ORGANOMETALLICS

Volume 12, Number 4, April 1993

Communications

Electrophilic Addition to an Iridathiacyclopentene Complex. Synthesis of the First Metallathiophene

John R. Bleeke,* Michael F. Ortwerth, and Michael Y. Chiang

Department of Chemistry, Washington University, St. Louis, Missouri 63130

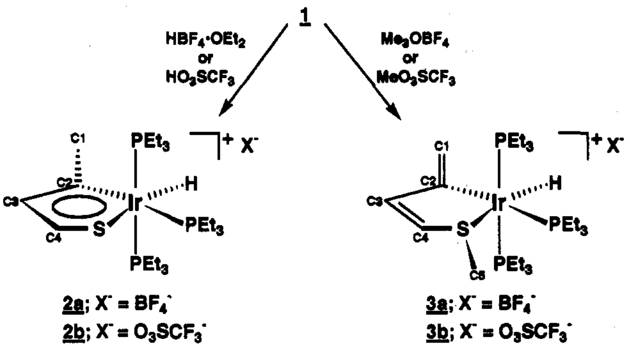
Received December 11, 1992

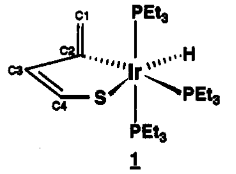
Summary: The reactivity of the unsaturated five-membered iridathiacycle $CH_2{=}\overline{C{-}CH{=}CH{-}S{-}Ir}(PEt_3)_3(H)$ *(1) toward simple electrophiles has been investigated. Protonation occurs at the basic exocyclic methylene carbon, generating* $[CH_3{-}\overline{C{\cdots}CH{\cdots}CH{\cdots}S{\cdots}Ir}(PEt_3)_3(H)]^+X^-$ *(**2a**,* $X^- = BF_4^-$*; **2b**,* $X^- = O_3SCF_3^-$*), the first example of a "metallathiophene". In contrast, methylation of 1 occurs at the nucleophilic sulfur center, producing* $[CH_2{=}\overline{C{-}CH{=}CH{-}S(CH_3){-}Ir}(PEt_3)_3(H)]^+X^-$ *(**3a**,* $X^- = BF_4^-$*; **3b**,* $X^- = O_3SCF_3^-$*). X-ray crystal structures of **2a** and **3b** have been obtained.*

During the past several years, we have been developing a new synthetic route to unsaturated metallacycles, which utilizes pentadienide reagents as the source of ring carbon atoms and exploits C–H bond activation in the key ring-forming step.[1] A notable success of this approach has been the high-yield synthesis of iridacyclohexadiene complexes[1] and the straightforward conversion of these species to aromatic "iridabenzenes".[2]

Heteroatom-containing metallacycles can also be produced via this synthetic strategy.[3] For example, we recently reported the synthesis of the novel unsaturated five-membered iridathiacycle 1 using potassium thiapentadienide as the source of ring carbon and sulfur atoms.[3b] We now describe the reactions of 1 with simple electrophiles, including its conversion to "iridathiophene", the first example of a transition-metal-containing analogue of thiophene.

Scheme I





1

As shown in Scheme I, treatment of compound 1 with strong acids and with methylating agents leads to electrophilic addition at two different sites. Proton attack occurs exclusively at the exocyclic carbon center (C1), producing "iridathiophene" (2),[4] while methylation occurs exclusively at the sulfur center, generating compound 3.[5,6] This reactivity pattern suggests that C1 is the most *basic*

---

[1] (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113.

[2] (a) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (b) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271.

[3] (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19. (b) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

