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Thiapentadienyl–Iridium–Phosphine Chemistry.[1] Synthesis of Sulfur-Containing Iridacycles via C–H Bond Activation[2]

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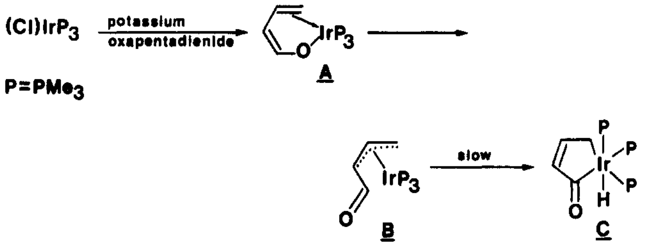
Summary: Treatment of $(Cl)Ir(PR_3)_3$ (R = Me, Et) with potassium thiapentadienide produces ((1,2,5-η)-5-thiapentadienyl)$Ir(PR_3)_3$ (**1**, R = Me; **2**, R = Et). While **1** is stable indefinitely in solution, **2** undergoes intramolecular activation of thiapentadienyl C–H bonds, producing a mixture of *mer*-(Ir—CH=CH—CH=CH—S)$(PEt_3)_3$(H) (**3**) and *mer*-(Ir—C(=CH_2)—CH=CH—S)$(PEt_3)_3$(H) (**4**). Over time, all of the six-membered thiairidacycle **3** converts to the thermodynamically favored five-membered-ring compound **4**.

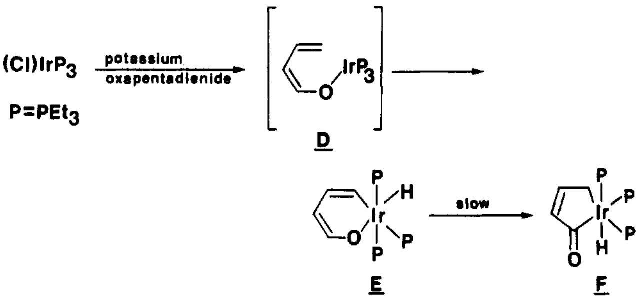
During the past decade, (pentadienyl)metal chemistry has developed rapidly.[3] In contrast, relatively little effort has been directed toward synthesizing and studying the reactivity of (heteropentadienyl)metal complexes, i.e., species in which one carbon of the pentadienyl chain has been replaced by a heteroatom. Like their all-carbon counterparts, heteropentadienyl ligands have the *potential* to bond to metals in a wide variety of different modes. However, little is currently known about the relative energetics of these modes. In order to address this issue, we have begun a systematic exploration of the synthesis of (heteropentadienyl)metal complexes, using halo–metal–phosphine compounds and anionic heteropentadienide reagents as our building blocks.

Our initial studies have focused on electron-rich heteropentadienyl–iridium(I)–phosphine complexes because these species have a propensity to undergo C–H bond activation, generating novel metallacyclic products. For example, we have shown[4] that treatment of $(Cl)Ir(PMe_3)_3$ with potassium oxapentadienide produces ((1,2,5-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (A, Scheme I), which quickly rearranges to ((1,2,3-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (B). This species then slowly undergoes metal-centered activation of the aldehydic (formyl) C–H bond to produce the iridacyclopentenone complex C. In contrast, treatment of $(Cl)Ir(PEt_3)_3$ with potassium oxapentadienide leads directly to an oxairidacyclohexadiene complex (E, Scheme II), presumably via C–H bond activation in 16e$^-$ (η^1-oxapentadienyl)$Ir(PEt_3)_3$ (D).[4] However, E also slowly converts to an iridacyclopentenone complex (F, Scheme II), probably through a series of steps similar to those outlined in Scheme I. We now report the results of a parallel study involving halo–iridium–phosphine precursors and the sulfur-containing heteropentadienide reagent potassium *thia*pentadienide.

