

# Sulfur-Hydrogen and Selenium-Hydrogen Bond Activation by Both Metal Centers in $[MM'(CO)_3(Ph_2PCH_2PPh_2)_2]$ ( $M, M' = Rh, Ir$ )

Robert McDonald and Martin Cowie\*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received September 28, 1992

The complexes  $[M_2(CO)_3(dppm)_2]$  ( $M = Rh$  (**1**),  $Ir$  (**2**);  $dppm = Ph_2PCH_2PPh_2$ ) react with  $H_2S$  to produce  $[M_2(CO)_2(\mu-S)(dppm)_2]$ ,  $CO$ , and  $H_2$ ; the reaction is immediate and quantitative for  $M = Rh$ , while for  $M = Ir$  a number of hydridic intermediates of general formula  $[Ir_2(H)_2(CO)_2(\mu-S)(dppm)_2]$  are observed, allowing a mechanism for  $H_2S$  addition and  $H_2$  elimination to be proposed. Reaction of  $H_2Se$  with **1** leads to several unidentified products, while with **2** hydridic products analogous to those observed in the  $H_2S$  reaction are among those formed. The reactions of  $[RhIr(CO)_3(dppm)_2]$  (**3**) with  $H_2S$  and  $H_2Se$  yield  $[RhIr(H)(CO)_2(\mu-XH)(dppm)_2]$  ( $X = S$  (**7**),  $Se$  (**8**)), which are proposed to have structures modeling the species formed by the first S-H bond addition to **1** or **2**; these undergo no further rearrangement or elimination of  $H_2$ . Reactions of the thiols or selenols  $RXH$  ( $X = S, R = Et, Ph; X = Se, R = Ph$ ) with **1** or **3** do not yield characterizable products; however with **2**, complexes of the form  $[Ir_2(XR)_2(CO)_2(\mu-CO)(dppm)_2]$  are obtained. One of these,  $[Ir_2(SPh)_2(CO)_2(\mu-CO)(dppm)_2]$  (**17**), has been characterized by X-ray crystallography and is shown to have the  $SPh$  ligands disposed on one side of the  $Ir_2P_4$  plane, while the one bridging and two terminal  $CO$  ligands are found on the opposite side. Complex **17** crystallizes with  $1/2$  equiv of dichloromethane solvent in the monoclinic space group  $C2/c$  with  $a = 19.532(7)$  Å,  $b = 22.030(6)$  Å,  $c = 14.333(6)$  Å,  $\beta = 102.82(4)^\circ$ ,  $V = 6014(7)$  Å<sup>3</sup>, and  $Z = 4$ . On the basis of 3319 unique observations and 349 parameters varied, the structure has been refined to  $R = 0.040$  and  $R_w = 0.053$ . Although, in contrast to the reactions of **2** with  $H_2S$  and  $H_2Se$ , net loss of  $CO$  does not occur in the formation of the dithiolate and diselenolate products, monitoring the reactions of **2** with  $RSH$  through use of variable-temperature multinuclear NMR spectroscopy indicates that dicarbonyl species such as  $[Ir_2(H)_2(SR)_2(CO)_2(dppm)_2]$  are intermediates.

## Introduction

Much effort has been directed toward understanding the interactions between sulfur-containing substrates and metal catalysts, much of it concerned with establishing how catalyst surfaces are poisoned by these compounds.<sup>1</sup> Other studies have focused upon chemical transformations of the sulfur-bearing species, including the mechanisms of hydrodesulfurization of sulfur-containing organic compounds present in hydrocarbon feedstock mixtures<sup>2</sup> and the utilization of hydrogen sulfide as an alternate source of hydrogen.<sup>3,4</sup> In some cases, the presence of sulfur-containing residues in a homogeneous catalyst precursor has been found to actually enhance activity of the catalyst.<sup>5</sup>

A fundamental step in the interaction between a catalyst and sulfur-containing substrates, such as hydrogen sulfide or thiols, is the oxidative addition of S-H bonds to the metal centers. In

the chemistry of mononuclear model complexes it has been found that sulfur tends to promote the formation of multinuclear complexes such that in the resultant products sulfur atoms (as  $HS^-$ ,  $RS^-$  or  $S^{2-}$  residues) often bridge two or three metal nuclei.<sup>3a-e,6</sup> Complexes in which the sulfur-containing ligands are present as purely terminal groups are also known.<sup>3a,f,g,6,7</sup>

Studies of oxidative additions of hydrogen sulfide, thiols, and disulfides to low-valent complexes of rhodium and iridium have focused mainly on mononuclear species;<sup>3a,d,6f,8b,9</sup> fewer studies have involved the interactions of sulfur-containing substrates with binuclear  $Rh$  or  $Ir$  complexes.<sup>10,11</sup> The reactions of bis(diphenylphosphino)methane-bridged low-oxidation-state di- and tri-