0276-7333/93/2312-0985$04.00/0 © 1993 American Chemical Society

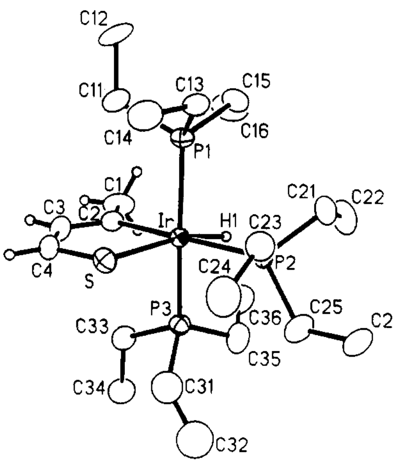


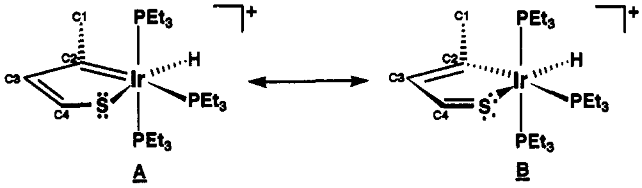
Figure 1. ORTEP drawing of $[CH_3{-}\overline{C\cdots CH\cdots CH\cdots S\cdots Ir}(PEt_3)_3(H)]^+BF_4^-$ (**2a**). Selected bond distances (Å): Ir–P1, 2.358(3); Ir–P2, 2.408(3); Ir–P3, 2.350(3); Ir–H1, 1.941; Ir–C2, 2.042(10); Ir–S, 2.383(3); C1–C2, 1.500(15); C2–C3, 1.362(15); C3–C4, 1.399(16); C4–S, 1.647(11). Selected bond angles (deg): S–Ir–C2, 82.3(3); Ir–C2–C1, 124.3(8); Ir–C2–C3, 118.0(8); C1–C2–C3, 117.7(10); C2–C3–C4, 121.2(10); C3–C4–S, 119.2(8); C4–S–Ir, 99.2(4).

site in the molecule but that sulfur, due to its greater polarizability and accessibility, is the better *nucleophile*.[7]

The solid-state structure of **2a**, as determined by single-crystal X-ray diffraction, is shown in Figure 1; key distances and angles are listed in the figure caption.[8] Unlike precursor **1**, in which the bonding around the metallacycle is fully localized, compound **2a** exhibits the delocalized bonding of an aromatic ring system. The Ir–C2, Ir–S, and C4–S ring bonds in **2a** have all shortened significantly (with respect to their distances in **1**)[9] to values which are intermediate between normal single and double bonds.[10] Similarly, the C–C bond distances within the ring have moved toward equalization, with C2–C3 shortening to 1.362(15) Å and C3–C4 lengthening to 1.399(16) Å. Overall, the circumference of the five-membered ring in **2a** has shrunk by 0.233 Å from its value in **1** (8.833 vs 9.066 Å).

Aromatic character is also suggested by the ^{1}H NMR spectrum of **2**.[11] H3 and H4 are shifted dramatically downfield to δ 7.58 and 10.08, respectively (vs δ 5.84 and 6.14 in precursor **1**). The ^{13}C NMR spectrum of **2** shows similar downfield shifts for the ring carbons with C2, C3, and C4 appearing at δ 245.8, 155.0, and 212.0, respectively.[11]

The structural and spectroscopic data described above suggest that several resonance structures contribute to the overall bonding picture in **2**. Structure A is supported by the short Ir–C2 distance and the downfield "carbene-like" chemical shift position of C2. Resonance form B, on the other hand, accounts for the short C4–S bond distance. The aromatic character of **2** can be explained qualitatively by noting that both resonance structures A and B possess a closed loop of six π-electrons. In A, a lone pair on sulfur contributes two π-electrons, while in B, a pair of metal-based d electrons completes the Hückel sextet.[12]



As shown in Scheme I, treatment of **1** with trimethyloxonium tetrafluoroborate or with methyl triflate leads to methylation at the sulfur center and production of $[CH_2{=}\overline{C{-}CH{=}CH{-}S(CH_3){-}Ir}(PEt_3)_3(H)]^+X^-$ (**3a**, $X^- = BF_4^-$; **3b**, $X^- = O_3SCF_3^-$).[13] The X-ray crystal structure of **3b** is shown in Figure 2; important bond distances and angles are listed in the caption.[14] As expected, the sulfur center in **3b** is *pyramidal*. Methyl carbon C5 lies 1.521 Å below the ring plane, and the C4–S–C5 angle is 98.9(3)°. Like precursor **1**, compound **3** is *not* aromatic, and this is reflected in the localized bonding around the ring. Particularly diagnostic are the ring C–C distances of 1.478(9) and 1.324(9) Å for C2–C3 and C3–C4, respectively. The circumference of the five-membered ring in **3b** is almost identical with that in **1** (9.059 Å in **3b** vs 9.066 Å in **1**). The ^{1}H NMR chemical shifts observed for the ring protons in **3** are also consistent with its formulation as a localized,

---

(4) In a typical reaction, $HBF_4{\cdot}OEt_2$ (41 mg, 0.25 mmol) was added under nitrogen to a cold (−30 °C) solution of compound **1** (160 mg, 0.25 mmol) in 15 mL of diethyl ether. After it was swirled briefly, the solution was stored overnight at −30 °C, causing **2a** to precipitate as a light brown powder. The powder was collected by filtration (yield 160 mg, 89%) and recrystallized from a 1:1 mixture of ethanol and diethyl ether, affording red-brown prisms of **2a**. Anal. Calcd for $C_{22}H_{51}BF_4IrP_3S$: C, 36.71; H, 7.16. Found: C, 36.27; H, 6.57.