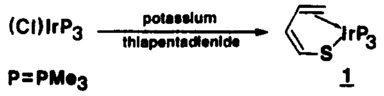
Scheme I



Scheme II



Scheme III



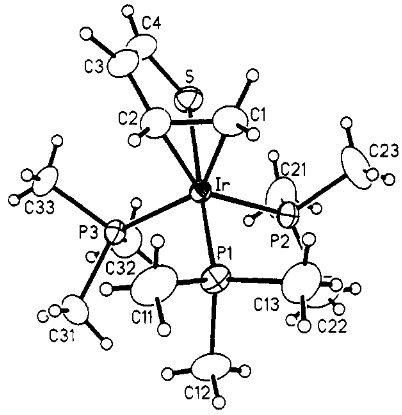


Figure 1. ORTEP drawing of ((1,2,5-η)-5-thiapentadienyl)$Ir(PMe_3)_3$ (**1**). Bond distances (Å): Ir–P1, 2.261 (3); Ir–P2, 2.293 (3); Ir–P3, 2.323 (2); Ir–S, 2.417 (3); Ir–C1, 2.110 (9); Ir–C2, 2.139 (9); C1–C2, 1.441 (15); C2–C3, 1.474 (15); C3–C4, 1.316 (18); C4–S, 1.758 (11). Bond angles (deg): P1–Ir–P2, 95.8 (1); P1–Ir–P3, 99.3 (1); P2–Ir–P3, 106.1 (1); P1–Ir–S, 174.4 (1); P2–Ir–S, 86.4 (1); P3–Ir–S, 85.0 (1); C1–Ir–C2, 39.6 (4); C1–C2–C3, 116.7 (9); C2–C3–C4, 121.0 (9); C3–C4–S, 120.8 (8).

Potassium thiapentadienide is synthesized from 2,5-dihydrothiophene[5] using the "cycloreversion" method of Kloosterziel.[6] Addition of this reagent to $(Cl)Ir(PMe_3)_3$ produces in high yield the η^3-thiapentadienyl[7] complex

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[1] Pentadienyl–Metal–Phosphine Chemistry. 24. Part 23: Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391.

[2] Metallacyclohexadiene and Metallabenzene Chemistry. 7. Part 6: Bleeke, J. R.; Bass, L.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213.

[3] For recent reviews, see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1251. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

[4] Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19.

[5] Everhardus, R. H.; Gräfing, R.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 153.

[6] Kloosterziel, H.; Van Drunen, J. A. A.; Galama, P. *J. Chem. Soc., Chem. Commun.* **1969**, 885.

[7] Several η^5-thiapentadienyl (or "butadienethiolate") metal complexes have recently been obtained by treating (η^5-thiophene)metal precursors with nucleophiles: (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (b) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909. (c) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875.

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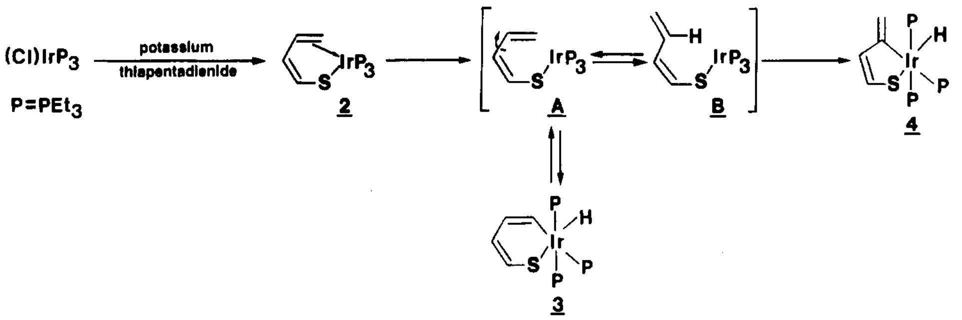
Scheme IV



