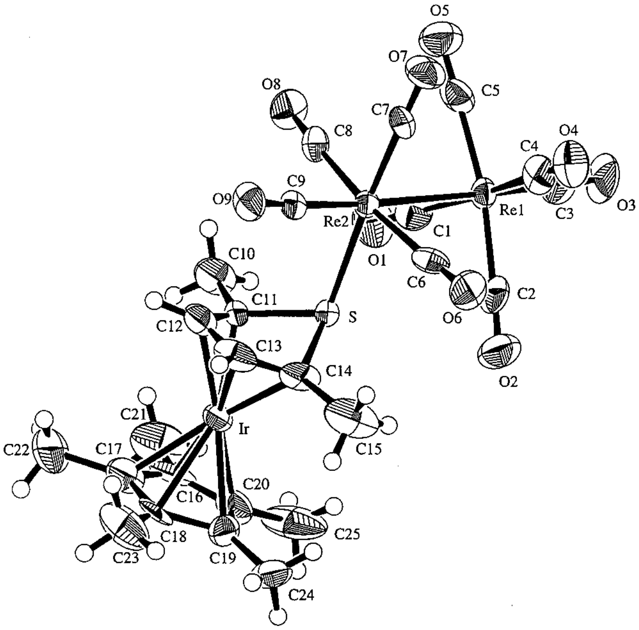


Figure 2. Thermal ellipsoid drawing of Cp*Ir(η-2,5-Me$_2$T$\cdot$-Re$_2$(CO)$_9$) (**6**).

Table 4. Selected Bond Distances (Å) and Angles (deg) with Esd's for Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me)[Re$_2$(CO)$_9$] (7)

	Distances		
Re(1)−S(1)	2.536(2)	Re(1)−Re(2)	3.0399(7)
Re(1)−C(12)	1.941(14)	Re(1)−C(11)	2.006(14)
Re(1)−C(14)	1.939(14)	Re(1)−C(13)	1.899(11)
Re(2)−C(22)	1.99(2)	Re(2)−C(21)	1.982(13)
Re(2)−C(24)	2.02(2)	Re(2)−C(23)	1.92(2)
S(1)−C(2)	1.741(10)	Re(2)−C(25)	2.03(2)
C(1)−C(2)	1.517(13)	C(2)−C(3)	1.405(13)
C(3)−C(4)	1.437(13)	C(4)−C(5)	1.453(13)
C(5)−O(1)	1.230(12)	C(5)−C(6)	1.49(2)
Ir−S(1)	2.391(2)	Ir(1)−C(2)	2.137(9)
Ir−C(3)	2.133(9)	Ir(1)−C(4)	2.162(9)
	Angles		
Re(2)−Re(1)−S(1)	87.60(6)	Re(2)−Re(1)−C(11)	86.0(3)
S(1)−Re(1)−C(11)	98.0(3)	Re(2)−Re(1)−C(12)	178.0(3)
S(1)−Re(1)−C(12)	90.4(3)	S(1)−Re(1)−C(13)	169.7(4)
Re(2)−Re(1)−C(13)	89.2(4)	S(1)−Re(1)−C(14)	81.1(4)
Re(2)−Re(1)−C(14)	85.5(4)	Re(1)−Re(2)−C(21)	83.5(3)
C(11)−Re(1)−C(14)	171.5(5)	C(21)−Re(2)−C(22)	169.0(5)
Re(1)−Re(2)−C(22)	85.6(4)	Re(1)−Re(2)−C(24)	84.5(4)
Re(1)−Re(2)−C(23)	177.8(5)	C(24)−Re(2)−C(25)	172.2(5)
Ir(1)−S(1)−Re(1)	134.04(11)	Ir(1)−S(1)−C(2)	59.8(3)
Re(1)−S(1)−C(2)	111.6(3)	C(1)−C(2)−C(3)	120.1(9)
S(1)−C(2)−C(1)	121.1(8)	C(3)−C(4)−C(5)	120.9(9)
S(1)−C(2)−C(3)	118.8(7)	C(4)−C(5)−C(6)	116.8(10)
C(2)−C(3)−C(4)	118.7(9)	O−C(5)−C(6)	121.8(10)
C(4)−C(5)−O(1)	121.5(10)		

