slippage is observed for the C_5H_4SPh ring.

Metallocenic systems containing functionalized Cp rings are desirable starting materials for the preparation of heterobimetallic systems.[21] Although it is unlikely that complex **3** can be utilized for this purpose, the possibility of generalizing this reaction pathway and the presence in the molecule of two reactive moieties (μ-$NSiMe_3$ and η^1:η^5-C_5H_4) give some new synthetic perspectives in this regard. We are unable at the moment to explain the reasons for the failure of formation of fulvalene in complex **2**. Further work is in progress.

Acknowledgment. We are indebted to the generosity of the Chemistry Department at the University of California, Los Angeles, CA, for making available the X-ray facility.

Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond angles and distances for **2** and **3** and a table of torsion angles for **3** (32 pages); listing of observed and calculated structure factors (42 pages). Ordering information if given on any current masthead page.

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[21] See for example: (a) Kool, L. B.; Ogasa, M.; Rausch, M. D.; Rogers, R. D. *Organometallics* **1989**, *8*, 1786. (b) Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* **1986**, *5*, 888.

2,5-Dimethylthiophene Coordination to Three Metal Centers in (η^4,S-μ_3-2,5-Me_2T)($IrCp^*$)[$Mo(CO)_2Cp$]$_2$

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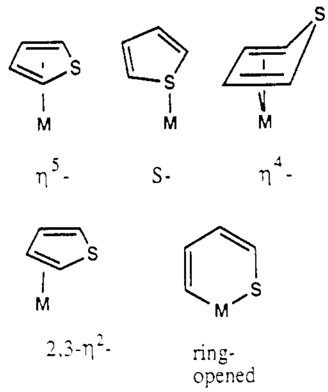
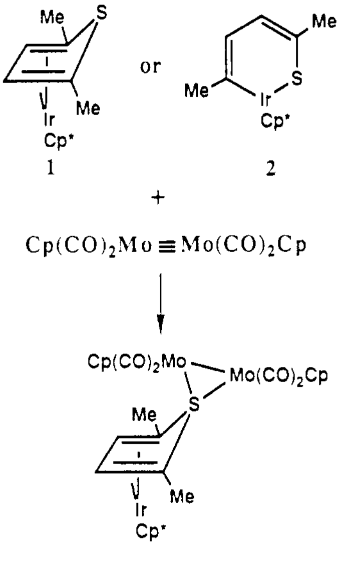
Summary: The reaction of $Cp^*Ir(\eta^4$-2,5-$Me_2T)$, where η^4-2,5-Me_2T is 2,5-dimethylthiophene coordinated through the four ring carbons, with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ gives (η^4,S-μ_3-2,5-Me_2T)($IrCp^*$)[$Mo(CO)_2Cp$]$_2$, in which the bridging thiophene is η^4-coordinated to the Ir and bonded via the sulfur to both Mo atoms. The same product is obtained from the ring-opened isomer of $Cp^*Ir(2,5$-$Me_2T)$. The structure of the product, which is the first example of a thiophene coordinated to three metal centers, was established by X-ray crystallography.

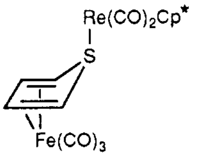
Recent interest in model studies[2] of the hydrodesulfurization of thiophenes has led to the discovery of several new modes of thiophene coordination to transition metals. Five types of coordination to one metal center (Chart I) have been reported. Of these, the η^5- and S-bound forms have been known the longest.[2] Indirect evidence[3] for η^4-thiophene in $Cp^*Ir(\eta^4$-thiophene) was followed by a full structural characterization[4] of $Cp^*Ir(\eta^4$-2,5-$Me_2T)$ (where 2,5-Me_2T is 2,5-dimethylthiophene and Cp^* is η^5-C_5Me_5) and then $Cp^*Rh(\eta^4$-TMT) (where TMT is tetramethylthiophene).[5] The 2,3-η^2-thiophene complex $(NH_3)_5Os(2,3$-η^2-thiophene$)^{2+}$ was recently[6] described, as was the ring-opened isomer of $Cp^*Ir(2,5$-$Me_2T)$.[7] There is only one example of a complex in which the thiophene is coordinated to two metals:[8]

Chart I



Scheme I





In this communication, we report the first complex, (η^4,S-μ_3-2,5-Me_2T)($IrCp^*$)[$Mo(CO)_2Cp$]$_2$, in which a thiophene is coordinated to three metals.