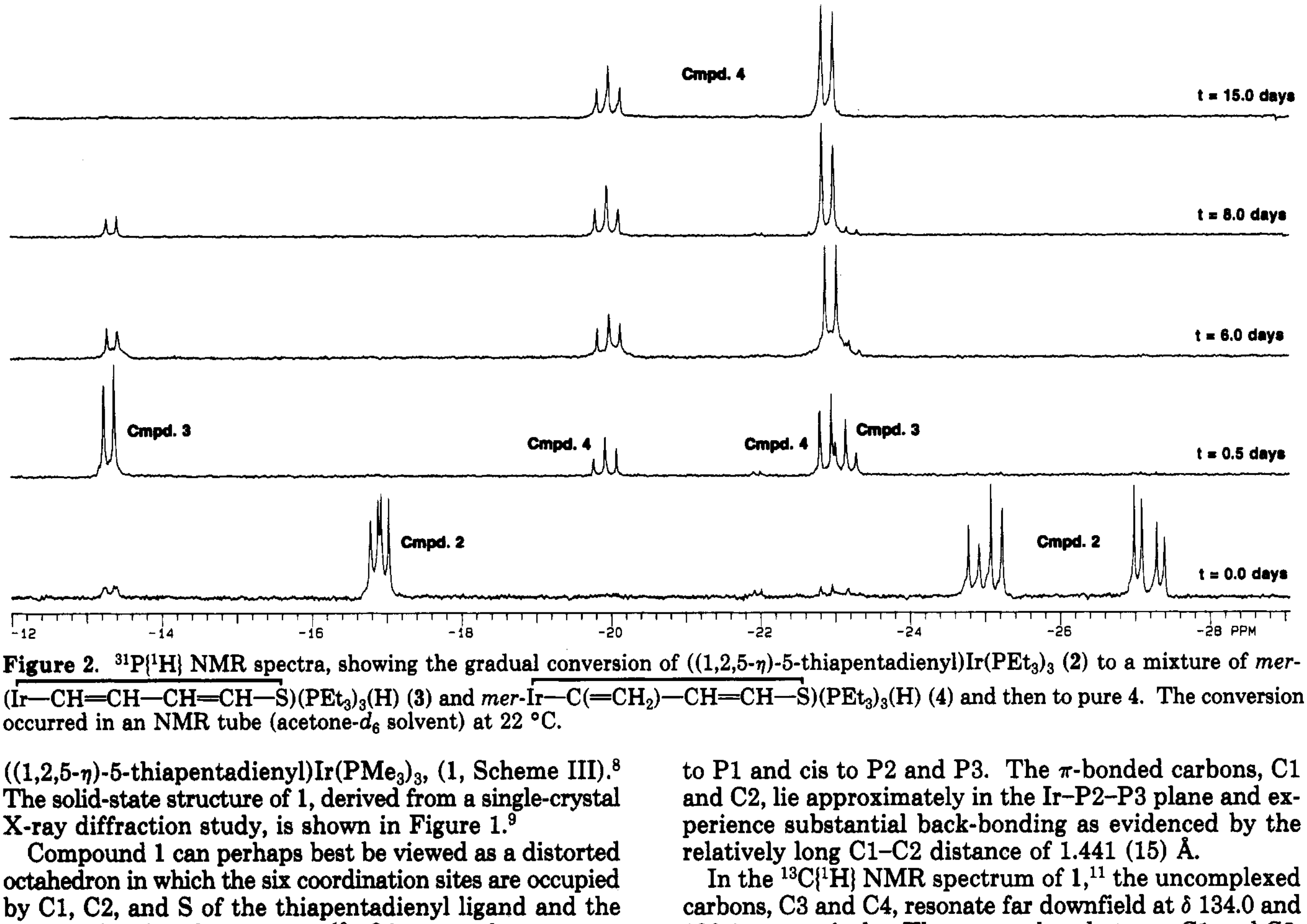


Figure 2. $^{31}P\{^1H\}$ NMR spectra, showing the gradual conversion of ((1,2,5-η)-5-thiapentadienyl)Ir(PEt_3)$_3$ (2) to a mixture of *mer*-($\overline{\mathrm{Ir{-}CH{=}CH{-}CH{=}CH{-}S}}$)($PEt_3$)$_3$(H) (3) and *mer*-$\overline{\mathrm{Ir{-}C({=}CH_2){-}CH{=}CH{-}S}}$($PEt_3$)$_3$(H) (4) and then to pure 4. The conversion occurred in an NMR tube (acetone-d_6 solvent) at 22 °C.