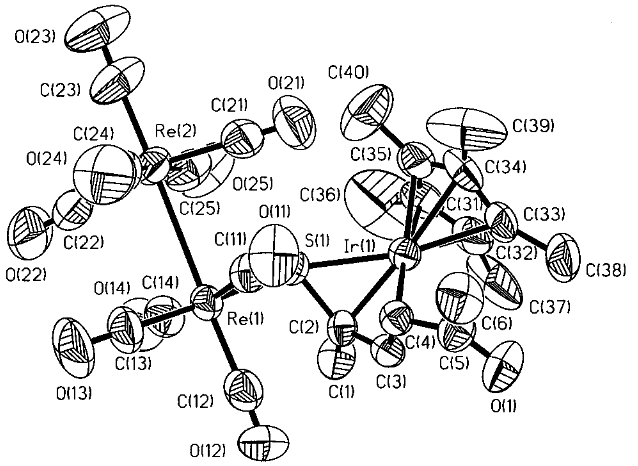
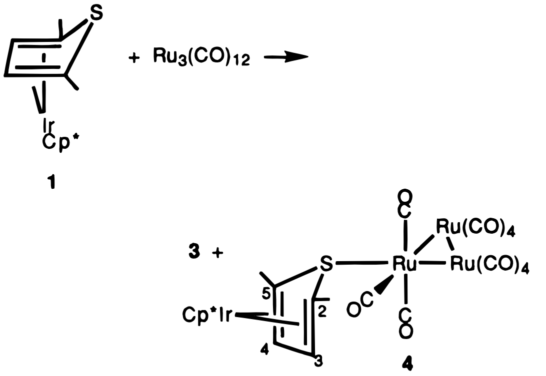


Figure 3. Thermal ellipsoid drawing of Cp*Ir(η^4-SC$_3$H$_2$-MeC(=O)Me)[Re$_2$(CO)$_9$] (**7**).



1

4

(3)

3 and **4** (eq 3). The structure (Figure 1) of the major product **4**, obtained in 45% yield, was established by an X-ray diffraction study of its orange-red crystals. It contains a triangular Ru$_3$(CO)$_{11}$ core very similar to that of Ru$_3$(CO)$_{12}$ and its monosubstituted products Ru$_3$-(CO)$_{11}$(L).[24] All of the CO groups are terminal, and the Ru−Ru−Ru angles lie within the range 59.4−60.3°. As in the structure of Ru$_3$(CO)$_{11}$(PPh$_3$)[25] and related compounds,[24a] the sulfur donor atom of the Cp*Ir(η^4-2,5-Me$_2$T) (**1**) ligand occupies an equatorial position in the plane of the Ru$_3$ triangle. However, the effect of ligand **1** on the Ru−Ru distances within the Ru$_3$ core is quite different than that of P-donor ligands.[24a] In a wide range of M$_3$(CO)$_{12-n}$(L)$_n$ complexes, where M = Fe, Ru, Os[24a] and L is a P- or As-donor ligand, the M−M bond *cis* to the L ligand is the longest. In **4**, where Ru(1)−Ru(2) = 2.865(2) Å, Ru(2)−Ru(3) = 2.868(2) Å, and Ru-(1)−Ru(3) = 2.842(2) Å, it is evident that the *cis* (Ru(1)−Ru(2)) bond is not the longest. It and Ru(2)−Ru(3) have the same distance, which is longer than the Ru(1)−Ru-(3) bond. The Ru−C(O) distances in **4** are generally longer for the axial CO groups (average 1.93 Å) than the equatorial CO's (average 1.90 Å), as was also observed for Ru$_3$(CO)$_{11}$(PPh$_3$).[25]