The title complex (**3**) was prepared by the reaction (Scheme I) of $Cp^*Ir(\eta^4$-2,5-$Me_2T)$ (**1**;[4] 25 mg, 0.057 mmol) with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (30 mg, 0.069 mmol)[9] in 30 mL of tetrahydrofuran at room temperature for 24 h. The resulting green solution was evaporated to dryness in vacuo, and the residue was chromatographed on neutral alumina with hexane/CH_2Cl_2/Et_2O (10:2:1) as the eluant. A green solution containing the product was eluted and evaporated to dryness; **3** was obtained as deep green

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[1] Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

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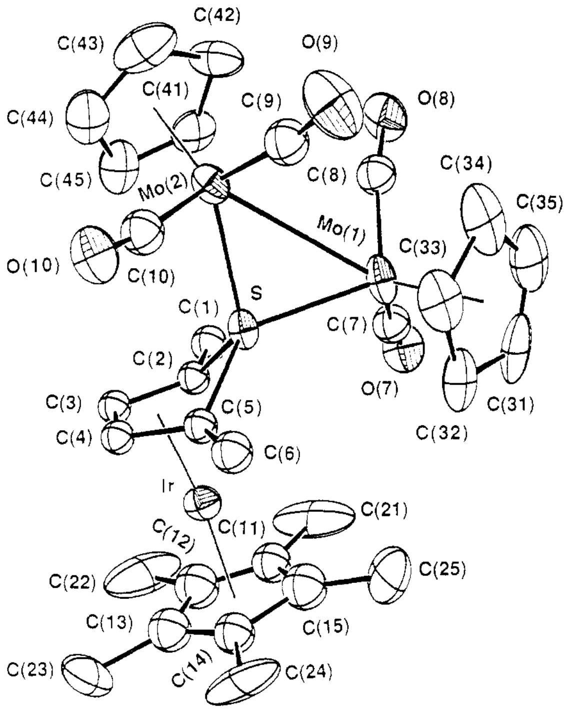

Figure 1. ORTEP drawing of (η^4,*S*-μ_3-2,5-Me_2T)(IrCp*)[Mo(CO)$_2$Cp]$_2$ (**3**). Selected bond distances (Å) and angles (deg): C(2)–S = 1.81 (2), C(5)–S = 1.83 (1), C(2)–C(3) = 1.44 (2), C(3)–C(4) = 1.48 (2), C(4)–C(5) = 1.40 (2), C(1)–C(2) = 1.55 (2), C(5)–C(6) = 1.52 (2), Mo(1)–S = 2.342 (3), Mo(2)–S = 2.343 (5), Mo(1)–Mo(2) = 3.144 (2), Mo(1)–C(7) = 1.92 (2), Mo(1)–C(8) = 1.95 (2), Mo(2)–C(9) = 1.90 (2), Mo(2)–C(10) = 1.97 (1), Ir–C(2) = 2.12 (2), Ir–C(3) = 2.14 (2), Ir–C(4) = 2.13 (2), Ir–C(5) = 2.14 (2); C(2)–S–C(5) = 81.7 (6), C(1)–C(2)–C(3) = 122 (1), C(4)–C(5)–C(6) = 124 (1), C(7)–Mo(1)–C(8) = 81.8 (8), C(9)–Mo(2)–C(10) = 80.3 (6), Mo(1)–S–Mo(2) = 84.3 (1), S–Mo(1)–Mo(2) = 47.9 (1), S–Mo(2)–Mo(1) = 47.9 (1).

crystals[10] in 38% yield after recrystallization of the residue from hexane/CH_2Cl_2 at −80 °C.

The structure of **3** determined by X-ray crystallography (Figure 1) contains a thiophene that is coordinated via the four ring carbon atoms (η^4) to the iridium and through its sulfur to the two Mo atoms. The structural features of the Cp*Ir(η^4-2,5-Me_2T) portion of **3** are nearly the same as that of free Cp*Ir(η^4-2,5-Me_2T) (**1**),[4] except the C–S bond distances (1.81 (2), 1.83 (1) Å) in **3** are slightly longer than the corresponding distances (1.76 (2), 1.79 (2) Å) in **1**. The thiophene ring is folded with an angle of 43.6 (8)° between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes, as compared with a 42° angle in **1**. The methyl carbons, C(1) and C(6), are in the C(2)–C(3)–C(4)–C(5) plane within experimental error, and the sulfur is 0.95 Å out of this plane. The S–Mo(1)–Mo(2) plane is essentially perpendicular to both the C(2)–C(3)–C(4)–C(5) (92.4 (5)°) and C(2)–S–C(5) (91.2 (5)°) planes. The Mo(1)–Mo(2) distance (3.144 (2) Å) is slightly shorter than that (3.235 (1) Å)[12] in $Cp(CO)_3MoMo(CO)_3Cp$, but not nearly as short a the metal–metal bond in $Cp(CO)_2Mo\equiv Mo(CO)_2Cp$ (2.448 (1) Å).[9,13] The CO ligands in **3** are terminal, unlike those in $Cp(CO)_2Mo\equiv Mo(CO)_2Cp$,[9] in which there are semibridging CO groups. Thus, it appears that the sulfur in **3** acts as a formal four-electron donor to the molybdenum dimer.

