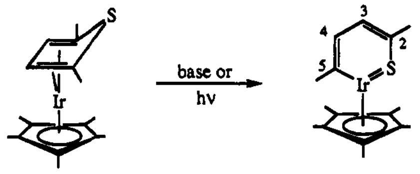
Iridathiabenzene, a Novel η^6 Heteroaromatic π-Ligand

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

Department of Chemistry and Ames Laboratory
Iowa State University, Ames, Iowa 50011

Received December 27, 1994

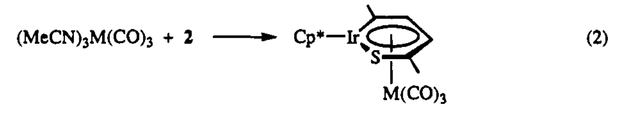
It was recently demonstrated that the η^4-2,5-dimethylthiophene complex Cp*Ir(η^4-2,5-Me_2T) (**1**) undergoes base[1] or ultraviolet light-catalyzed[2] rearrangement (eq 1) to an isomer, Cp*Ir(*C*,*S*-2,5-Me_2T) (**2**), in which the Ir is inserted into a C−S bond of the thiophene. The planarity of the 6-membered ring in **2**, the near equivalence of the C−C bond distances in this ring, and the downfield chemical shifts (δ 7.34 and 7.47) of H3 and H4 suggested that the π-system of the ring is delocalized. For these reasons, **2** was described as an iridathiabenzene, a derivative of benzene in which two CH units are replaced by S and IrCp*. This delocalized description is supported by a recent MO calculation.[3] Complex **2** undergoes a variety of reactions,[2,4,5] but they all result in products in which the π-system is disrupted. In this Communication, we show that the 6-membered ring in **2** is capable of forming η^6 complexes that are analogs of well-known η^6-arene derivatives. Moreover, **2** is a more strongly coordinating ligand than the arenes.



1 **2**

(1)

The series of complexes [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]M$(CO)_3$, where M = Cr, Mo, and W, containing **2** as an η^6-coordinated ligand were prepared in >92% yield according to eq 2.



(2)

M = Cr(**3**), Mo(**4**), W(**5**)

Typically, 0.080 mmol of solid $(MeCN)_3M(CO)_3$[6] was added to a tetrahydrofuran (30 mL) solution of **2** (0.068 mmol) at −50 °C. Upon slowly (3−8 h) warming to room temperature, the reaction mixture turned from red to purple. Pure, purple, air-stable **3**, **4**, and **5**[7] were obtained by chromatography on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluent. Complex **4** was also prepared by reacting the η^6-toluene complex (η^6-$C_6H_5CH_3$)Mo$(CO)_3$ (0.066 mmol)[8] with **2** (0.057 mmol) in hexanes for 6 h at room temperature; the 94% isolated yield of **4** demonstrates that the 6-membered ring of **2** is more strongly coordinating than toluene. The greater donor ability of the iridathiabenzene as compared with toluene is indicated by the lower ν(CO) values (in hexane) for **4** (1957 vs, 1894 s, 1880 s) than for (η^6-$C_6H_5CH_3$)Mo$(CO)_3$ (1985 vs, 1914 vs).

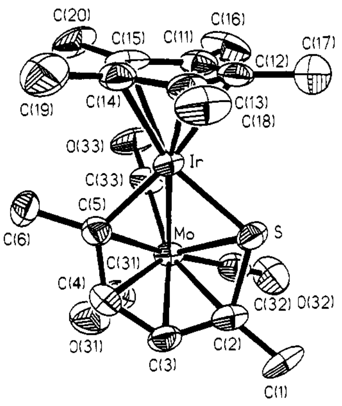


Figure 1. Thermal ellipsoid drawing at 50% probability of [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]Mo$(CO)_3$ (**4**), shown without hydrogen atoms for clarity. Selected bond distances (Å) are Ir−S = 2.241(3), S−C(2) = 1.745(13), C(2)−C(3) = 1.385(19), C(3)−C(4) = 1.433(18), C(4)−C(5) = 1.409(17), Ir−C(5) = 1.999(13), Ir−Mo = 2.967(1), Mo−S = 2.615(3).