- (1) (a) Bonzel, H. P.; Ku, R. *J. Chem. Phys.* **1973**, *58*, 4617. (b) Bartholemew, C. H.; Agrawal, P. K.; Katzer, J. R. *Adv. Catal.* **1982**, *31*, 135. (c) Billy, J.; Abon, M. *Surf. Sci.* **1984**, *146*, L525. (d) Trenary, M.; Uram, K. J.; Yates, J. T., Jr. *Surf. Sci.* **1985**, *157*, 512. (e) Wong, P. C.; Zhou, M. Y.; Hui, K. C.; Mitchell, K. A. R. *Surf. Sci.* **1985**, *163*, 172. (f) Protopopoff, E.; Marcus, P. *Surf. Sci.* **1986**, *169*, L237. (g) Koestner, R. J.; Salmerson, M.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1986**, *172*, 668.
- (2) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394.
- (3) See, for example, the following representative studies. (a) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44. (b) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4617. (c) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620. (d) Mueting, A. M.; Boyle, P. D.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 271. (e) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3663. (f) Rabinovich, D.; Parkin, G. J. *Am. Chem. Soc.* **1991**, *113*, 5904. (g) Jessop, P. G.; Lee, C.-L.; Rastar, G.; James, B. R.; Lock, C. J. L.; Faggiani, R. *Inorg. Chem.* **1992**, *31*, 4601.
- (4) (a) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175. (b) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622. (c) Barnabas, A. F.; Sallin, D.; James, B. R. *Can. J. Chem.* **1989**, *67*, 2009.
- (5) (a) Kalck, P.; Poilblanc, R.; Martin, R.-P.; Rovera, A.; Gaset, A. *J. Organomet. Chem.* **1980**, *195*, C9. (b) Kalck, P.; Frances, J.-M.; Pfister, P.-M.; Southern, T. G.; Thorez, A. *J. Chem. Soc., Chem. Commun.* **1983**, 510. (c) Kalck, P. *Polyhedron* **1988**, *7*, 2441. (d) Bayón, J. C.; Esteban, P.; Real, J.; Claver, C.; Ruiz, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1579. (e) Bayón, J. C.; Real, J.; Claver, C.; Polo, A.; Ruiz, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1056. (f) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.
- (6) (a) Escaffre, P.; Thorez, A.; Kalck, P.; Besson, B.; Perron, R.; Colleuille, Y. *J. Organomet. Chem.* **1986**, *302*, C17. (b) Kalck, P.; Senocq, F.; Siani, M.; Thorez, A. *J. Organomet. Chem.* **1988**, *350*, 77. (c) Bianchini, C.; Meli, A.; Laschi, F.; Vacca, A.; Zanello, P. *J. Am. Chem. Soc.* **1988**, *110*, 3913. (d) Shaver, A. L.; Uhm, H. L.; Singleton, E.; Liles, D. C. *Inorg. Chem.* **1989**, *28*, 847. (e) Wei, G.; Liu, H.; Huang, Z.; Huang, L.; Kang, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1839. (f) Carlton, L.; Bulbulia, Z. *J. Organomet. Chem.* **1990**, *389*, 139. (g) Osakada, K.; Yamamoto, T.; Yamamoto, A.; Takenaka, A.; Sasada, Y. *Inorg. Chim. Acta* **1985**, *105*, L9.
- (7) (a) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Inorg. Chim. Acta* **1984**, *90*, L5. (b) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022. (c) Cecconi, F.; Innocenti, P.; Midollini, S.; Moneti, S.; Vacca, A.; Ramirez, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1129.
- (8) (a) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689. (b) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (c) Liaw, W.-F.; Kim, C.; Darenbourg, M. Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 3591. (d) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Young, D. J. *Inorg. Chem.* **1990**, *29*, 1496. (e) Darenbourg, M. Y.; Longridge, E. M.; Payne, V.; Reibenspies, J.; Riordan, C. G.; Springs, J. J.; Calabrese, J. C. *Inorg. Chem.* **1990**, *29*, 2721.

Table I. Infrared Spectroscopic Data<sup>a</sup> for the Compounds

compound	solid <sup>b</sup>	solution <sup>c</sup>
[RhIr(H)(SH)(CO) <sub>2</sub> (dppm) <sub>2</sub> ] (7)	1931 (vs), 1906 (vs)	1948 (vs), 1920 (vs)
[RhIr(H)(SeH)(CO) <sub>2</sub> (dppm) <sub>2</sub> ] (8)	2053 (vs), 2004 (vs)	2047 (s), 2009 (vs)
[Ir <sub>2</sub> (SEt) <sub>2</sub> (CO) <sub>2</sub> (μ-CO)(dppm) <sub>2</sub> ] (11)	1957 (s), 1943 (vs), 1702 (w)	1957 (sh), 1946 (vs, br), 1700 (w)
[Ir <sub>2</sub> (SPh) <sub>2</sub> (CO) <sub>2</sub> (μ-CO)(dppm) <sub>2</sub> ] (16)	1957 (s), 1946 (vs), 1720 (s)	1963 (sh), 1949 (vs), 1721 (s)
[Ir <sub>2</sub> (SPh) <sub>2</sub> (CO) <sub>2</sub> (μ-CO)(dppm) <sub>2</sub> ] (17)	1963 (s), 1951 (vs), 1700 (m)	1964 (vs), 1953 (vs), 1703 (m)
[Ir <sub>2</sub> (H) <sub>2</sub> (SPh) <sub>2</sub> (CO) <sub>2</sub> (dppm) <sub>2</sub> ] (18)	2152 (w, br), <sup>d</sup> 2044 (s), 1932 (vs)	2152 (w, br), <sup>d</sup> 2050 (vs), 1953 (vs)
[Ir <sub>2</sub> (SePh) <sub>2</sub> (CO) <sub>2</sub> (μ-CO)(dppm) <sub>2</sub> ] (20)	1959 (vs), 1947 (vs), 1708 (s)	1954 (vs, br), 1709 (vs)
[Ir <sub>2</sub> (H) <sub>2</sub> (SePh) <sub>2</sub> (CO) <sub>2</sub> (dppm) <sub>2</sub> ] (21)		2162 (w, br), <sup>d</sup> 2049 (vs), 1987 (s)

<sup>a</sup> Abbreviations used: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad. <sup>b</sup> Nujol mull on KBr disk. Values are  $\nu(\text{CO})$  except when indicated otherwise. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solution in KCl cells. <sup>d</sup>  $\nu(\text{Ir-H})$ .

platinum complexes with H<sub>2</sub>S, H<sub>2</sub>Se, thiols, selenols, disulfides, and diselenides have been the subject of several reports from the research group of Puddephatt,<sup>12</sup> while James and co-workers have investigated the addition of H<sub>2</sub>S to [Pd<sub>2</sub>X<sub>2</sub>(dppm)<sub>2</sub>] (X = Cl, Br, I), yielding [Pd<sub>2</sub>X<sub>2</sub>(μ-S)(dppm)<sub>2</sub>] and H<sub>2</sub> under ambient conditions.<sup>4</sup> Our interest in the binuclear oxidative-addition reactions of the [MM'(CO)<sub>3</sub>(dppm)<sub>2</sub>] (MM' = Rh,<sup>13</sup> Ir,<sup>14</sup> RhIr<sup>15</sup>; dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) compounds, which contain rhodium and iridium centers of low oxidation state, prompted investigations into the interactions of these complexes with hydrogen sulfide, hydrogen selenide, thiols, and selenols. A primary goal in these studies was to discover how adjacent metals could be involved in the activation of S-H and Se-H bonds.

### Experimental Section

General experimental conditions were as previously described.<sup>15</sup> The thiol and disulfide reagents were obtained from Aldrich and used as received. The complexes [Rh<sub>2</sub>(CO)<sub>3</sub>(dppm)<sub>2</sub>] (1),<sup>13</sup> [Ir<sub>2</sub>(CO)<sub>3</sub>(dppm)<sub>2</sub>] (2)<sup>14</sup> and [RhIr(CO)<sub>3</sub>(dppm)<sub>2</sub>] (3)<sup>15</sup> were prepared as previously reported. All other chemicals were used as received without further purification. Infrared and NMR spectroscopic parameters for the compounds prepared are found in Tables I and II, respectively.