(5) In a typical reaction, methyl triflate (39 mg, 0.24 mmol) was added under nitrogen to a cold (−30 °C) solution of compound **1** (150 mg, 0.24 mmol) in 15 mL of diethyl ether. After it was swirled briefly, the solution was stored overnight at −30 °C. The resulting precipitate was collected by filtration (yield 160 mg, 84%) and recrystallized from a 1:1 mixture of ethanol and diethyl ether, affording yellow crystals of **3b**. Anal. Calcd for $C_{24}H_{53}F_3IrO_3P_3S_2$: C, 36.21; H, 6.72. Found: C, 36.60; H, 6.24.

(6) While it is possible that the site of *initial* proton attack is also the sulfur center, low-temperature (−80 °C) NMR monitoring of the protonation reaction shows the immediate appearance of **2** with no evidence for a kinetically formed intermediate.

(7) Gutsche, C. D.; Pasto, D. J. *Fundamentals of Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1975; pp 446–448.

(8) Crystal data for **2a**: red-brown prism, 0.16 × 0.30 × 0.38 mm; orthorhombic, space group $P2_12_12_1$, $a = 10.903(3)$ Å, $b = 15.760(4)$ Å, $c = 17.952(4)$ Å, $V = 3084.7(13)$ Å^3, $Z = 4$, $d_{calcd} = 1.549$ g/cm^3, $\mu = 45.85$ cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, θ–2θ scanning technique, 4268 unique reflections with $3.5° < 2\theta < 50.0°$ collected, 2968 reflections with $I > 3\sigma(I)$ used in refinement; semiempirical absorption correction; $R = 0.0273$; $R_w = 0.0321$; GOF = 0.88. The hydride ligand (H1) was located but not refined.

(9) A preliminary structure of compound **1** was reported in ref 3b. We have since obtained a higher quality structure with the following average ring bond distances: Ir–C2, 2.104 (11) Å; C2–C3, 1.477(17) Å; C3–C4, 1.328(18) Å; C4–S, 1.713(13) Å; S–Ir, 2.444(3) Å.

(10) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; Appendix E and references therein.

(11) Spectroscopic data for **2**: ^{1}H NMR (CD_2Cl_2, 22 °C, 300 MHz) δ 10.08 (m, 1, H4), 7.58 (m, 1, H3), 3.17 (m, 3, H1's), 1.84 (m, 6, PEt_3 CH_2's), 1.60 (m, 6, PEt_3 CH_2's), 1.52 (m, 6, PEt_3 CH_2's), 0.94 (m, 9, PEt_3 CH_3's), 0.82 (m, 18, PEt_3 CH_3's), −14.28 (q, $J_{H-P} = 14.8$ Hz, 1, Ir–H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 75 MHz) δ 245.8 (d of t, $J_{C-P} = 75.9$, 6.4 Hz, C2), 212.0 (d, $J_{C-P} = 12.2$ Hz, C4), 155.0 (s, C3), 43.5 (d, $J_{C-P} = 5.6$ Hz, C1), 19.2 (m, PEt_3 CH_2's), 8.46 (s, axial PEt_3 CH_3's), 8.11 (s, equatorial PEt_3 CH_3's); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 121 MHz, referenced to external H_3PO_4) δ −17.1 (d, $J_{P-P} = 24.9$ Hz, 2, axial PEt_3's), −28.8 (t, $J_{P-P} = 24.9$ Hz, 1, equatorial PEt_3).

(12) Fenske–Hall molecular orbital calculations have been performed on a related mangana*furan* system. See: DeShong, P.; Slough, G. A.; Sidler, D. R.; Rybczynski, P. J.; von Philipsborn, W.; Kunz, R. W.; Bursten, B. E.; Clayton, T. W., Jr. *Organometallics* **1989**, *8*, 1381.

(13) A small quantity of compound **2** is also produced in the methylation reactions. The origin of this product is under investigation.

(14) Crystal data for **3b**: yellow prism, 0.26 × 0.28 × 0.42 mm; monoclinic, space group $P2_1/c$, $a = 10.374(3)$ Å, $b = 17.003(7)$ Å, $c = 19.007(6)$ Å, $\beta = 93.82(2)°$, $V = 3343(1)$ Å^3, $Z = 4$, $d_{calcd} = 1.581$ g/cm^3, $\mu = 43.02$ cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, ω scanning technique, 5875 unique reflections with $3.5° < 2\theta < 50.0°$ collected, 3846 reflections with $I > 3\sigma(I)$ used in refinement; semiempirical absorption correction; $R = 0.0232$; $R_w = 0.0262$; GOF = 0.79. The position of the hydride ligand (H1) was inferred from the positions of the heavy atoms in the molecule. In Figure 2, it was placed at an idealized position with Ir–H1 = 1.75 Å and angle S–Ir–H1 = 180°.

