The heat of reaction, ΔH_2, for the binding of *cis*-cyclooctene to the solvated intermediate **2** to generate *cis*-**1** was found to be −14.3 ± 0.9 kcal/mol. This is somewhat more exothermic than the −12.2 kcal/mol olefin–metal bond enthalpy found in (1-hexene)$Cr(CO)_5$.[7c] A much more dramatic effect is seen in the enthalpy of binding of *trans*-cyclooctene to intermediate **2**. In this case, $\Delta H_2 = -19.5 \pm 2.5$ kcal/mol. Thus, the metal–olefin bond in *trans*-**1** is more than 5 kcal/mol stronger than that in *cis*-**1**; i.e., $\Delta\Delta H_2 \approx 5$ kcal/mol.

Coordination of an olefin to a metal results in greater sp^3 hybridization at the olefinic carbons, the limiting case being formation of a metallacyclopropane complex.[15] If the hybridization change reduces strain by introducing greater flexibility into the olefin, then the metal–olefin interaction should be stronger.[3–6,15] Thus, our result that $\Delta\Delta H_2 \approx 5$ kcal/mol is consistent with the observation that *trans*-cyclooctene has ~10.4 kcal/mol of strain relative to *cis*-cyclooctene.[16,17] An estimate of the strain relief possible in the *cis*/*trans*-cyclooctene system is seen upon cyclopropanation of the double bond to form the corresponding *cis*- and *trans*-bicyclo[6.1.0]nonanes. The heats of formation of these two bicyclononanes differ by less than 1 kcal/mol.[18] Thus, while coordination of the cyclooctene double bond to $Cr(CO)_5$ relieves half of the strain associated with the trans double bond relative to the cis double bond, cyclopropanation relieves nearly *all* of this strain. In addition to rehybridization, different steric interactions may also contribute to $\Delta\Delta H_2$, although we believe that this effect is minimal (vide infra).

The rate of substitution of solvent in intermediate **2** by both *cis*- and *trans*-cyclooctene exhibited an apparent first-order dependence on the concentration of the cyclooctene. The data are plotted in Figure 1. The rates of these two substitution processes are nearly identical with second-order rate constants k_2 for *cis*- and *trans*-cyclooctene, respectively, of $(1.4 \pm 0.3) \times 10^7$ and $(1.7 \pm 0.2) \times 10^7$ L/(mol s) (Table I).[19] These rate constants are very similar to previously reported rate constants for reaction of intermediate **2** with a number of different ligands.[7c,20] From comparisons of the rates and enthalpies of reaction of α-methyl-substituted and unsubstituted pyridine and THF ligands with $Cr(CO)_5S$ in heptane solution, it is apparent that steric influences which have an effect on the enthalpy of reaction also have a substantial effect on the rate of reaction.[21] The lack of a substantial difference in the rate constants k_2 for *cis*- and *trans*-cyclooctene supports the conclusion that strain relief and not steric bulk is the primary component in $\Delta\Delta H_2$.

Acknowledgment. We acknowledge the National Institutes of Health (Grant No. GM-42704-01) and the donors of the Petroleum Research Fund, administered by the American Chemical Society for financial support of this research and Professor Tom Flood for helpful discussions.

Registry No. *trans*-1, 92937-36-5; *cis*-1, 92889-73-1.

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(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(16) This is the average of two values: 11.4 kcal/mol (Rogers, D. W.; von Voithenberg, H.; Allinger, N. L. *J. Org. Chem.* **1978**, *43*, 360–361) and 9.3 kcal/mol (Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133–4136).

(17) Although crystallographic data are unavailable for complexes *cis*-1 and *trans*-1, ^{13}C NMR data confirm the greater sp^3 hybridization at the olefinic carbons in the trans complex compared to that in the cis complex.[6b] Further support for a substantial change in hybridization is found in comparison of X-ray data of the free *trans*-cyclooctene moiety to those of Fe-*trans*-cyclooctene complexes. The double-bond dihedral angle *decreases* from 138° in the free *trans*-cyclooctene structure to 125° upon complexation in $Fe(CO)_3$(*trans*-cyclooctene)$_2$. See ref 6c and: Ermer, O.; Mason, S. A. *Acta Crystallogr.* **1982**, *B38*, 2200–2206. Such a decrease in the dihedral angle must substantially reduce the strain inherent in the *trans*-cyclooctene moiety.