**Preparation of Compounds.** (a) [RhIr(H)(SH)(CO)<sub>2</sub>(dppm)<sub>2</sub>]-CH<sub>2</sub>Cl<sub>2</sub> (7). An atmosphere of H<sub>2</sub>S was placed over a solution of 3 (150 mg, 131 μmol) in THF (5 mL), causing a color change from red-orange to deep red-brown. The solution was allowed to stir for 2 h, and then was evaporated to dryness under an N<sub>2</sub> stream. The brown residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the resultant solution filtered and reduced in volume, at which point addition of ether (15 mL) caused precipitation of a medium red-brown powder (91 mg, 56%). Anal. Calcd for C<sub>53</sub>Cl<sub>2</sub>H<sub>48</sub>IrO<sub>2</sub>P<sub>4</sub>RhS: C, 51.38; H, 3.91. Found: C, 51.42; H, 3.88.

(b) [RhIr(H)(SeH)(CO)<sub>2</sub>(dppm)<sub>2</sub>] (8). Hydrogen selenide was placed over a solution of 3 in THF (150 mg, 131 μmol in 5 mL) causing a color change from deep orange to red-brown within 10 min. The solution was stirred for 2 h then evaporated under a stream of N<sub>2</sub> to ca. 2 mL; addition of ether (15 mL) caused precipitation of a dark brown solid. This material was recrystallized from THF/ether, resulting in isolation of 105 mg (67%) of the product as a medium-brown powder.<sup>16</sup>

(c) [Ir<sub>2</sub>(SET)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>] (11). To a solution of 2 (100 mg, 80.8 μmol) in THF (5 mL) was added ethanethiol (12.0 μmol, 10.0 mg, 162 μmol), causing initially a slight lightening of the orange solution and then a change in color to light yellow within 20 min. The reaction mixture was left to stir for a further 2 h, during which time formation of a light yellow precipitate occurred. The solution volume was reduced to ca. 2 mL, causing a darkening of the supernatant liquid to red-orange. Placing the mixture under a CO atmosphere resulted in regeneration of the light yellow color. Addition of hexanes (20 mL) under CO completed precipitation of the light yellow product, which was dried under an N<sub>2</sub> stream and then briefly under vacuum, to give 79 mg (72% yield) of lemon-yellow powder. Anal. Calcd for C<sub>57</sub>H<sub>54</sub>Ir<sub>2</sub>O<sub>3</sub>P<sub>4</sub>S<sub>2</sub>: C, 50.36; H, 4.00. Found: C, 50.10; H, 4.38. (This compound has been found to be susceptible to decomposition via CO loss, more so in solution than in the solid state.)

(d) [Ir<sub>2</sub>(SPh)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>]-1/2CH<sub>2</sub>Cl<sub>2</sub> (17). Thiophenol (16.6 μL, 17.8 mg, 162 μmol) was added to a solution of 2 in THF (100 mg, 80.8 μmol in 5 mL), causing an immediate color change from orange to golden yellow. The reaction was stirred for a further 2 h, allowing formation of a yellow precipitate. Addition of hexanes (20 mL) completed precipitation, and the product was washed with hexanes then dried under a stream of N<sub>2</sub>, resulting in isolation of 83 mg (71%) of golden-yellow powder. Crystalline samples for microanalysis and an X-ray study were grown from CH<sub>2</sub>Cl<sub>2</sub>/ether. Anal. Calcd for C<sub>65.5</sub>H<sub>55</sub>ClIr<sub>2</sub>O<sub>3</sub>P<sub>4</sub>S<sub>2</sub>: C, 52.52; H, 3.70. Found: C, 52.47; H, 4.18.

(e) [Ir<sub>2</sub>(SePh)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>] (20). A THF solution of diphenyl diselenide (25.2 mg, 80.8 μmol in 1 mL) was added to a solution of 2 (100 mg, 80.8 μmol) in THF (5 mL). The reaction mixture immediately changed from clear and orange to cloudy and lighter orange. The mixture was stirred for 1 h, after which precipitation of the product was completed via addition of ether (15 mL). Yield was 87 mg (69%) of light orange-yellow powder. Anal. Calcd for C<sub>6</sub>H<sub>54</sub>Ir<sub>2</sub>O<sub>3</sub>P<sub>4</sub>Se<sub>2</sub>: C, 50.39; H, 3.51. Found: C, 49.55; H, 3.81.<sup>16</sup>

**Reaction of 1 with H<sub>2</sub>S.** Hydrogen sulfide was placed over a solution of 1 (150 mg, 142 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), resulting in an immediate change in the solution color from red-orange to brown. The mixture was stirred for a further 2 h and then evaporated to 5 mL, and the product precipitated via addition of hexanes (20 mL). The brown solid isolated was shown by <sup>31</sup>P{<sup>1</sup>H} and infrared spectroscopy to be the previously-characterized complex [Rh<sub>2</sub>(CO)<sub>2</sub>(μ-S)(dppm)<sub>2</sub>].<sup>17a</sup>

**Reaction of 2 with H<sub>2</sub>S at Room Temperature.** Hydrogen sulfide was placed over a solution of 2 (30 mg, 24.2 μmol) in THF-*d*<sub>8</sub> (0.6 mL) in an NMR sample tube, and the sample was shaken vigorously. The solution immediately underwent a color change from orange to light yellow; <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, and <sup>1</sup>H{<sup>31</sup>P} NMR experiments showed the sample to contain a mixture of isomers of [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>2</sub>(μ-S)(dppm)<sub>2</sub>]<sup>17b,18</sup> (as confirmed by comparison of these spectra with those obtained from a study of H<sub>2</sub> addition to [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-S)(dppm)<sub>2</sub>]<sup>18</sup>, together with small amounts of [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-S)(dppm)<sub>2</sub>]<sup>17b</sup> and [Ir<sub>2</sub>(CO)<sub>2</sub>(μ-S)(μ-CO)(dppm)<sub>2</sub>].<sup>17b</sup>

**Reaction of 2 with H<sub>2</sub>Se at Room Temperature.** Hydrogen selenide was placed over a stirred solution of 2 (30 mg, 24.2 μmol) in THF-*d*<sub>8</sub> (1.0 mL). An immediate color change from orange to yellow occurred, and the solution was allowed to stir at room temperature for 2 h. The solution