((1,2,5-η)-5-thiapentadienyl)Ir(PMe_3)$_3$, (1, Scheme III).[8] The solid-state structure of 1, derived from a single-crystal X-ray diffraction study, is shown in Figure 1.[9]

Compound 1 can perhaps best be viewed as a distorted octahedron in which the six coordination sites are occupied by C1, C2, and S of the thiapentadienyl ligand and the three PMe_3 phosphorus atoms.[10] Of course, the geometry is distorted because of the rigidity of the thiapentadienyl ligand. The σ-bonded sulfur atom lies approximately trans to P1 and cis to P2 and P3. The π-bonded carbons, C1 and C2, lie approximately in the Ir–P2–P3 plane and experience substantial back-bonding as evidenced by the relatively long C1–C2 distance of 1.441 (15) Å.

In the $^{13}C\{^1H\}$ NMR spectrum of 1,[11] the uncomplexed carbons, C3 and C4, resonate far downfield at δ 134.0 and 126.4, respectively. The π-complexed atoms, C1 and C2, resonate at δ 18.4 and 41.0, respectively, and appear as doublets due to phosphorus coupling. The three phosphorus atoms are inequivalent and appear as an AXY pattern in the $^{31}P\{^1H\}$ NMR spectrum.

When (Cl)Ir(PEt_3)$_3$ is substituted for (Cl)Ir(PMe_3)$_3$ in the above reaction system, a more complex chemistry is observed. As shown in Scheme IV, the initial reaction product is the analogue of 1, ((1,2,5-η)-5-thiapentadienyl)Ir(PEt_3)$_3$ (2). This species can be isolated and crystallized in pure form from diethyl ether/pentane.[12] The

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[8] Synthesis of 1: Under nitrogen, trimethylphosphine (0.38 g, 5.0 mmol) was added dropwise to a cold (−78 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.75 g, 0.84 mmol) in 30 mL of tetrahydrofuran (THF). Excess potassium thiapentadienide (0.42 g, 3.4 mmol) in 15 mL of THF was then added dropwise, and the solution was warmed to room temperature. The volatiles were removed under vacuum, and the residue was extracted with pentane. After removal of the pentane, the residue was redissolved in a minimal quantity of diethyl ether. Addition of several drops of pentane, followed by cooling to −30 °C, produced yellow crystals of 1; yield 0.52 g, 62%. Anal. Calcd for $C_{13}H_{32}IrP_3S$: C, 30.88; H, 6.39. Found: C, 30.56; H, 6.34.

[9] Crystal data for 1: pale yellow needle, 0.10 × 0.16 × 0.53 mm; monoclinic, space group $P2_1/n$, a = 9.488 (4) Å, b = 15.366 (9) Å, c = 13.598 (9) Å, β = 98.99 (4)°, V = 1958 (2) Å^3, Z = 4, d_{calcd} = 1.715 g/cm^3, μ = 71.24 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, $\theta/2\theta$ scanning technique; 3426 unique reflections with $3.5° < 2\theta < 50°$ collected, 2370 reflections with $F > 6.0\sigma(F)$ used in refinement; semiempirical absorption correction (ψ scans); R = 2.81%, R_w = 3.02%, GOF = 1.04, data-to-parameter ratio 13.2:1.

[10] The structure is analogous to those of ((1,2,5-η)-pentadienyl)Ir(PEt_3)$_3$ and ((1,2,5-η)-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$, which we reported earlier.[1]

[11] Spectroscopic data for 1 (carbon atoms in the chain are numbered by starting from the end opposite sulfur): ^1H NMR ($CD_3C(O)CD_3$, 22 °C, 300 MHz) δ 5.72 (m, 1, H3), 5.17 (m, 1, H4), 2.67 (m, 1, H2), 1.59 (m, 9, PMe_3), 1.51 (m, 18, PMe_3's), 1.37 (m, 1, H1), 1.10 (m, 1, H1); $^{13}C\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 75 MHz) δ 134.0 (s, C3), 126.4 (d, J_{C-P} = 15.6 Hz, C4), 41.0 (d, J_{C-P} = 24.6 Hz, C2), 23.1 (m, PMe_3), 20.2 (m, PMe_3), 19.4 (m, PMe_3), 18.4 (d, J_{C-P} = 30.9 Hz, C1); $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 121 MHz, referenced to external H_3PO_4) δ −37.0 (dd, J_{P-P} = 17.6, 16.0 Hz), −51.6 (dd, J_{P-P} = 42.3, 17.6 Hz), −52.1 (dd, J_{P-P} = 42.3, 16.0 Hz); IR (KBr pellet) 2980–2900 (vs), 1575 (m), 1546 (m), 1420 (s), 1300 (s), 1279 (s), 1152 (m), 1103 (m), 963 (vs), 943 (vs), 852 (s), 776 (m), 715 (s), 682 (s), 666 (s), 538 (m), 492 (m) cm^{-1}.