Structural features of the Cp*Ir(η^4-2,5-Me$_2$T) (**1**) part of **4** are very similar to those in complexes of structure type **C**, as in Cp*Ir(η^4,*S*-μ_2-2,5-Me$_2$T)Fe(CO)$_4$.[15] The 2,5-Me$_2$T ligand is folded with a 39.3° dihedral angle between the C(2)−C(3)−C(4)−C(5) and C(2)−S−C(5) planes. The S is 0.837 Å out of the four-carbon plane, and the Ir−S distance is a long 2.913 Å, probably indicating an antibonding interaction between the Ir and S atoms, as described by Harris[26] for other Lewis acid adducts of Cp*Ir(η^4-2,5-Me$_2$T). The folded 2,5-Me$_2$T ligand in **4** is also observed in the following type **C** structure compounds: Cp*Rh(η^4,*S*-μ_2-2,5-Me$_2$T)Fe(CO)$_4$,[27] (η^5-Me$_4$T)Ru(η^4,*S*-μ_2-Me$_4$T)Fe(CO)$_4$,[28] (η^6-C$_6$Me$_6$)$_3$Ru$_3$-

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[24] (a) Bruce, M. I. *Coord. Chem. Rev.* **1987**, *76*, 1. (b) Bruce, M. I.; Matisons, J. G.; Nicolson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.

[25] Forbes, E. J.; Goodhand, N.; Jones, D. L.; Hamor, T. A. *J. Organomet. Chem.* **1979**, *182*, 143.

[26] Harris, S. *Organometallics* **1994**, *13*, 2628.

[27] Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002.

[28] Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1992**, *11*, 3497.

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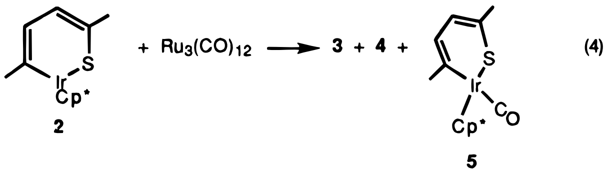
(η^4,S-μ_2-Me_4T)$_2$,[18] and $(CO)_3Fe$(η^4,S-μ_2-T)$Re(CO)_2Cp$.[29] Within the 2,5-Me_2T ring, the C−C bond distances (C(2)−C(3) = 1.42(2) Å, C(3)−C(4) = 1.43(2) Å, C(4)−C(5) = 1.46(2) Å) are the same within the experimental error limits; the C(2)−S (1.78(1) Å) and C(5)−S (1.77(1)) bond lengths are longer than those in thiophene itself (1.714(1) Å).[4]

The IR spectrum of **4** in the ν(CO) region (2088 s, 2059 w, 2035 vs, 2021 m, 2004 vs cm^{-1}) is generally similar to that (2097 m, 2047 s, 2031 sh, 2026 sh, 2017 s, 2001 w, 1986 w)[24b] of $Ru_3(CO)_{11}(PPh_3)$ and related molecules, but relative intensities of the bands vary from one $Ru_3(CO)_{11}(L)$ compound to another. The ^1H NMR spectrum of **4** contains signals for the equivalent H3 and H4 protons at δ 4.63 s and for the CH_3 groups at 1.28 s; these chemical shifts are similar to those of other Cp*Ir(η^4-2,5-Me_2T) Lewis acid adducts.[14−16]