- (9) (a) Cooke, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 170. (b) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2516. (c) Bolton, E. S.; Havlin, R.; Knox, G. R. *J. Organomet. Chem.* **1969**, *18*, 153. (d) Senoff, C. V. *Can. J. Chem.* **1970**, *48*, 2444. (e) Kemmit, R. D. W.; Rimmer, D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3155. (f) Gaines, T.; Roundhill, D. M. *Inorg. Chem.* **1974**, *13*, 2521. (g) Collman, J. P.; Rothrock, R. K.; Stark, R. A. *Inorg. Chem.* **1977**, *16*, 437. (10) Balch, A. L.; Labadie, J. W.; Delker, G. *Inorg. Chem.* **1979**, *18*, 1224. (11) Cotton, F. A.; Lahuerta, P.; Latorre, J.; Sanaú, M.; Solana, I.; Schwotzer, W. *Inorg. Chem.* **1988**, *27*, 2131. (12) (a) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 3776. (b) Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4280. (c) Hadj-Bagheri, N.; Puddephatt, R. J.; Manojlović-Muir, L.; Stefanović, A. *J. Chem. Soc., Dalton Trans.* **1990**, 535. (13) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (b) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285. (14) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637. (15) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564. (16) The purity of several of the solid compounds obtained could not be confirmed by elemental analysis; although hydrogen percentages were satisfactory, carbon results were consistently ~1% below the calculated values, apparently due to the formation of iridium carbides. Nevertheless the compounds were spectroscopically pure, as found by NMR and IR spectroscopy.

- (17) (a) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726. (b) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. (18) (a) Vaartstra, B. A.; O'Brien, K. N.; Eisenberg, R.; Cowie, M. *Inorg. Chem.* **1988**, *27*, 3668. (b) Vaartstra, B. A. Ph.D. Thesis, University of Alberta, 1989, Chapter 5. (c) O'Brien, K. N. Ph.D. Thesis, University of Rochester, 1987, Chapter 5.

Table II. Nuclear Magnetic Resonance Spectroscopic Data<sup>a</sup> for the Compounds

compound	$\delta(^{31}\text{P}\{\text{H}\})^b$	$\delta(^{13}\text{C}\{\text{H}\})^c$	$\delta(^1\text{H})^c$
$[\text{Ir}_2(\text{H})(\mu\text{-SH})(\text{CO})_2(\text{dppm})_2]$ (5)	-16.5 (m), -27.1 (m) <sup>d</sup>	173.2 (s, br, 1 C), 164.8 (s, br, 1 C) <sup>d</sup>	-1.07 (s, br, 1 H), -13.03 (t, 1 H, $^2J_{\text{P-H}} = 9.8$ Hz) <sup>d</sup>
$[\text{RhIr}(\text{H})(\mu\text{-SH})(\text{CO})_2(\text{dppm})_2]$ (7)	-5.04 (dm, $^2J_{\text{Rh-P}} = 103.8$ Hz), <sup>e</sup> -19.49 (m)	183.4 (dt, 1 C, $^1J_{\text{Rh-C}} = 55.7$ Hz, $^2J_{\text{P(Rh)-C}} = 8.4$ Hz), 167.2 (t, 1 C, $^2J_{\text{P(Ir)-C}} = 6.4$ Hz)	8.07-6.91 (m, 40 H), 6.52 (m, 2 H), 4.21 (m, 2 H), -2.91 (t, 1 H, $^2J_{\text{P(Rh)-H}} = 6.4$ Hz), -10.74 (t, 1 H, $^2J_{\text{P(Ir)-H}} = 12.8$ Hz)
$[\text{RhIr}(\text{H})(\mu\text{-SeH})(\text{CO})_2(\text{dppm})_2]$ (8)	-11.04 (dm, $^2J_{\text{Rh-P}} = 103.5$ Hz), <sup>e</sup> -23.41 (m) <sup>f</sup>	181.0 (dt, 1 C, $^1J_{\text{Rh-C}} = 57.3$ Hz, $^2J_{\text{P(Rh)-C}} = 8.3$ Hz), 165.5 (s, br, 1 C)	8.06-6.98 (m, 40 H), 6.71 (m, 2 H), 4.06 (m, 2 H), -4.90 (t, 1 H, $^2J_{\text{P(Rh)-H}} = 6.8$ Hz), -11.80 (t, 1 H, $^2J_{\text{P(Ir)-H}} = 12.4$ Hz)
$[\text{Ir}_2(\text{SEt})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (11)	-13.94 (s)	221.6 (m, 1 C), 176.4 (t, 2 C, $^2J_{\text{P-C}} = 7.0$ Hz)	7.61-6.97 (m, 40 H), 6.08 (m, 2 H), 5.34 (m, 2 H), 0.21 (t, 6 H, $^3J_{\text{H-H}} = 7.2$ Hz), -0.49 (qrt, 4 H, $^3J_{\text{H-H}} = 7.2$ Hz)
$[\text{Ir}_2(\text{H})_2(\text{SEt})_2(\text{CO})_2(\text{dppm})_2]$ (12)	-6.1 (s) <sup>g</sup>	171.3 (m, br, 2 C) <sup>g</sup>	5.42 (m, 2 H), 4.20 (m, 2 H), -9.10 (qnt) <sup>g</sup> $^3J_{\text{H-H}} = 7.2$ Hz)
$[\text{Ir}_2(\text{H})_2(\text{SEt})_2(\text{CO})_2(\text{dppm})_2]$ (13)	-8.4 (m), -12.8 (m) <sup>g</sup>	160.7 (br, 1 C), 159.9 (br, 1 C) <sup>g</sup>	5.66 (m, 2 H), 5.48 (m, 2 H), -9.37 (t, 1 H, $^2J_{\text{P-H}} = 14.4$ Hz), -13.06 (t, 1 H, $^2J_{\text{P-H}} = 14.4$ Hz) <sup>g</sup>
$[\text{Ir}_2(\text{H})(\text{SEt})(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (14)	-1.7 (m), -11.1 (m) <sup>h</sup>	<i>i</i>	-10.20 (t, 1 H, $^2J_{\text{P-H}} = 14.0$ Hz) <sup>h</sup>
$[\text{Ir}_2(\text{SEt})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (15)	-15.4 (m), -29.0 (m) <sup>h</sup>	<i>i</i>	<i>i</i>
$[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (16)	-13.39 (m), -26.96 (m)	227.4 (m, 1 C), 182.3 (dt, 1 C, $^2J_{\text{C-C}} = 24.9$ Hz, $^2J_{\text{P-C}} = 12.4$ Hz), 177.3 (t, 1 C, $^2J_{\text{P-C}} = 19.3$ Hz)	7.68-6.04 (m, 50 H), 4.76 (m, 2 H), 4.45 (m, 2 H)
$[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (17)	-15.06 (s)	216.7 (m, 1 C), 177.3 (t, 2 C, $^2J_{\text{P-C}} = 6.8$ Hz)	7.70-6.73 (m, 50 H), 5.86 (m, 2 H), 4.91 (m, 2 H)
$[\text{Ir}_2(\text{H})_2(\text{SPh})_2(\text{CO})_2(\text{dppm})_2]$ (18)	-5.31 (s)	171.1 (t, 1 C, $^2J_{\text{P-C}} = 5.4$ Hz)	7.62-6.76 (m, 50 H), 6.54 (br, 2 H), 4.10 (br, 2 H), -11.58 (qnt, 2 H)
$[\text{Ir}_2(\text{H})(\text{SPh})(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (19)	0.5 (m), -11.4 (m) <sup>g</sup>	232.7 (m, 1 C), 180.3 (t, 1 C, $^2J_{\text{P-C}} = 11.5$ Hz), 176.3 (t, 1 C, $^2J_{\text{P-C}} = 7.5$ Hz) <sup>g</sup>	-9.98 (t, 1 H, $^2J_{\text{P-H}} = 10.0$ Hz) <sup>g</sup>
$[\text{Ir}_2(\text{SePh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ (20)	-17.68 (s)	215.7 (m, 1 C), 176.1 (t, 2 C, $^2J_{\text{P-C}} = 6.5$ Hz)	7.70-6.08 (m, 50 H), 6.03 (m, 2 H), 5.21 (m, 2 H)
$[\text{Ir}_2(\text{H})_2(\text{SePh})_2(\text{CO})_2(\text{dppm})_2]$ (21)	-6.77 (s)	171.5 (t, 1 C, $^2J_{\text{P-C}} = 5$ Hz)	7.82-6.72 (m, 50 H), 6.12 (m, 2 H), 4.29 (m, 2 H), -11.58 (qnt, 2 H)