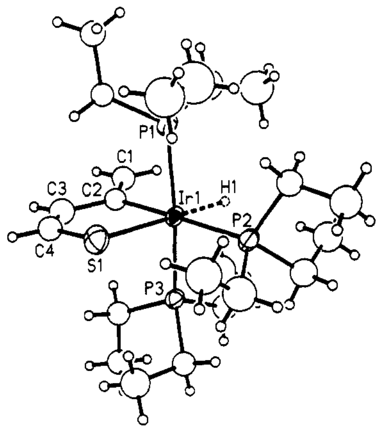

Figure 3. ORTEP drawing of *mer*-(Ir—C(=CH_2)—CH=CH—S)$(PEt_3)_3$(H) (4). Compound 4 crystallized with two independent molecules in the unit cell; therefore, *average* bond distances and angles are reported below. Bond distances (Å): Ir–P1, 2.334 (9); Ir–P2, 2.364 (8); Ir–P3, 2.334 (8); Ir–S, 2.450 (8); Ir–C2, 2.131 (29); C1–C2, 1.306 (42); C2–C3, 1.482 (44); C3–C4, 1.267 (45); C4–S, 1.717 (35). Bond angles (deg): P1–Ir–P2, 99.1 (3); P1–Ir–P3, 164.4 (3); P2–Ir–P3, 93.1 (3); C1–C2–C3, 121.8 (29); C2–C3–C4, 125.2 (32); C3–C4–S, 124.0 (28); C4–S–Ir, 95.3 (12); S–Ir–C2, 84.5 (8); Ir–C2–C3, 110.8 (20); Ir–C2–C1, 127.2 (24).

NMR spectra of 2[13] are completely analogous to those of 1, described above. However, when 2 is stirred in tetrahydrofuran, it undergoes additional chemistry, converting first to a mixture of *mer*-(Ir—CH=CH—CH=CH—S)$(PEt_3)_3$(H) (3, Scheme IV) and *mer*-(Ir—C(=CH_2)—CH=CH—S)$(PEt_3)_3$(H) (4, Scheme IV) and then slowly to pure 4. Reproduced in Figure 2 is a series of $^{31}P\{^1H\}$ NMR plots, showing the gradual conversion of 2 to 4 *in an NMR tube* over a period of 15 days. This conversion probably involves $16e^-$ η^1-thiapentadienyl species (A and B in Scheme IV) as key intermediates.[14] Metal-centered activation of a C1–H bond in A would produce the six-membered-ring compound 3, while analogous activation of C2–H in B would generate the five-membered metallacycle 4.

Although pure 3 has not been obtained, its identity has been established through a series of NMR experiments conducted on mixtures of 3 and 4.[15] Particularly diagnostic for the thiairidacyclohexadiene ring structure[16] is the $^{13}C\{^1H\}$ NMR spectrum, which shows four CH-type carbons in the downfield region (δ 122.8–121.1). These carbon peaks correlate with four downfield proton peaks (δ 7.18–5.70) in the 2D ^{13}C–^1H HMQC spectrum. The $^{31}P\{^1H\}$ NMR spectrum is an A_2X (doublet/triplet) pattern, indicating that the three phosphines adopt a *mer* arrangement. Furthermore, C1 is strongly coupled to phosphorus (J_{C-P} = 72 Hz), requiring that it reside trans to PEt_3 and, therefore, cis to the hydride.

Pure compound 4 can be obtained by stirring the mixture of 3 and 4 in tetrahydrofuran for several days or by refluxing the mixture in tetrahydrofuran for 3 h.[17] The X-ray crystal structure of 4,[18] shown in Figure 3, exhibits an essentially planar five-membered ring[19] (mean deviation of the ring atoms is 0.02 Å). The sum of the five internal angles in the ring is 539.8° (very close to the theoretical value of 540°), but the individual angles range from 84.5° (S–Ir–C2) to 125.2° (C2–C3–C4). As in the six-membered metallacycle 3, the hydride resides cis to the carbon atom that it was originally bonded to (C2 in this case) and trans to the sulfur atom.