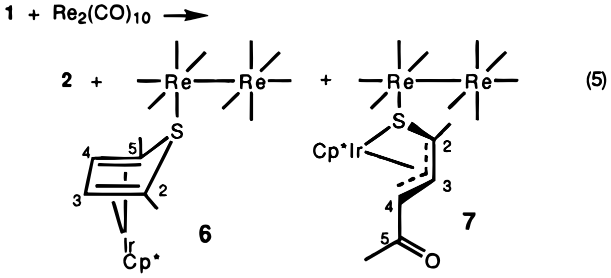
The mechanism of the formation of **4** in reaction 3 has not been investigated. However, kinetic studies[30,31] of the substitution of CO groups in $Ru_3(CO)_{12}$ by phosphines indicate that both dissociative and associative pathways are possible. Since CO dissociation from $Ru_3(CO)_{12}$ occurs very slowly at and below room temperature,[30,31] the formation of **4** in reaction 3 presumably occurs by the associative pathway in which $Ru_3(CO)_{12}$ undergoes attack by the strongly nucleophilic sulfur of Cp*Ir(η^4-2,5-Me_2T) (**1**).

The carbon−hydrogen elemental analysis of the minor product **3** (17% yield) in reaction 3 corresponds to the composition Cp*Ir(2,5-Me_2T)$Ru_2(CO)_8$, but a molecular ion was not observed in the mass spectrum. Crystals of **3** were too small to characterize structurally by X-ray diffraction. The ^1H NMR spectrum shows inequivalent H3 and H4 protons at δ 5.22 d and 4.18 d and inequivalent CH_3 groups at δ 2.71 s and 2.39 s, which suggests that **3** contains a six-membered ring as in **2**. While it is possible to propose structures for **3**, they would be only speculative at this time.

The reaction of **2** with $Ru_3(CO)_{12}$ (eq 4), under the same room-temperature conditions as the reaction of **1** (eq 3), also gives products **3** and **4**. This is not surprising, since isomers **1** and **2** have been observed previously to give the same products in their reactions, as noted in the Introduction. In reaction 4, **3** and **4** are formed in nearly equal amounts (29% and 32%, respectively). In addition, a significant amount (27%) of **5** is formed. Since **5** is known[21] to form in the reaction of **2** with CO, it could originate in eq 4 from the reaction of **2** with CO that is liberated in the formation of **4**. Alternatively, it could form by direct transfer of CO from $Ru_3(CO)_{12}$ to **2**.



Reactions of 1 and 2 with $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$. Isomer **1** reacts with $Re_2(CO)_{10}$ in THF solvent at room temperature over a 40 h period to give (eq 5) some (18% yield) of the thermodynamically (eq 1) more stable isomer **2** in addition to the two dimeric rhenium compounds Cp*Ir(η^4-2,5-Me_2T·$Re_2(CO)_9$) (**6**) and Cp*Ir(η^4-SC_3H_2MeC(=O)Me)[$Re_2(CO)_9$] (**7**), isolated in 34 and 31% yields, respectively. Orange-yellow **6** has the composition Cp*Ir(η^4-2,5-Me_2T·$Re_2(CO)_9$), which is supported by its carbon−hydrogen elemental analysis; the heaviest ion observed in the mass spectrum is M^+ − 5CO. The ^1H NMR spectrum contains peaks for H3,-H4 at δ 4.59 s and for the equivalent methyl groups at δ 1.26 s, which are characteristic of the Cp*Ir(η^4-2,5-Me_2T) ligand coordinated through the sulfur as discussed for compound **4**.