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(19) The apparent positive intercepts in Figure 1 may be due to reaction with impurities. Although the scatter in our data makes us wary of drawing any conclusions based on the *y* intercepts, this point deserves to be addressed. The only likely impurity in these experiments is water in the heptane. Given the low solubility of water in hydrocarbons (~3 mmol at 298 K; see: Goldman, S. *Can. J. Chem.* **1974**, *52*, 1668), water will have a noticeable effect on k_{obsd} only at the lower concentrations of cyclooctene (≲0.03 M). However, the rate constants k_2 are derived from the *slopes* of the plots in Figure 1, and therefore the values of k_2 we obtained are *not dependent* on reaction with an impurity in the solvent. Since the enthalpic data have no concentration dependence, the contribution of reaction with the impurity either is negligible or has an enthalpy of reaction very similar to that of the reactions being examined. We thank the reviewers for bringing up these points.

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(21) For example, in heptane solution, pyridine reacts with $Cr(CO)_5S$ more exothermically (2.3 kcal/mol) and faster (10 times) than does 2-picoline.[7c]

Cyclopentadiene Functionalization versus Fulvalene Formation in the Oxidation of $[(\eta^1{:}\eta^5\text{-}C_5H_4)ZrCp(PMe_3)]_2$: Preparation and Crystal Structures of $[(\eta^1{:}\eta^5\text{-}C_5H_4)ZrCp]_2[\mu\text{-}NSiMe_3]$ and $[(\eta^1{:}\eta^5\text{-}C_5H_4)][\mu\text{-}NSiMe_3][CpZrSPh][Cp(C_5H_4SPh)Zr]$

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Summary: Oxidation of $[CpZr(PMe_3)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ (**1**) by Me_3SiN_3 led to the formation of the dinuclear imido-bridged complex $[CpZr(\eta^1{:}\eta^5\text{-}C_5H_4)]_2(\mu\text{-}NSiMe_3)$ (**2**). Reaction of **2** with PhSSPh cleaved one of the two Zr–$(\eta^1{:}\eta^5\text{-}C_5H_4)$ bonds, forming the asymmetric dinuclear complex $[(\eta^1{:}\eta^5\text{-}C_5H_4)][\mu\text{-}NSiMe_3][CpZrSPh][Cp(C_5H_4SPh)Zr]$ (**3**). Crystal data for **2** and **3** are as follows: **2**, orthorhombic, space group $Pn2_1a$, $a = 17.140$ (1) Å, $b = 24.973$ (1) Å, $c = 10.259$ (1) Å, $Z = 8$, $R = 0.032$ ($R_w = 0.040$) for 2979 observed reflections; **3**, triclinic, space group $P\bar{1}$, $a = 9.943$ (1) Å, $b = 10.742$ (1) Å, $c = 15.417$ (2) Å, $\alpha = 75.736$ (9)°, $\beta = 79.58$ (1)°, $\gamma = 87.59$ (1)°, $Z = 2$, $R = 0.024$ ($R_w = 0.032$) for 6572 observed reflections.

The most attractive characteristic of the fulvalene dianion as a ligand is its ability to enforce very short contacts between two metals (up to the metal–metal bond range),[1]

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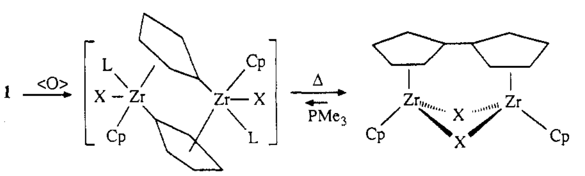
(1) See for example: (a) Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518. (b) Gambarotta, S.; Chiang, M. Y. N. *Organometallics* **1987**, *6*, 897.