The solution-phase NMR spectra of 4[20] are fully con-

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(12) Synthesis of 2: Under nitrogen, triethylphosphine (0.59 g, 5.0 mmol) was added dropwise to a stirred solution of $[(cyclooctene)_2Ir(Cl)]_2$ (0.75 g, 0.84 mmol) in 30 mL of tetrahydrofuran (THF). The volatiles were removed under vacuum, and the resulting residue was redissolved in 30 mL of THF and cooled to 0 °C. Potassium thiapentadienide (0.21 g, 1.7 mmol) in 15 mL of THF was then added dropwise. After the mixture was stirred for 4 h, the volatiles were removed under vacuum. The residue was extracted with pentane and crystallized at −30 °C from a concentrated diethyl ether solution containing several drops of pentane; yield 0.91 g, 86%. Anal. Calcd for $C_{22}H_{50}IrP_3S$: C, 41.81; H, 7.99. Found: C, 41.60; H, 8.07.

(13) Spectroscopic data for 2 (carbon atoms in the chain are numbered by starting from the end opposite sulfur): ^1H NMR ($CD_3C(O)CD_3$, 22 °C, 500 MHz) δ 5.73 (m, 1, H3), 5.07 (m, 1, H4), 2.88 (m, 1, H2), 2.10–1.71 (m, 18, PEt_3CH_2's), 1.51 (m, 1, H1), 1.24 (m, 1, H1), 1.12–1.03 (m, 27, PEt_3 CH_3's); $^{13}C\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 75 MHz) δ 134.0 (s, C3), 126.0 (d, J_{C-P} = 17.2 Hz, C4), 39.1 (d, J_{C-P} = 33.5 Hz, C2), 23.2 (d, J_{C-P} = 21.1 Hz, PEt_3CH_2's), 20.0 (d, J_{C-P} = 21.1 Hz, PEt_3CH_2's), 19.9 (d, J_{C-P} = 29.2 Hz, PEt_3CH_2's), 15.8 (d, J_{C-P} = 36.2 Hz, C1), 10.0 (s, PEt_3CH_3's), 8.9 (s, PEt_3CH_3's); $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 121 MHz, referenced to external H_3PO_4) δ −16.9 (dd, J_{P-P} = 17.5, 12.5 Hz, 1), −25.0 (dd, J_{P-P} = 36.8, 17.5 Hz, 1), −27.2 (dd, J_{P-P} = 36.8, 12.5 Hz, 1); IR (KBr pellet): 2981–2875 (vs), 1575 (s), 1457 (vs), 1413 (s), 1370 (s), 1300 (m), 1258 (s), 1159 (m), 1103 (m), 1034 (vs), 928 (s), 857 (m), 759 (vs), 695 (vs), 667 (vs), 604 (s), 527 (m), 505 (m), 443 (s) cm^{-1}.

(14) Formation of these $16e^-$ species would be favored in the sterically crowded tris(triethylphosphine) system but not in the less congested tris(trimethylphosphine) system.

(15) Spectroscopic data for 3 (carbon atoms in the chain are numbered by starting from the end opposite sulfur): ^1H NMR ($CD_3C(O)CD_3$, 22 °C, 500 MHz) δ 7.18 (m, 1, H1), 6.43 (m, 1, H2), 5.79 (m, 1, H4), 5.70 (m, 1, H3), 2.09–1.69 (m, 18, PEt_3CH_2's), 1.13–1.02 (m, 27, PEt_3CH_3's), −16.74 (m, 1, Ir–H); $^{13}C\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 150 MHz) δ 122.8 (s, C3), 122.7 (s, C4), 122.6 (s, C2), 121.1 (d of t, J_{C-P} = 72, 16 Hz, C1), 21.1 (d, J_{C-P} = 24.0 Hz, PEt_3CH_2's), 17.5 (virtual t, J_{C-P} = 32.0 Hz, mutually *trans* PEt_3CH_2's), 8.6 (s, PEt_3CH_3's), 8.4 (s, PEt_3CH_3's); $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 121 MHz, referenced to external H_3PO_4) δ −13.3 (d, J_{P-P} = 16.7 Hz, 2), −23.4 (t, J_{P-P} = 16.7 Hz, 1).