The structure (Figure 2) of **6**, which was established by an X-ray diffraction study, shows that it is a CO-substituted product of $Re_2(CO)_{10}$ with the sulfur-coordinated Cp*Ir(η^4-2,5-Me_2T) (**1**) ligand in an equatorial position. The structure is similar to that of $Re_2(CO)_9(CNBu^t)$, in which the isocyanide is also equatorial.[32,33] As in $Re_2(CO)_{10}$ and $Re_2(CO)_9(CNBu^t)$,[32,33] the equatorial ligands in the halves of the molecule are staggered with respect to each other. The Re−Re bond distance (3.051(1) Å) in **6** is similar to that (3.048(2) Å) in $Re_2(CO)_9(CNBu^t)$ but is slightly longer than that in $Re_2(CO)_{10}$ (3.041(1) Å). Excluding the Re−CO bond to C(7), which is *trans* to the sulfur ligand, the average Re−CO bond distance (1.99 Å) to the equatorial CO ligands is longer than the average Re−CO distance (1.93 Å) to the axial CO ligands; the same difference was noted in $Re_2(CO)_{10}$[34] and $Re_2(CO)_9(CNBu^t)$[32] and was attributed to competition of trans CO ligands for π-bonding electrons on the metals. Increased π-bonding to CO accounts for the shorter Re−C(7) distance (1.91(2) Å) to the CO *trans* to the relatively poorly π-accepting sulfur of ligand **1**. The geometry of the Cp*Ir(η^4-2,5-Me_2T) ligand in **6** is very similar to that in **4**. The sulfur is bent out of the C(11)−C(12)−C(13)−C(14) plane by 0.883 Å away from the Ir. Also, the Cp* plane (C(16)−C(20)) is nearly coplanar (3.6° dihedral angle) with the C(11)−C(12)−C(13)−C(14) plane. As in the other complexes of Cp*Ir(η^4-2,5-Me_2T), the C−S bond lengths (1.82(1), 1.84(1) Å) are significantly longer than those (1.714(1) Å)[4] in thiophene itself.

The other rhenium complex formed in reaction 5, **7**, was unexpected. X-ray diffraction studies of pale yellow crystals of **7** show that it has a structure (Figure 3) in which one of the CO groups in $Re_2(CO)_{10}$ is substituted by the sulfur of the acyl−thiolate ligand in Cp*Ir(η^4-

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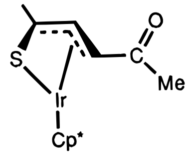
E:



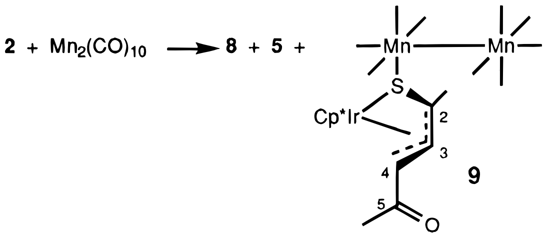
$SC_3H_2MeC({=}O)Me$) (**E**),whose structure was established previously.[35] In fact, the bond distances and angles in the Cp*Ir(η^4-$SC_3H_2MeC({=}O)Me$) portion of **7** are the same within experimental error as those in **E**. As in **E**, the η^4-$SC_3H_2MeC({=}O)Me$ ligand in **7** is coordinated to the Ir through the sulfur and the three carbon atoms (C(2), C(3), C(4)), which form an η^3-allyl group. The C(2)−C(3) (1.405(13) Å) and C(3)−C(4) (1.437(13)) distances of this group are the same within experimental error. Even the Ir−S bond length (2.391(2) Å) in **7** is the same as that in **E**, despite coordination of the sulfur to Re. The $Re_2(CO)_9$ portion of **7** is very similar to that in **6**. The equatorial ligands on the two Re atoms are staggered with respect to each other. As in **6**, the average Re−CO distance to the equatorial CO groups (1.98 Å) is longer than to the axial CO's (1.94 Å). Also, the Re−C(13) distance to the CO *trans* to the sulfur is the shortest Re−CO bond in the molecule. The Re−Re distance (3.0399(7) Å) is slightly shorter than that (3.051(1) Å) in **6** but is the same as in $Re_2(CO)_{10}$ (3.041(1) Å).[34] The ^{1}H NMR spectrum of **7** shows doublets for H(3),H(4) at δ 5.67 and 2.63, while singlets for the methyl groups are observed at δ 2.27 and 2.03. These chemical shifts are the same as those for **E**.