<sup>a</sup> Abbreviations used: br = broad, s = singlet, d = doublet, t = triplet, qrt = quartet, qnt = quintet, m = multiplet. Data were obtained in CD<sub>2</sub>Cl<sub>2</sub> solvent at 25 °C unless otherwise noted. <sup>b</sup> Vs 85% H<sub>3</sub>PO<sub>4</sub>. <sup>c</sup> Vs TMS. <sup>d</sup> At -60 °C in THF-*d*<sub>8</sub>. <sup>e</sup> Rh-P. <sup>f</sup> Ir-P. <sup>g</sup> At -20 °C in CD<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup> At -20 °C in THF-*d*<sub>8</sub>. <sup>i</sup> Data not obtained for this unstable intermediate.

was found by multinuclear (<sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, and <sup>1</sup>H{<sup>31</sup>P}) NMR spectroscopy to consist of several species; elucidation of their structures is discussed below.

**X-ray Data Collection.** Diffusion of ether into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution containing a mixture of complexes **16** and **17** produced red-orange crystals of **17**, several of which were mounted and flame-sealed in glass capillaries under N<sub>2</sub> and solvent vapor to minimize decomposition and/or solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K $\alpha$  radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 20.0° ≤ 2θ ≤ 24.0°. The monoclinic diffraction symmetry and the systematic absences (*hkl*, *h* + *k* ≠ 2*n*; *h0l*, *l* ≠ 2*n*) were consistent with the space groups *Cc* or *C2/c* (the latter was confirmed as the correct space group by the successful solution and refinement of the structure).

Intensity data were collected at 22 °C by using the  $\theta/2\theta$  scan technique, covering reflections with indices of the form *h*, *k*, ±*l* to a maximum 2θ = 50.0°. Of the data collected, 6718 reflections were unique after merging. Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three reflections were chosen as intensity standards, being remeasured after every 120 min of X-ray exposure time. The intensities of these standards remained approximately constant over the duration of data collection; thus, no decomposition correction was applied. The data were measured and processed in the usual way, with a value of 0.04 for *p*<sup>19</sup> employed to downweight intense reflections; 3319 reflections were considered observed ( $F_o^2 \geq 3\sigma(F_o^2)$ ) and were used in subsequent calculations. Absorption corrections were applied to the data according

Table III. Crystallographic Data for  $[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2] \cdot 1/2\text{CH}_2\text{Cl}_2$  (17)

formula	C <sub>65.5</sub> H <sub>55</sub> Ir <sub>2</sub> O <sub>3</sub> P <sub>4</sub> S <sub>2</sub>	fw	1498.06
<i>a</i> , Å	19.532 (7)	space group	<i>C2/c</i> (No. 15)
<i>b</i> , Å	22.030 (6)	<i>T</i> , °C	22
<i>c</i> , Å	14.333 (6)	$\lambda$ , Å	0.71069
$\beta$ , deg	102.82 (4)	$\mu$ , cm <sup>-1</sup>	46.65
<i>V</i> , Å <sup>3</sup>	6014 (7)	$R(F_o)$ <sup>a</sup>	0.040
<i>Z</i>	4	$R_w(F_o)$ <sup>b</sup>	0.053
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.654		

$$^a R(F_o) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w(F_o) = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2}$$

to the method of Walker and Stuart.<sup>20,21</sup> See Table III for crystal data and more information on the X-ray data collection.

**Structure Solution and Refinement.** The structure of compound **17** was solved in the space group *C2/c* using standard Patterson and Fourier techniques. Full-matrix least-squares refinements proceeded so as to minimize the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$ . Atomic scattering factors and anomalous dispersion terms were taken from the usual tabulations.<sup>22-24</sup> Positional parameters for the hydrogens attached to the carbon atoms of the complex were calculated from the geometries about the attached carbon. These hydrogens were located 0.95 Å from their attached C atoms, given thermal parameters 20% greater than the

(19) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.(20) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(21) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

(22) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.(24) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

**Table IV.** Positional and Thermal Parameters of Selected Atoms of  $[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2] \cdot 1/2\text{CH}_2\text{Cl}_2$  (**17**)<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>
Ir	0.06143(2)	0.20069(2)	0.32402(3)	2.642(7)
S	0.0756(1)	0.0889(1)	0.3345(2)	3.66(7)
P(1)	-0.0017(1)	0.1875(1)	0.4435(2)	3.09(6)
P(2)	-0.1322(1)	0.1972(1)	0.2874(2)	3.01(6)
O(1)	0.1726(4)	0.2694(4)	0.4635(6)	5.8(2)
O(2)	0.000	0.3212(4)	0.250	4.0(3)
C(1)	0.1318(5)	0.2415(5)	0.4110(7)	3.6(3)
C(2)	0.000	0.2680(6)	0.250	2.6(3)
C(3)	-0.0893(5)	0.1562(5)	0.3936(7)	3.4(2)
C(51)	0.1523(8)	0.0645(7)	0.427(1)	7.1(4)
C(52)	0.1643(8)	0.0013(6)	0.463(1)	8.3(4)
C(53)	0.2076(7)	-0.0185(5)	0.5125(9)	5.9(3)
C(54)	0.2710(9)	0.0216(7)	0.555(1)	10.7(5)
C(55)	0.2685(8)	0.0776(7)	0.5364(9)	7.4(4)
C(56)	0.2102(8)	0.0998(8)	0.472(1)	8.5(5)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter defined as  $1/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$ . Parameters for phenyl carbon atoms of the dppm groups and atoms of the solvent molecule are given in the supplementary material.