(16) Several other related thiametallacyclohexadienes have recently been synthesized via metal-centered cleavage of C–S bonds in thiophenes: (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chen, J.; Daniels, L. M.; Angelici, R. J. *Polyhedron* **1990**, *9*, 1883. (c) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559. (d) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (e) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171.

(17) Synthesis of 4: Under nitrogen, compound 2 (0.91 g, 1.44 mmol) was refluxed for 3 h in 50 mL of tetrahydrofuran. The solution was then cooled to room temperature, and the volatiles were removed under vacuum. Compound 4 was extracted from the resulting residue with pentane and crystallized at −30 °C from a concentrated diethyl ether solution containing several drops of pentane; yield 0.83 g, 91%. Anal. Calcd for $C_{22}H_{50}IrP_3S$: C, 41.81; H, 7.99. Found: C, 41.00; H, 8.19.

(18) Crystal data for 4: orange-yellow plate, 0.08 × 0.20 × 0.34 mm; triclinic, space group $P\bar{1}$, a = 9.683 (2) Å, b = 15.666 (5) Å, c = 18.301 (6) Å, α = 95.25 (3)°, β = 90.66 (2)°, γ = 93.38 (2)°; V = 2759.3 (14) $Å^3$, Z = 4, d_{cald} = 1.521 g/cm^3, μ = 50.95 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, ω scanning technique; 9777 unique reflections with $3.5° < 2\theta < 50°$ collected, 4264 reflections with $F > 6.0\sigma(F)$ used in refinement; face-indexed numerical absorption correction; R = 5.76%, R_w = 6.59%, GOF = 1.32, data-to-parameter ratio 15.9:1.

(19) Compound 4 is structurally related to a family of thiametallacyclopentene complexes which contain an oxygen atom in place of the exocyclic methylene carbon. (a) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30. (b) Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1979**, *168*, 403. (c) Guerchais, J. E.; LeFloch-Perennou, F.; Petillon, F. Y.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc., Chem. Commun.* **1979**, 410. (d) Petillon, F. Y.; LeFloch-Perennou, F.; Guerchais, J. E.; Sharp, D. W. A. *J. Organomet. Chem.* **1979**, *173*, 89. (e) Ashby, M. T.; Enemark, J. H. *Organometallics* **1987**, *6*, 1318.

(20) Spectroscopic data for 4 (carbon atoms in the chain are numbered by starting from the end opposite sulfur): ^1H NMR ($CD_3C(O)CD_3$, 22 °C, 300 MHz) δ 6.14 (m, 1, H3 or H4), 5.90 (m, 1, H1), 5.84 (m, 1, H4 or H3), 4.96 (m, 1, H1), 2.12–1.61 (m, 18, PEt_3CH_2's), 1.13–1.01 (m, 27, PEt_3CH_3's), −15.63 (q, J_{H-P} = 16 Hz, 1, Ir–H); $^{13}C\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 75 MHz) δ 161.9 (d of t, J_{C-P} = 76.7, 14.2 Hz, C2), 144.4 (s, C4 or C3), 142.7 (d, J_{C-P} = 11.1 Hz, C3 or C4), 120.6 (d, J_{C-P} = 10.3 Hz, C1), 21.2 (d, J_{C-P} = 23.9 Hz, PEt_3CH_2's), 18.1 (virtual t, J_{C-P} = 32.8 Hz, mutually trans PEt_3CH_2's), 8.7 (s, PEt_3CH_3's), 8.5 (s, PEt_3CH_3's); $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, 22 °C, 121 MHz, referenced to external H_3PO_4) δ −19.9 (t, J_{P-P} = 18.7 Hz, 1), −22.9 (d, J_{P-P} = 18.7 Hz, 2); IR (KBr pellet) 3028 (m), 2991–2877 (vs), 2095 (s), 1542 (s), 1457 (s), 1422 (s), 1372 (m), 1305 (m), 1256 (m), 1030 (vs), 1004 (m), 828 (s), 778 (vs), 758 (vs), 711 (vs), 656 (m), 623 (m), 419 (m) cm^{-1}.

sistent with the solid-state structure. The downfield region of the $^{13}C\{^1H\}$ NMR spectrum consists of four signals at δ 161.9 (C2), 144.4 and 142.7 (C3 and C4), and 120.6 (C1). C2 appears as a doublet (J = 76.7 Hz) of triplets (J = 14.2 Hz), due to phosphorus coupling. The $^{31}P\{^1H\}$ NMR spectrum is an AX_2 (triplet/doublet) pattern, as expected for a planar metallacycle with a *mer* arrangement of phosphine ligands.