The formation of **7** in reaction 5 raises questions about the origin of the oxygen atom in the acyl group and the mechanism of the reaction. Although we do not now have answers to these questions, they require an explanation because **7** is formed in reasonable yield (31%). Moreover, the yield of **7** is twice as high (66%) when it is prepared from the Cp*Ir(*C,S*-2,5-Me_2T) isomer (**2**) and $Re_2(CO)_{10}$ under the same conditions (room temperature, THF solvent, 30 h) as reaction 5. There are three possible sources of the oxygen atom in **7**. One is O_2, which is known[22] to react with both **1** and **2** at room temperature in toluene over a 12 h period to form the acyl−thiolate **E**. This is an unlikely source, since neither **1** nor **2** reacts with adventitious O_2 to give **E** when stirred under a N_2 atmosphere under the reaction conditions; however, $Re_2(CO)_{10}$ is known[36] to catalyze the O_2 oxidation of cyclohexanone to adipic acid. Since the conditions (96 °C, 600 psi of O_2) for this reaction are much more strenuous than those in eq 5, it is unlikely that $Re_2(CO)_{10}$ catalyzes the oxidation of **1** and **2** to give **E**, which subsequently coordinates to the rhenium. A second possible source of oxygen is the THF solvent. Transfer of the THF oxygen atom to form a Mo=O oxo complex has been observed to occur when $Mo_3S_7Br_4$ is treated with P(*n*-Bu)$_3$ in THF.[36] Nucleophilic attack of the phosphine on O-coordinated THF is proposed to lead to the observed products $Mo_2O_2S_2Br_4^{2-}$ and $(n\text{-}Bu)_3P(CH_2)_4P(n\text{-}Bu)_3^{2+}$. In reaction 5 and the analogous reaction of **2** with $Re_2(CO)_{10}$, there is no basic nucleophile such as a phosphine. If THF were the source of oxygen, another mechanism for oxygen atom transfer would likely be involved. The third possible source of the oxygen atom is the CO in $Re_2(CO)_{10}$. There are a few examples in which an oxygen atom is transferred from a CO ligand to an oxygen acceptor. This type of reaction occurs between $Re_2(CO)_{10}$ and $Cp_2Ta(CH_2)(CH_3)$, which gives $Cp_2Ta({=}O)(CH_3)$.[38] However, this is a reaction quite different from those involving **1** and **2**. Reaction 5 and the corresponding reaction of **2** with $Re_2(CO)_{10}$ require further study before this oxygen atom transfer is understood.

Like $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$ also reacts with **1** and **2**; however, the products are quite different. The reaction of compound **1** with $Mn_2(CO)_{10}$ at room temperature for 24 h in THF solvent yields (eq 6) only products resulting from the transfer of CO from Mn to Ir. The Cp*Ir(CO)$_2$ (**8**)[15,39] product (42%) nominally forms by displacement of the η^4-2,5-Me_2T ligand; however, it probably does not result from a reaction between **1** and free CO, since **1** and CO react[21] to give **5**. Thus, **8** presumably results from a more direct transfer of CO from $Mn_2(CO)_{10}$. Product **5** (53%) in eq 6 could result from the reaction of **1** with CO.

$$\mathbf{1} + Mn_2(CO)_{10} \rightarrow \underset{\mathbf{8}}{Cp^*Ir(CO)_2} + \underset{\mathbf{5}}{Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)} \quad (6)$$

The reaction (eq 7) of **2** with $Mn_2(CO)_{10}$ under the same conditions (room temperature, 24 h, THF solvent) also gives compounds **8** (31%) and **5** (44%). In addition, a smaller yield (23%) of pale yellow crystalline Cp*Ir(η^4-$SC_3H_2MeC({=}O)Me$)[$Mn_2(CO)_9$] (**9**), the manganese analog of the rhenium complex **7**, was isolated. The structure of **9** was assigned on the basis of its ^{1}H NMR spectrum, which contains doublets for H3 and H4 at δ 5.68 and 2.65 and singlets for the methyl groups at δ 2.27 and 2.03; the positions of these signals are almost identical with those for **7**. Also, the IR spectrum of **9** (2056 s, 2001 vs, 1971 m, 1920 s, 1722 s, 1656 s cm^{-1}) in the ν(CO) region is very similar to that for **7** (2097 w, 2034 s, 1988 vs, 1952 m, 1912 s, 1723 s, 1653 s cm^{-1}). Although the yield of **9** in reaction 7 is much lower than that (66%) resulting from the reaction of **2** with $Re_2(CO)_{10}$, the incorporation of the oxygen atom into **9** poses the same mechanistic questions that were discussed for **7**.