Scheme I



<O>= R_3PX_2[R=n-Bu,Me; X=Cl,Br,I; L=PMe$_3$], PhSSPh[X=SPh]; Me_2PPMe_2 [X=PMe$_2$]

giving considerable potential for modeling[2] and reactivity studies.[3] In spite of these promising features, however, the chemistry of the fulvalene-containing systems is quite poorly developed, probably due to the limited availability of synthetic pathways.[4] Diversified fulvalene complexes are almost invariably present among the products obtained from the attempted syntheses of low-valent early-transition-metal metallocenes.[5] In these cases, the binucleating fulvalene ligand is probably formed via the reductive coupling of two bridging $\eta^1{:}\eta^5$-C_5H_4 rings,[1b,6] which are in turn formed in a spontaneous *deactivation* of the highly reactive low-valent metallocenes "Cp_2M".[7]

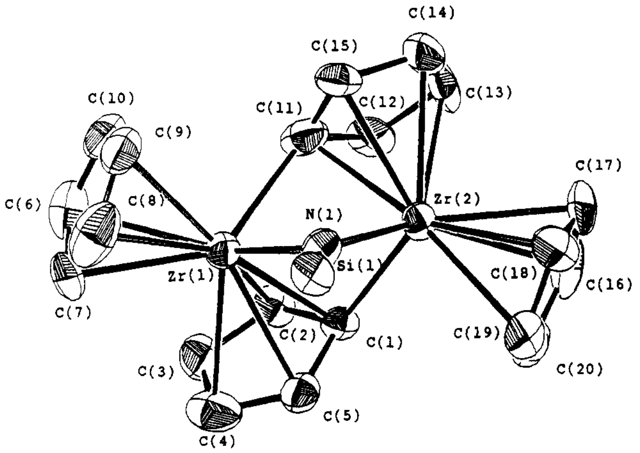


Figure 1. ORTEP drawing of **2** showing the labeling scheme (50% probability level). Hydrogen atoms and methyl groups on silicon have been omitted for clarity reasons. Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): Zr1–N1 = 2.136 (8), Zr2–N1 = 2.103 (9), Si1–N1 = 1.716 (9), Zr1–C1 = 2.41 (1), Zr2–C1 = 2.32 (1), Zr1–C11 = 2.31 (1), Zr2–C11 = 2.41 (1), Zr1···Zr2 = 3.073 (1); Zr1–N1–Zr2 = 92.9 (3), Zr1–C1–Zr2 = 80.9 (3), Zr1–C11–Zr2 = 81.1 (4), N1–Zr1–C11 = 82.4 (4).

We have recently found that the simple oxidation of $[\mathrm{CpZr(PMe_3)}(\eta^1{:}\eta^5\text{-}\mathrm{C_5H_4})]_2$ (**1**) with an appropriate reagent rationalizes this type of reaction into a synthetically useful route to *cis*- and *trans*-fulvalene Zr(III) and -(IV) compounds (Scheme I).[1b,8] The high degree of rotational freedom of the fulvalene around the C–C linkage can be inhibited in these complexes with bridging ancillary ligands able to impose a rigid cis configuration on the two metal centers.[8b] Bridging imido groups (μ-NR) may be particularly desirable for this purpose because of their electronic flexibility[9] and the possibility of adjusting their steric bulk by varying the size of the organic fragment attached to the bridging nitrogen.[10]

These reasons prompted us to study the oxidation of **1** with organic substrates that may function as possible sources of nitrene fragments. In this paper, we wish to describe the result of the reaction of **1** with an organic azide.

The reaction of complex **1** with Me_3SiN_3 proceeded slowly at room temperature but was completed within a few minutes in boiling toluene, evolving dinitrogen and giving a deep blue solution from which $[\mathrm{CpZr}(\eta^1{:}\eta^5\text{-}\mathrm{C_5H_4})]_2[\mu\text{-}\mathrm{NSiMe_3}]$ (**2**) can be isolated in high yield (88%) as deep blue crystals (eq 1).[11] Fulvalene did not form in

$$\underset{\mathbf{1}}{[\mathrm{CpZr(PMe_3)}(\eta^1{:}\eta^5\text{-}\mathrm{C_5H_4})]_2} + \mathrm{Me_3SiN_3} \xrightarrow{-\mathrm{N_2}} \underset{\mathbf{2}}{[\mathrm{CpZr}(\eta^1{:}\eta^5\text{-}\mathrm{C_5H_4})]_2(\mu\text{-}\mathrm{NSiMe_3})} \quad (1)$$