A comparison of the (oxapentadienyl)iridium chemistry (Schemes I and II) with that of the analogous (thiapentadienyl)iridium system (Schemes III and IV) reveals some interesting differences. The oxapentadienyl chemistry appears to be driven by the favorable thermodynamics of forming C–O double bonds; hence, the final products are carbonyl-containing ring compounds. In contrast, C–S double bonds are relatively weak[21] and, as a result, all of the products in the (thiapentadienyl)iridium reaction systems contain C–S single bonds.[22] In both systems, however, five-membered rings are thermodynamically preferred over six-membered rings.

In summary, we have shown that treatment of (Cl)Ir$(PR_3)_3$ (R = Me, Et) with potassium thiapentadienide leads to the production of ((1,2,5-η)-5-thiapentadienyl)Ir$(PR_3)_3$ complexes. While the PMe_3 compound is stable in solution, its PEt_3 analogue undergoes intramolecular C–H bond activation processes, producing five- and six-membered thiairidacycles. The further reactivity of these novel species is currently under investigation in our laboratories.

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Supplementary Material Available: Structure determination summaries for 1 and 4, listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for 1 and 4, and ORTEP drawings of both independent molecules of 4 (19 pages). Ordering information is given on any current masthead page.

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[21] Typical bond energies for C=O and C=S are 799 and 573 kJ/mol, respectively: Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1972; Appendix F and references therein.

[22] In addition, the "soft" sulfur center of the thiapentadienyl ligand interacts more strongly with the $Ir(PR_3)_3$ moiety than does the "harder" oxygen center of oxapentadienyl.

Secondary Bonding in Organobismuth Compounds. Comparison of the Structures of 2,2′,5,5′-Tetramethyl-1,1′-dibismaferrocene and 2,2′,5,5′-Tetramethylbibismole

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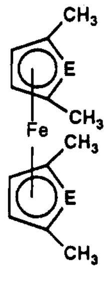
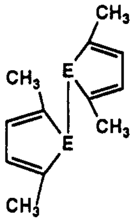
Summary: **The reaction of 1-phenyl-2,5-dimethylbismole (5) with lithium in THF followed by $FeCl_2$ gave red-black crystals of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (3), while the reaction of 5 with sodium in liquid ammonia followed by 1,2-dichloroethane gave green crystals of 2,2′,5,5′-tetramethylbibismole (4). Single-crystal X-ray diffraction studies show that 3 adopts a ferrocene-like arrangement with a close (3.688 (1) Å) inter-ring Bi⋯Bi contact, while 4 has a zigzag chain of Bi atoms with close intermolecular contacts of 3.6595 (5) Å.**

The structures of many main-group compounds exhibit short contacts between formally nonbonded atoms, which indicate a secondary bonding.[1,2] We recently reported the crystal structure of the distibaferrocene 1, which shows an inter-ring Sb⋯Sb contact that is well below the van der Waals distance.[3] The corresponding thermochromic bistibole 2 crystallizes so that Sb atoms are aligned in chains with a similar short intermolecular separation.[4,5] Since secondary bonding is generally more important for heavier atoms,[1] it is of interest to examine the corresponding bismuth compounds. We report here on the synthesis of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (3) and on a comparison of its crystal structure with that of 2,2′,5,5′-tetramethylbibismole (4).



1 E = Sb

3 E = Bi



2 E = Sb

4 E = Bi

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[1] Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

[2] Ashe, A. J., III. *Adv. Organomet. Chem.* **1990**, *30*, 77.

[3] Ashe, A. J., III; Diephouse, T. R.; Kampf, J. W.; Al-Taweel, S. *Organometallics* **1991**, *10*, 2068. Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

[4] Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207.

[5] Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876.

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