**Table V.** Selected Distances (Å) in  $[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2] \cdot 1/2\text{CH}_2\text{Cl}_2$  (**17**)

(a) Bonded <sup>a</sup>			
Ir–Ir'	2.8286(6)	P(1)–C(11)	1.810(9)
Ir–S	2.480(2)	P(1)–C(21)	1.825(9)
Ir–P(1)	2.339(2)	P(2)–C(3)	1.809(9)
Ir–P(2')	2.333(2)	P(2)–C(31)	1.825(9)
Ir–C(1)	1.868(9)	P(2)–C(41)	1.792(9)
Ir–C(2)	2.049(9)	O(1)–C(1)	1.15(1)
S–C(51)	1.84(1)	O(2)–C(2)	1.17(1)
P(1)–C(3)	1.837(8)		
(b) Non-Bonded			
P(1)···P(2)	3.003(3)	S···S'	3.378(4)

<sup>a</sup> Primed atoms are related to unprimed ones via the crystallographic 2-fold axis passing through C(2)O(2) and the center of the Ir–Ir' bond.

equivalent isotropic *B*'s of their associated carbons, and included as fixed contributions. Peaks due to the Cl atoms of the solvent molecule were found to be symmetrically disposed about the crystallographic 2-fold axis of symmetry at  $1/2, y, 1/4$ , and were found to have electron density roughly half of that expected (being comparable to the typical value for a carbon atom). This suggested a half-molecule of dichloromethane per complex molecule; thus, Cl was input at half-occupancy, and refined satisfactorily. The central carbon atom of the  $\text{CH}_2\text{Cl}_2$  molecule was located on the 2-fold axis at a distance and angle appropriate for a Cl–C–Cl unit, as found through use of difference Fourier electron density maps; however, this carbon atom did not refine well and so was included as a fixed contribution. For this reason the solvent molecule's hydrogen atoms were not included. There was no evidence for secondary extinction therefore no extinction correction was applied.

The final model for complex **17**, with 349 parameters varied, converged to values of  $R = 0.040$  and  $R_w = 0.053$ . In the final difference Fourier map the 10 highest residuals (1.6–0.9 e/Å<sup>3</sup>) were found in the area of the solvent molecule and the thiophenolate group (a typical carbon in an earlier synthesis had an electron density of 3.5 e/Å<sup>3</sup>). The positional and thermal parameters for the non-hydrogen atoms of complex **17** are given in Table IV, and selected bond lengths and angles are given in Tables V and VI, respectively.

## Results and Discussion

When hydrogen sulfide is passed through a THF solution of  $[\text{Rh}_2(\text{CO})_3(\text{dppm})_2]$  (**1**) at room temperature, the previously-synthesized  $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$ <sup>17a</sup> is obtained instantaneously as the only product. Oxidative addition of both S–H bonds of  $\text{H}_2\text{S}$  to **1** has apparently taken place, with concomitant loss of CO and  $\text{H}_2$  to give the final species. A similar transformation, observed in the reactions of  $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$  with

**Table VI.** Selected Angles (deg) in  $[\text{Ir}_2(\text{SPh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2] \cdot 1/2\text{CH}_2\text{Cl}_2$  (**17**)

(a) Bond Angles <sup>a</sup>			
Ir'–Ir–S	96.32(5)	P(1)–Ir–C(2)	97.22(6)
Ir'–Ir–P(1)	92.97(6)	P(2')–Ir–C(1)	90.7(3)
Ir'–Ir–P(2')	91.12(5)	P(2')–Ir–C(2)	92.12(6)
Ir'–Ir–C(1)	151.2(3)	C(1)–Ir–C(2)	104.9(4)
Ir'–Ir–C(2)	46.3(2)	Ir–S–C(51)	113.3(4)
S–Ir–P(1)	84.35(8)	Ir–P(1)–C(3)	111.0(3)
S–Ir–P(2')	86.24(8)	Ir'–P(2)–C(3)	111.1(3)
S–Ir–C(1)	112.5(3)	Ir–C(1)–O(1)	176.2(9)
S–Ir–C(2)	142.6(2)	Ir–C(2)–Ir'	87.4(5)
P(1)–Ir–P(2')	170.10(8)	Ir–C(2)–O(2)	136.3(2)
P(1)–Ir–C(1)	90.0(3)	P(1)–C(3)–P(2)	110.9(5)
(b) Torsion Angles			
S–Ir–Ir'–S'	3.59(9)	P(1)–Ir–Ir'–P(2)	5.3(1)

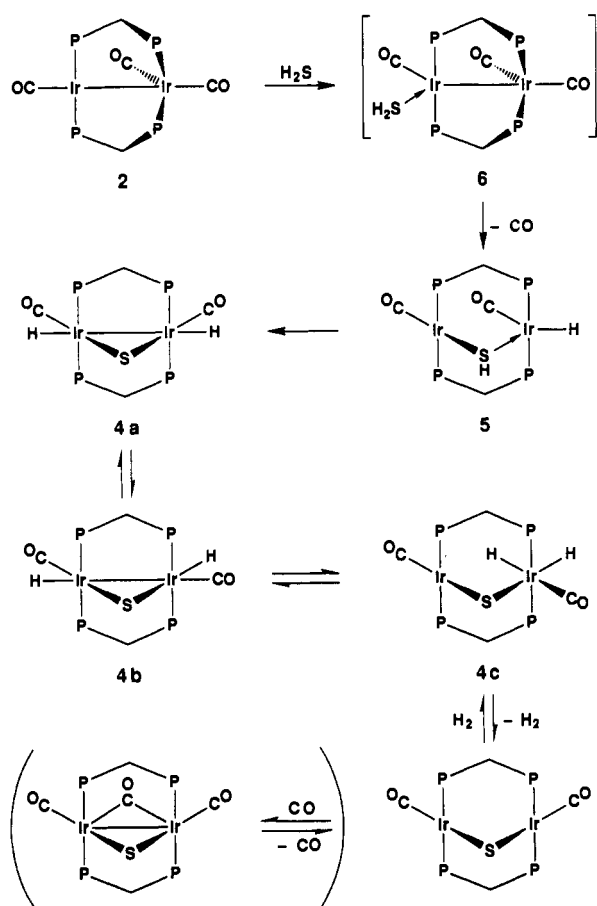
<sup>a</sup> Primed atoms are related to unprimed ones via the crystallographic 2-fold axis passing through C(2)O(2) and the center of the Ir–Ir' bond.