The formation of **3** from the reaction of **1** and $Cp(CO)_2Mo\equiv Mo(CO)_2Cp$ appears to be promoted by the strong donor ability of the sulfur in **1**; this donating character has already been demonstrated[4,14] in the reaction of **1** with $Me_2S{\cdot}BH_3$ to form the sulfur adduct Cp*Ir(η^4-2,5-$Me_2T{\cdot}BH_3$). Clearly, the η^4-coordination of thiophene to the iridium activates the thiophene to react with $Cp(CO)_2Mo\equiv Mo(CO)_2Cp$, since there is no reaction between the molybdenum dimer and either thiophene or 2,5-Me_2T under the conditions used to prepare **3**.

Rather remarkably, the ring-opened isomer **2** (Scheme I) (25 mg, 0.057 mmol) also reacts with $Cp(CO)_2Mo\equiv Mo(CO)_2Cp$ (30 mg, 0.069 mmol) in 30 mL of THF to give **3** in 44% isolated yield. This reaction occurs at 0–15 °C over an 8-h period, conditions even milder than those used in the reaction of **1**. At this point, the mechanisms of the reactions of the molybdenum dimer with **1** and **2** are not understood, but it is possible that the known[7] isomerization of **1** to **2** is involved. Further studies of **3** and related derivatives are in progress.

Acknowledgment. We thank Dr. Lee M. Daniels for the crystal structure determination of **3**. The loan of $IrCl_3$ from Johnson Matthey, Inc., is greatly appreciated.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes and dihedral angles (16 pages); a listing of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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[10] Anal. Calcd for $C_{30}H_{33}O_4SIrMo_2$: C, 41.24; H, 3.81. Found: C, 41.46; H, 3.86. IR (CH_2Cl_2, ν(CO)): 1910 s, 1870 vs, 1828 s, 1805 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.29 (s, 5 H, Cp), 5.16 (s, 5 H, Cp), 4.73 (s, 1 H), 4.62 (s, 1 H), 1.98 (s, 15 H, Cp*), 0.947 (s, 3 H, CH_3), 0.873 (s, 3 H, CH_3). EIMS: *m/e* 878 (M^+, based on ^{98}Mo). Melting point: >230 °C dec.

[11] Crystal data for **3**: dark green crystal, 0.19 × 0.15 × 0.08 mm, monoclinic, *C*2/*c*, a = 30.767 (8) Å, b = 9.670 (1) Å, c = 26.952 (6) Å, β = 124.05 (1)°, V = 6644 (2) Å^3, Z = 8, ρ_{calcd} = 1.917 g/cm^3, μ(Mo Kα) = 49.64 cm^{-1}. Diffraction data: Enraf-Nonius CAD4 diffractometer, Mo radiation (λ = (Kα) = 0.71073 Å), graphite monochromator, range 4.0° $< 2\theta <$ 45.0°, 4431 reflections, 4335 unique data, 2712 observed data ($I > 3\sigma(I)$), crystal temperature −20 (1) °C, ω–2θ scans, corrected for absorption, Lorentz, and polarization effects. Solution and refinement: centric space group indicated by intensity statistics; Ir and Mo positions given by direct methods, other atoms taken from difference maps; hydrogen atoms not included; one molecule of CH_2Cl_2 in the lattice refined as a disordered model of two independent units with the total occupancy restrained to unity; refinement of 294 parameters converged with R_F = 0.0465, R_{wF} = 0.0609, and goodness of fit 1.05; largest peak in the final difference Fourier map 1.4 (1) e/Å^3.

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Easy Double Metalation of a Diphosphinomethane Ligand: Structure of the Remarkable Octagold Cage Complex $[Au_8Cl_2\{\mu_3\text{-}(MeO)_2PCHP(OMe)_2\}_2\{\mu_4\text{-}(MeO)_2PCP(OMe)_2\}_2]{\cdot}CHCl_3$

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Summary: Reaction of AuCC-*t*-Bu with $(MeO)_2PCH_2P(OMe)_2$ (dmopm), followed by recrystallization first from CH_2Cl_2 and then from $CHCl_3$, gave the title cage complex, which contains four fused nine-membered rings and the first structurally characterized example of a $[\mu_4\text{-}R_2PCPR_2]^{2-}$ ligand, formed by easy deprotonation of dmopm.

The ligands $R_2PCH_2PR_2$ (R = alkyl, aryl, alkoxy, aryloxy) are often used as binucleating ligands and have been

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