(7)

Reactions of 1 and 2 with [(η^6-C_6H_6)RuCl$_2$]$_2$. The Cp*Ir(η^4-2,5-Me_2T) (**1**) isomer reacts (eq 8) with [(η^6-

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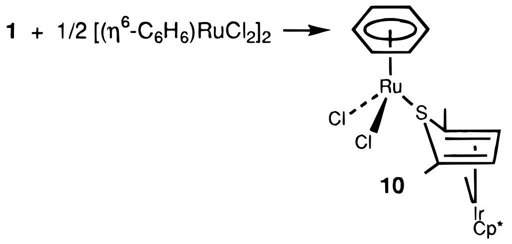
$C_6H_6)RuCl_2]_2$ at 35 °C in benzene over a 4 h period to give a high isolated yield (80%) of orange crystalline Cp*Ir(η^4-2,5-Me_2T·Ru(η^6-C_6H_6)Cl_2) (**10**). This composition is supported by carbon−hydrogen elemental analyses and a molecular ion in the mass spectrum. In the ^1H NMR spectrum, the singlet at δ 5.55 is assigned to η^6-benzene, while singlets at δ 4.79 and 1.46 may be assigned to the H3,H4 and methyl groups, respectively. The chemical shifts of these protons are characteristic of the 2,5-Me_2T group in a Cp*Ir(η^4-2,5-Me_2T) (**1**) ligand that is sulfur-coordinated to a metal center, as in **4** and **6**. The formation of **10** results from cleavage of the bridging Cl−Ru bonds. There is no evidence for a product in which the benzene is replaced by the η^6-iridathiabenzene group Cp*Ir(*C*,*S*-2,5-Me_2T) (**2**).



(8)

The reaction of **2** with [(η^6-C_6H_6)$RuCl_2$]$_2$ under the same conditions as reaction 8 yields (69%) the dark red product **11**. Unfortunately, crystals of **11** suitable for X-ray diffraction were not obtained; however, its composition based on carbon−hydrogen elemental analysis and the molecular ion in the mass spectrum corresponds to Cp*Ir(2,5-Me_2T)[(η^6-C_6H_6)$RuCl_2$] (**11**). While the elemental compositions of **10** and **11** are the same, the structure of **11** must be quite different from that of **10**, since the two methyl groups in the original 2,5-Me_2T ligand are inequivalent in **11** (δ 2.28, 1.98) in the ^1H NMR spectrum. The original H3,H4 protons in the 2,5-Me_2T ligand are also inequivalent (δ 5.37 d, 5.28 d) in **11**. This pattern suggests the presence of a ring-opened 2,5-Me_2T ligand of the type in **2**. The chemical shift of the η^6-benzene in **11** (δ 5.73) is similar to that in **10** (δ 5.55). On the basis of present evidence, it is not possible to assign an unequivocal structure to **11**. It is interesting to note, however, that isomers **1** and **2** give quite different products in their reactions with [(η^6-C_6H_6)-$RuCl_2$]$_2$. This is surprising in view of other reactions of **1** and **2** cited in the Introduction as well as others described in this present report; **1** and **2** usually give the same products, although the yields may be different.

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Supporting Information Available: For **4**, **6**, and **7**, tables of atomic coordinates and complete bond distances, angles, torsion angles, and least-squares planes (37 pages). Ordering information is given on any current masthead page.

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