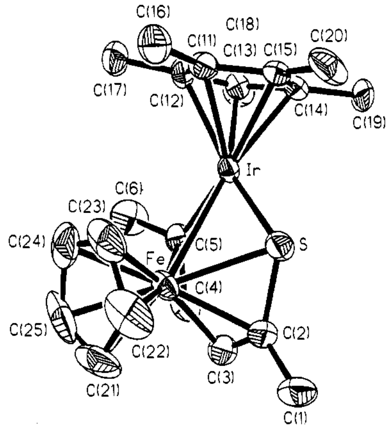
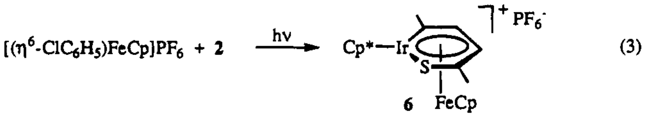


Figure 2. Thermal ellipsoid drawing at 50% probability of [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]FeCp$^+$ (**6**), shown without hydrogen atoms for clarity. Selected bond distances (Å) are Ir−S = 2.212(2), S−C(2) = 1.742(9), C(2)−C(3) = 1.375(13), C(3)−C(4) = 1.413(12), C(4)−C(5) = 1.389(11), Ir−C(5) = 2.004(8), Ir−Fe = 2.758(1), Fe−S = 2.332(2).

The notable tendency of **2** to give η^6 complexes is further demonstrated by its formation (eq 3) of the cationic complex [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]FeCp$^+$ (**6**). When a CH_2Cl_2 solution



6

(3)

of the chlorobenzene complex [(η^6-ClC_6H_5)FeCp]PF_6 (0.092 mmol)[9] and **2** (0.114 mmol) is photolyzed with a 450 W mercury ultraviolet lamp, **6** was produced and subsequently crystallized

---

[†] Iowa State University Molecular Structure Laboratory.

(1) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

(2) Chen, J.; Angelici, R. J. *J. Appl. Organomet. Chem.* **1992**, *6*, 479.

(3) Harris, S. *Organometallics* **1994**, *13*, 2628.

(4) Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; Vol. 3, pp 1433−1443.

(5) Chen, J.; Angelici, R. J. *Organometallics* **1992**, *11*, 992.

(6) (a) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433. (b) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

(7) **3**: mp 183−184 °C dec; IR (hexane) ν(CO) 1950 vs, 1893 s, 1880 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.86 (d, 1 H), 5.46 (d, 1 H), 2.72 (s, 3 H), 2.52 (s, 3 H), 2.07 (s, 15 H); MS (*m/e*) 576 (M$^+$, based on ^{52}Cr). Anal. Calcd for $C_{19}H_{23}O_3SIrCr$: C, 39.64; H, 4.03. Found: C, 39.00; H, 3.98. **4**: mp 188−189 °C dec; IR (hexane) ν(CO) 1957 vs, 1894 s, 1880 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.00 (d, 1 H), 5.81 (d, 1 H), 2.69 (s, 3 H), 2.54 (s, 3 H), 2.06 (s, 15 H); MS (*m/e*) 622 (M$^+$, based on ^{98}Mo). Anal. Calcd for $C_{19}H_{23}O_3SIrMo$: C, 36.83; H, 3.74. Found: C, 37.17; H, 3.83. **5**: mp 194−195 °C dec; IR (hexane) ν(CO) 1955 vs, 1888 s, 1878 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.89 (d, 1 H), 5.81 (d, 1 H), 2.83 (s, 3 H), 2.72 (s, 3 H), 2.05 (s, 15 H); MS (*m/e*) 708 (M$^+$, based on ^{184}W). Anal. Calcd for $C_{19}H_{23}O_3SIrW$: C, 32.25; H, 3.28. Found: C, 32.68; H, 3.21.