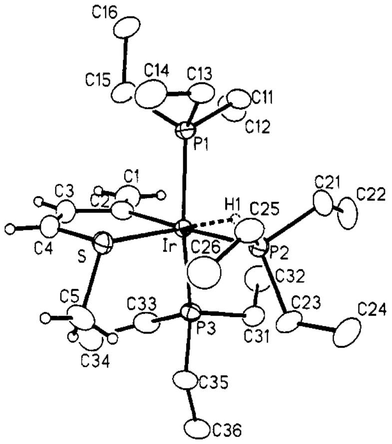


Figure 2. ORTEP drawing of [CH_2=C—CH=CH—S-(CH_3)—Ir(PEt_3)$_3$(H)]$^+O_3SCF_3^-$ (**3b**). Selected bond distances (Å): Ir–Pl, 2.367(2); Ir–P2, 2.398(2); Ir–P3, 2.359(2); Ir–C2, 2.091(6); Ir–S, 2.419(2); C1–C2, 1.330(9); C2–C3, 1.478(9); C3–C4, 1.324(9); C4–S, 1.747(6). Selected bond angles (deg): S–Ir–C2, 82.8(2); Ir–C2–C1, 129.1(5); Ir–C2–C3, 115.6(4); C1–C2–C3, 115.2(6); C2–C3–C4, 123.4(6); C3–C4–S, 118.6(5); C4–S–C5, 98.9(3); C4–S–Ir, 99.5(2); C5–S–Ir, 119.2(2).

nonaromatic system.[15] H3 and H4 resonate at δ 6.45 and 6.00, respectively, significantly upfield from their positions in **2**.

The pyramidal geometry about sulfur causes the trans-diaxial phosphines (P1 and P3 in Figure 2) to be inequivalent. Hence, these phosphines give rise to separate signals in the $^{31}P\{^1H\}$ NMR spectrum at −80 °C.[15] However, as the temperature of the sample is raised, these peaks broaden and ultimately coalesce at about −25 °C. The free energy of activation ($\Delta G^{\ddagger}$) at the coalescence temperature is calculated to be 11.3 kcal/mol.[16] Two reasonable mechanisms for this exchange process can be envisaged: (a) inversion of the pyramidal sulfur or (b) dissociation of sulfur, followed by C4–S bond rotation and reattachment to iridium. While the calculated activation energy is unusually low for inversion about sulfonium sulfur,[17] the planar intermediate would be stabilized by overlap of the filled sulfur pπ orbital with the ring's carbon π-system. Furthermore, the presence of the metal and its ligands may promote inversion, because bulky substituents generally lower the barrier to sulfonium inversion.[17] A resolution of this interesting mechanistic question must await further experimentation.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8520680 and CHE-9003159) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of $IrCl_3 \cdot 3H_2O$ from Johnson-Matthey Aesar/Alfa is gratefully acknowledged. Washington University's X-Ray Crystallography Facility was funded by the NSF's Chemical Instrumentation Program (Grant CHE-8811456).

Supplementary Material Available: Structure determination summary tables and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for **2a** and **3b** (16 pages). Ordering information is given on any current masthead page.

OM920791G

---

(15) Spectroscopic data for **3**: ^1H NMR (CD_2Cl_2, 22 °C, 300 MHz) δ 6.45 (m, 2, H3 and H1), 6.00 (d, J_{H-H} = 4 Hz, 1, H4), 5.49 (m, 1, H1), 2.61 (m, 3, S–CH_3), 2.04–1.52 (m, 18, PEt_3 CH_2's), 1.28–0.92 (m, 27, PEt_3 CH_3's), −16.37 (q, J_{H-P} = 15.5 Hz, 1, Ir–H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, 75 MHz) δ 156.0 (s, C3), 154.8 (d of t, J_{C-P} = 83.2, 17.1 Hz, C2), 134.1 (d, J_{C-P} = 8.1 Hz, C1), 124.9 (d, J_{C-P} = 7.2 Hz, C4), 26.5 (s, S–CH_3), 20.7 (d, J_{C-P} = 23.9 Hz, equatorial PEt_3 CH_2's), 18.4 (virtual t, J_{C-P} = 30.3 Hz, axial PEt_3 CH_2's), 8.41 (s, axial PEt_3 CH_3's), 8.34 (s, equatorial PEt_3 CH_3's); $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, −80 °C, 121 MHz, referenced to external H_3PO_4) δ −20.1 (t, J_{P-P} = 18.4 Hz, 1, equatorial PEt_3), −20.9 (dd, J_{P-P} = 295, 18.4 Hz, 1, axial PEt_3), −23.0 (dd, J_{P-P} = 295, 18.4 Hz, 1, axial PEt_3).

(16) (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 223. (b) Lowry, T. H.; Richardson, T. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1976; p 194.

(17) Anderson, K. K. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Ed.; Wiley: Chichester, England, 1981; Part 1, pp 229–266.