$\text{H}_2\text{S}$  to yield  $[\text{Pd}_2\text{X}_2(\mu\text{-S})(\text{dppm})_2]$  and  $\text{H}_2$ , has been investigated by James and co-workers.<sup>4</sup> Both of these systems are important in illustrating how adjacent metal centers can work in concert to activate two H–X bonds belonging to the same substrate, and it is of interest to obtain information pertaining to the involvement of each metal in the overall process. Monitoring the reaction of **1** with  $\text{H}_2\text{S}$  by  $^31\text{P}\{\text{H}\}$  NMR spectroscopy at low temperature has failed to detect intermediates; as the mixture is warmed in 10° increments from –80 °C to room temperature, signals due to **1** decrease in intensity while those due to  $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  increase, with conversion being complete by the time the temperature reaches –50 °C. The lack of observable intermediates is not totally surprising, as previous attempts to add  $\text{H}_2$  to  $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  revealed no hydridic species.<sup>17a</sup> Furthermore, dppm-bridged dirhodium complexes containing hydride ligands are found to be fewer in number and generally less stable<sup>13a,25</sup> than similar diiridium species.<sup>14,15a,17b,18,26–30</sup> Owing to our failure to observe intermediates in the reaction between  $\text{H}_2\text{S}$  and **1**, we turned to the analogous diiridium system in attempts to obtain models for possible intermediates in the “double oxidative addition” of  $\text{H}_2\text{S}$  and the subsequent reductive elimination of  $\text{H}_2$ .

The complex  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$  (**2**) reacts with hydrogen sulfide in an analogous fashion, but the course of the reaction can be followed spectroscopically and several intermediates can be identified before formation of the ultimate product, the previously-synthesized sulfide-bridged A-frame complex  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$ ,<sup>17b</sup> is complete. Among the species observed by  $^31\text{P}\{\text{H}\}$  and  $^1\text{H}$  NMR when  $\text{H}_2\text{S}$  is bubbled through a THF solution of **2** at room temperature are the sulfide-bridged dicarbonyl dihydride complexes **4a–c** shown in Scheme I. Intermediate **4a** is the result of oxidative addition of two S–H bonds to complex **2**, one to each metal, with concomitant loss of CO, while **4b** and **4c** are the products of a series of hydride migrations about the bimetallic core, a process that has been described elsewhere.<sup>29</sup> The complexes  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  and  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$  are also present in minor amounts, the former resulting from  $\text{H}_2$  elimination from **4c**, with the latter the result of CO uptake by the sulfide-bridged A-frame complex (the CO being a byproduct of the initial reaction of **2**

- (25) (a) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637. (b) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 1290. (c) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 4207. (d) Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417. (e) Wang, W.-D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833. (26) Sutherland, B. R.; Cowie, M. *Can. J. Chem.* **1986**, *64*, 464. (27) McDonald, R.; Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1987**, *26*, 3333. (28) McDonald, R.; Cowie, M. *Organometallics* **1990**, *9*, 2468. (29) Vaartstra, B. A.; Cowie, M. *Inorg. Chem.* **1989**, *28*, 3138. (30) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801.

Scheme I

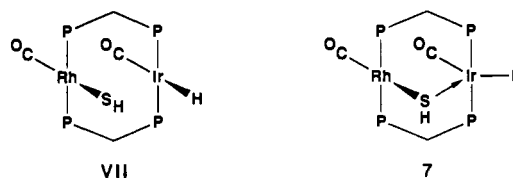


with  $\text{H}_2\text{S}$  to produce 5). If this THF solution is refluxed for 2 h under a slow  $\text{N}_2$  stream, or if it is allowed to stir under  $\text{N}_2$  at room temperature for 2 days, conversion of all species to  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  results. Products 4a–c are identical to those characterized in an earlier investigation of  $\text{H}_2$  addition to  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$ ,<sup>18</sup> demonstrating the reversibility of this step. It is important to note however, that the conversion of 2 to the sulfide-bridged species is *not* reversible; therefore, the reaction of the sulfide-bridged A-frame with  $\text{H}_2$  stops at compounds 4a–c and does *not* result in the reductive elimination of  $\text{H}_2\text{S}$ . Monitoring the reaction of 2 with  $\text{H}_2\text{S}$  by variable-temperature multinuclear NMR spectroscopy provides insight into the initial steps of activation of the S–H bonds, and an intermediate, formulated as  $[\text{Ir}_2(\text{H})(\text{CO})_2(\mu\text{-SH})(\text{dppm})_2]$  (5), may be observed and characterized at  $-60^\circ\text{C}$  in  $\text{THF}-d_8$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 5 shows two pseudotriplet resonances at  $\delta -16.5$  and  $-27.1$  indicative of two different chemical environments for the phosphorus nuclei, and the highfield region of the  $^1\text{H}$  NMR spectrum shows a broad singlet at  $\delta -1.07$  and a triplet at  $\delta -13.03$  ( $^2J_{\text{P-H}} = 9.8$  Hz). Irradiation of the lower-field phosphorus resonance results in a collapse of the highest-field  $^1\text{H}$  resonance to a singlet, confirming that it corresponds to a terminally-bound iridium hydride. Although the  $^1\text{H}$  resonance at  $\delta -1.07$  is unaffected when either of the phosphorus resonances is irradiated, indicating no discernible coupling to either set of phosphorus nuclei, it is likely due to a sulfhydryl group bridging the two metals. Resonances similar in appearance and chemical shift to this one have been observed in the  $^1\text{H}$  NMR spectra of the series of complexes  $[\text{Ir}_2(\text{H})_2(\mu\text{-SH})(\mu\text{-SR})(\mu\text{-H})(\text{PPh}_3)_4]^{n+}$  ( $\text{R} = \text{H}, \text{Pr}^i; n = 1; \text{R} = \text{vacant}; n = 0$ ),<sup>3d</sup> which have been shown by X-ray crystallography to contain bridging SH units. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at  $-60^\circ\text{C}$  of 5 prepared by using  $^{13}\text{C}$ -enriched compound 2 shows, in addition to less-intense signals due to 2 and the hydridic products 4a–c, two resonances of equal intensity (broadened singlets at  $\delta 173.2$  and  $164.8$ ) attributable

to this intermediate. All resonances due to intermediate 5 disappear upon warming, being replaced by those as described in the ambient-temperature reaction.