(8) (a) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1514. (b) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(9) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2261.

0002-7863/95/1517-6362$09.00/0

from acetone/Et_2O as a dark purple solid in 80% yield.[10] The higher field chemical shift of the cyclopentadienyl protons in **6** (δ 4.46) as compared with that in $[(\eta^6\text{-}ClC_6H_5)FeCp]^+$ (δ 5.19) suggests that the iridathiabenzene ligand is more strongly electron-donating than chlorobenzene.

X-ray diffraction studies of **4**[11] and **6**[12] show (Figures 1 and 2) that the iridathiabenzene ring in **2** is η^6-coordinated to the Mo and Fe. All of the atoms in the 6-membered rings in both structures lie in the same plane (±0.07 Å), and bond distances (Å) within the rings (see captions in Figures 1 and 2) are the same, within experimental error, as those in uncoordinated **2**:[1] Ir−S = 2.203(2), S−C(2) = 1.713(6), C(2)−C(3) = 1.375(9), C(3)−C(4) = 1.41(1), C(4)−C(5) = 1.394(9), and Ir−C(5) = 1.986(6). Thus, as in η^6-arene complexes,[13] the iridathiabenzene is not significantly distorted by its η^6 coordination to the metal in **4** or **6**.

In conclusion, the iridathiabenzene ring in **2** is a more strongly coordinating η^6 ligand than arenes. Studies of the reactivity of the η^6-iridathiabenzene ligand in these complexes are in progress.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82. We thank Johnson Matthey, Inc. for a loan of $IrCl_3$.

Supplementary Material Available: Description of the data collection and structure solution, tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes for **4** and **6** (35 pages); listing of calculated and observed structure factors for **4** and **6** (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA944155G

---

[10] **6**: mp 199−200 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.81 (d, 1 H), 5.99 (d, 1 H), 4.46 (s, 5 H), 3.15 (s, 3 H), 2.96 (s, 3 H), 2.14 (s, 15 H); MS (FAB, 3-nitrobenzyl alcohol matrix) (*m/e*) 561 ($M^+ - PF_6$). Anal. Calcd for $C_{21}H_{28}SPF_6IrFe$: C, 35.75; H, 4.00. Found: C, 36.35; H, 4.20.

[11] Crystallographic data for 4: MW = 619.6; crystal system, monoclinic, space group $P2_1/c$; $a = 9.196(2)$ Å, $b = 15.282(4)$ Å, $c = 14.943(4)$ Å, $\beta = 106.66(2)°$; $V = 2011.8(9)$ Å^3, $d_{calcd} = 2.046$ Mg/m^3 for $Z = 4$ at 22 ± 1 °C, $\mu = 7.349$ mm^{-1} (Mo Kα). Diffraction data were collected at 22 ± 1 °C with a Siemens P4/RA automated diffractometer. A total of 7907 reflections were collected. Of the 3558 independent reflections, 2169 were considered observed, having $F > 6.0\sigma(F)$. $R = 3.48$, and $R_w = 3.75$. Details of data collection and refinement are given in the supplementary material.

[12] Crystallographic data for **6**: MW = 705.5; crystal system, monoclinic, space group $P2_1/c$; $a = 10.677(1)$ Å, $b = 13.530(2)$ Å, $c = 16.279(2)$ Å, $\beta = 100.95(1)°$; $V = 2308.8(5)$ Å^3, $d_{calcd} = 2.030$ Mg/m^3 for $Z = 4$ at 223 ± 1 K, $\mu = 6.601$ mm^{-1} (Mo Kα). Diffraction data were collected at 223 ± 1 K with an Enraf-Nonius CAD4 automated diffractometer. A total of 8473 reflections were collected. Of the 4053 independent reflections, 2866 were considered observed, having $F > 4.0\sigma(F)$. $R = 3.08$, and $R_w = 3.39$. Details of data collection and refinement are given in the supplementary material.

[13] Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.