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(10) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

this reaction, as the presence of two intact bridging η^1:η^5-C_5H_4 rings in complex **2** has been demonstrated by an X-ray crystal structure.[12] The asymmetric unit consists of two crystallographically independent but chemically equivalent molecules. The geometry of one of these is shown in Figure 1. Each molecule consists of two CpZr fragments bridged by one μ-$NSiMe_3$ imido group and two η^1:η^5-C_5H_4 rings. The sterically demanding μ-$NSiMe_3$ group forces the two bridging rings quite close together without affecting their geometries, which appear to be quite normal and similar to those in the Ti complex $[CpTi(PMe_3)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$.[13] The comparable distances of the two bridgehead carbon atoms from the two zironium atoms (Zr1–C1 = 2.41 (1) Å, Zr2–C1 = 2.32 (1) Å, Zr1–C11 = 2.31 (1) Å, Zr2–C11 = 2.41 (1) Å) are considerably longer than those observed in other zirconium alkyl systems.[14] The imido group Me_3SiN is placed in the region between the two η^1:η^5-Cp rings, forming significantly short Zr–N distances (Zr1–N1 = 2.136 (8) Å, Zr2–N1 = 2.103 (9) Å) suggestive of appreciable pπ–dπ N→Zr interactions.[15] The N–Si bond length (N1–Si1 = 1.716 (9) Å) is also quite short.[16] Finally, the surprisingly short Zr···Zr nonbonding distance (Zr1···Zr2 = 3.073 (1) Å), which is shorter than in metallic zirconium (3.1789 Å),[17] and the very narrow angle formed by the imido group with the two Zr atoms suggest that the interaction of the zirconium centers with the two bridging rings is also strong. These structural features indicate the presence of a considerable electronic delocalization in this system, further emphasized by the very unusual deep blue color of this tetravalent zirconium species.

Compound **2** is surprisingly stable and provides a rare example of η^1:η^5-Cp rings being observed in a tetravalent zirconium species. In spite of the short distance between the two bridgehead carbon atoms (C1···C11 = 2.893 Å) and the high oxidation state of the metal atoms, the reductive elimination to form fulvalene could not be achieved through either thermolysis or photolysis. Nevertheless, the cleavage of the Zr–(η^1:η^5-C_5H_4) σ bond has been obtained by reaction with the mild oxidizing reagent PhSSPh. However, in this case the reaction took an unexpected pathway, forming the new dinuclear species $[(\eta^1{:}\eta^5\text{-}C_5H_4)][\mu\text{-}NSiMe_3][CpZrSPh][Cp(C_5H_4SPh)Zr]$ (**3**) through a slow reaction in toluene (eq 2).[18]

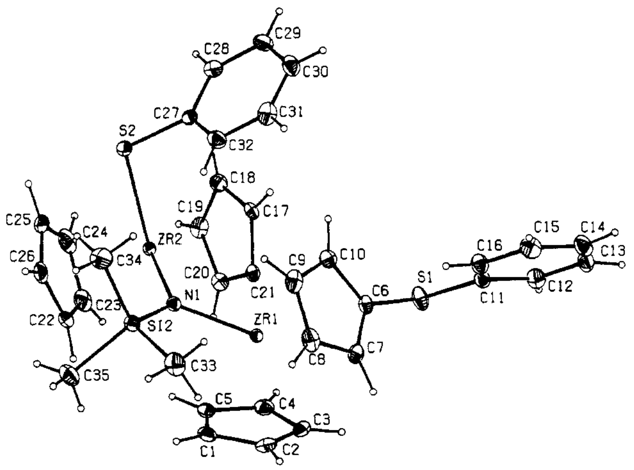
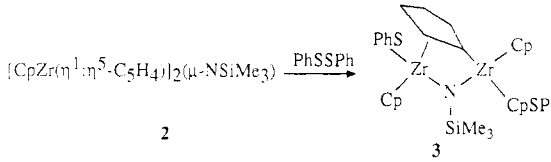


Figure 2. ORTEP drawing of **3** showing the labeling scheme (50% probability level). Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): Zr1–N1 = 2.076 (2), Zr2–N1 = 2.131 (2), N1–Si = 1.749 (2), Zr2–S2 = 2.5614 (6), Zr1···Zr2 = 3.3762 (5); Zr1–N1–Zr2 = 106.71 (7), Zr2–S2–C27 = 108.46 (6), N1–Zr2–S2 = 105.69 (4), C6–S1–C11 = 102.14 (9).



(2)

2

3

Complex **3** can be regarded as a product of the metathetic reaction between an S–S bond and one of the two Zr–(η^1:η^5-C_5H_4) σ bonds of **2**. The structure of **3**, as demonstrated by X-ray analysis,[19] showed several remarkable features. The complex is dinuclear, with the two asymmetric CpZr fragments linked by the bridging μ-$NSiMe_3$ group and the residual η^1:η^5-C_5H_4 ring. The two inequivalent Zr atoms bear the SPh and CpSPh groups, respectively. The geometry of the bridging imido group is normal and compares well with that of complex **2**. In contrast to the case of **2**, however, the bridging η^1:η^5-C_5H_4 ring in **3** is symmetrically η^5-bonded to Zr2, while the bridgehead carbon atom reaches a noticeably short bond distance with the second Zr atom (Zr1–C21 = 2.250 (2) Å). This value is also not far from that found in $[Cp_2ZrCCR]_2$, where the short Zr–C(acetylide) distance (Zr–C = 2.188 Å) is explained in terms of significant Zr→C π conjugation and resulting carbenoid character.[20] Finally, a small ring

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(11) A toluene solution of **1** (5.0 g, 8.4 mmol) in toluene (200 mL) was treated with Me_3SiN_3 (1.1 g, 9.5 mmol). The resulting solution slowly turned purple, with evolution of nitrogen. After 12 h the solution was boiled and it turned deep blue. Blue prisms of **2** separated upon concentration, filtration, and cooling at –30 °C (3.9 g, 7.4 mmol, 88% yield). Anal. Cacld (found) for $C_{23}H_{27}Zr_2NSi$: C, 52.37 (52.29); H, 5.12 (5.09); Zr, 34.53 (34.49); N, 2.65 (2.58); Si, 5.31 (5.29). ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ 6.61 (m, 4 H, C_5H_4), 5.25 (s, 10 H, Cp), 6.23 (m, 2 H, C_5H_4), 5.64 (m, 2 H, C_5H_4), 0.04 (s, 9 H, $SiMe_3$). ^{13}C NMR (75 MHz, benzene-d_6 25 °C): δ 153.2 (s, C_5H_4), 133.4 (d, J_{C-H} = 168.1 Hz, C_5H_4), 124.9 (d, J_{C-H} = 172.7 Hz, C_5H_4), 114.6 (d, J_{C-H} = 170.3 Hz, C_5H_4), 109.7 (d, J_{C-H} = 172.7 Hz, Cp), 108.3 (d, J_{C-H} = 168.1 Hz, C_5H_4), 5.7 (q, J_{C-H} = 115.2 Hz, $SiMe_3$).

(12) **2** crystallizes as orthorhombic prisms in the space group $Pn2_1a$. Cell data: a = 17.140 (1) Å, b = 24.973 (1) Å, c = 10.259 (1) Å, Z = 8, R = 0.032, R_w = 0.040, GOF = 1.32 for a fit of 486 variables to 2979 observations. The structure was solved by standard Patterson methods; hydrogen atom positions were located and not refined. Details on crystal data and refinement are given as supplementary material.

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(18) A solution of **2** (0.83 g, 1.6 mmol) in toluene (80 mL) was treated with PhSSPh (0.4 g, 1.8 mmol). The resulting solution gradually changed from blue to bright yellow, and bright yellow solid separated during the slow reaction. After 24 h, the mixture was boiled and filtered while hot. After the solution slowly cooled at room temperature, bright yellow crystals of **3** separated (1.0 g, 1.3 mmol, 81% yield). Anal. Calcd (found) for $C_{35}H_{37}NS_2SiZr_2$: C, 56.32 (56.87); H, 4.99 (5.00); Zr, 24.44 (24.26); Si, 8.59 (8.48). ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ 7.54 (pseudo d, 2 H, SPh), 7.16–7.06 (m, 4 H, SPh), 6.97–6.86 (m, 4 H, SPh), 6.29 (m, 1 H, C_5H_4), 6.13 (m, 1 H, C_5H_4), 6.08 (m, 2 H, CpSPh), 6.03 (m, 1 H, CpSPh), 6.00 (m, 1 H, CpSPh), 5.99 (s, 5 H, Cp), 5.92 (s, 5 H, Cp), 5.68 (m, 1 H, C_5H_4), 5.41 (m, 1 H, C_5H_4), 0.39 (s, 9 H, $SiMe_3$).

(19) **3** is triclinic with space group $P\bar{1}$. Cell data: a = 9.943 (1) Å, b = 10.742 (1) Å, c = 15.417 (2) Å, α = 75.736 (9)°, β = 79.58 (1)°, γ = 87.59 (1)°, Z = 2, R = 0.024 (R_w = 0.032) for a fit of 520 variables to 6572 observations. The structure was solved by standard Patterson methods and subsequent partial structure expansion; hydrogen atom positions were located and refined isotropically. Details on crystal data and refinement are given as supplementary material.

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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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2,5-Dimethylthiophene Coordination to Three Metal Centers in $(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[Mo(CO)_2Cp]_2$

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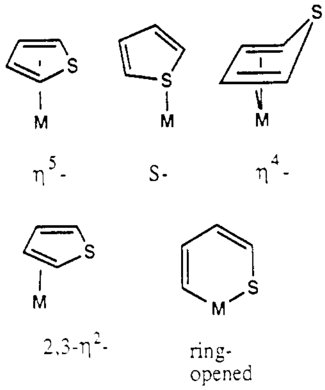
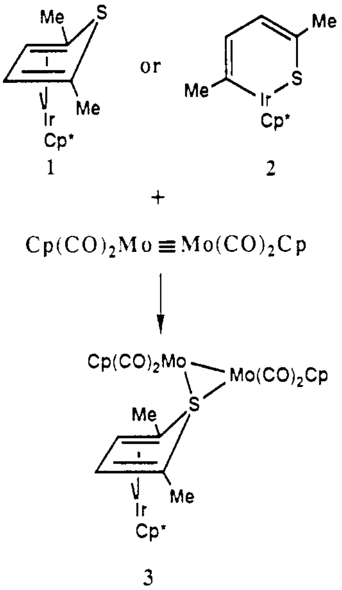
Summary: The reaction of $Cp^*Ir(\eta^4$-2,5-$Me_2T)$, where η^4-2,5-Me_2T is 2,5-dimethylthiophene coordinated through the four ring carbons, with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ gives $(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[Mo(CO)_2Cp]_2$, in which the bridging thiophene is η^4-coordinated to the Ir and bonded via the sulfur to both Mo atoms. The same product is obtained from the ring-opened isomer of $Cp^*Ir(2,5\text{-}Me_2T)$. The structure of the product, which is the first example of a thiophene coordinated to three metal centers, was established by X-ray crystallography.

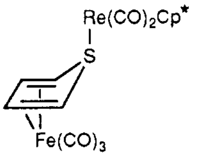
Recent interest in model studies[2] of the hydrodesulfurization of thiophenes has led to the discovery of several new modes of thiophene coordination to transition metals. Five types of coordination to one metal center (Chart I) have been reported. Of these, the η^5- and S-bound forms have been known 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 $(NH_3)_5Os(2,3\text{-}\eta^2\text{-thiophene})^{2+}$ was recently[6] described, as was the ring-opened isomer of $Cp^*Ir(2,5\text{-}Me_2T)$.[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, $(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[Mo(CO)_2Cp]_2$, 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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