On the basis of these data, the reaction of  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$  (2) with  $\text{H}_2\text{S}$  may be proposed to proceed as shown in Scheme I. Intermediate 6, unlike the other species illustrated, was not observed; however, the formulation shown is supported by related investigations of the oxidative additions of  $\text{H}_2\text{S}$  and thiols to the isoelectronic heterobimetallic complex  $[\text{RhRe}(\text{CO})_4(\text{dppm})_2]$ .<sup>31</sup> Coordination of  $\text{H}_2\text{S}$  at the coordinatively unsaturated Ir center in 2 is not unexpected, and although such adducts are not common, a few are known.<sup>8a,32</sup> It does not appear likely that the reaction of 2 with  $\text{H}_2\text{S}$  takes place via acid/base dissociation of hydrogen sulfide, i.e. involving initial protonation of the tricarbonyl 1 or 2 followed by reaction of the so-formed protonated complex with  $\text{SH}^-$  to give the dihydride species. Hydrogen sulfide is a weak acid in aqueous solution ( $K_1 = 9.1 \times 10^{-8}$ ) and would be expected to be even weaker in THF. Furthermore, although the reaction of  $[\text{Ir}_2(\text{CO})_2(\mu\text{-H})(\mu\text{-CO})(\text{dppm})_2][\text{BF}_4]^{14}$  with  $\text{NaSH}$  at room temperature does proceed to give a mixture of  $[\text{Ir}_2(\text{H})_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  isomers and  $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$ , the reaction time required is 24 h, which is clearly inconsistent with the rapid rate observed for the reaction of 2 with  $\text{H}_2\text{S}$ .

It was anticipated that further insight into the reactivity of hydrogen sulfide toward compounds 1 and 2 would be gained by studies of the reaction of  $\text{H}_2\text{S}$  with the mixed-metal analogue  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  (3). Unlike the transformation observed for the homobimetallic tricarbonyls, this reaction does *not* ultimately yield the sulfide-bridged, hydride-free dicarbonyl derivative. Instead, the only product observed is  $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-SH})(\text{dppm})_2]$  (7). The infrared and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of this complex indicate that two terminal CO groups are present, and the couplings in the NMR indicate that one is on each metal. The highfield region of the  $^1\text{H}$  NMR spectrum shows two triplet resonances, at  $\delta -2.91$  ( $^2J_{\text{P-H}} = 6.4$  Hz) and  $-10.74$  ( $^2J_{\text{P-H}} = 12.8$  Hz). Decoupling the iridium-bound phosphorus nuclei causes the high-field  $^1\text{H}$  signal to collapse to a singlet, leaving the other unaffected, while decoupling the rhodium-bound phosphorus nuclei causes the lower-field triplet to collapse to a singlet without altering the appearance of the higher-field triplet. Thus the latter signal is consistent with a hydride ligand that is terminally bound to iridium, whereas the former resonance appears to be due to a sulfhydryl ligand interacting with the rhodium center. The lack of obvious coupling of the sulfhydryl hydrogen to the iridium-bound phosphorus nuclei suggests a terminal SH group as in structure VII. However we favor the bridged structure



shown for 7 owing to the strong tendency of these groups to bridge and to the tendency of RhIr systems to obtain a 16/18-electron configuration.<sup>28,29,33,34</sup> In this case the bridging S–H group would compensate for the loss of a donor electron pair

- (31) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 3339.  
 (32) (a) Herberhold, M.; Süß, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 366. (b) Harris, P. J.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1009. (c) Urban, G.; Sünkel, K.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 329. (d) Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830. (e) Sellmann, D.; Lechner, P.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 552. (f) Sellmann, D.; Lechner, P.; Knoch, F.; Moll, M. *J. Am. Chem. Soc.* **1992**, *114*, 922.  
 (33) (a) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060. (b) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743. (c) Mague, J. T. *Organometallics* **1986**, *5*, 918. (d) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 4039. (e) Jenkins, J. A. Ph.D. Thesis, University of Alberta, 1991, Chapter 6.

Table VII. NMR Spectroscopic Parameters for the Species Observed in the Reaction of  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$  (**2**) with  $\text{H}_2\text{Se}^a$ 

compound	core structure <sup>a</sup>	$\delta(^{31}\text{P}\{\text{H}\})$	$\delta(^1\text{H})$
9a		-7.33 (s)	-9.86 (pseudoquintet)
9b		-8.62 (m), -14.35 (m)	-9.79 (t, $^2J_{\text{P-H}} = 12.0$ Hz), -12.70 (t, $^2J_{\text{P-H}} = 13.8$ Hz)
9c		-7.06 (s)	-11.04 (pseudoquintet)
9d		-4.81 (m), -12.04 (m)	-9.48 (dt, $^2J_{\text{P-H}} = 13.8$ Hz, $^2J_{\text{H-H}} = 5.6$ Hz), -12.03 (dt, $^2J_{\text{P-H}} = 18.0$ Hz, $^2J_{\text{H-H}} = 5.6$ Hz)
9e		-12.58 (m), -21.83 (m)	-5.34 (t, $^2J_{\text{P-H}} = 5.5$ Hz), -11.22 (t, $^2J_{\text{P-H}} = 13.4$ Hz)
9f		-17.45 (m), -28.65 (m)	-3.61 (br), -12.59 (t, $^2J_{\text{P-H}} = 11.2$ Hz)
10		-6.83 (s)	

<sup>a</sup> The bridging dppm groups have been omitted for clarity.

upon removal of CO from iridium. A selenium-containing analogue of **7**,  $[\text{RhIr}(\text{H})(\mu\text{-SeH})(\text{CO})_2(\text{dppm})_2]$  (**8**), has been prepared in much the same manner and is found to possess spectroscopic parameters very similar to those for the sulfur-containing species (see Table II).

As noted above, complex **7** does not undergo further hydride rearrangements and does not reductively eliminate  $\text{H}_2$ . The fact that only one S-H bond of  $\text{H}_2\text{S}$  is activated by **3** is in distinct contrast, not only to the reactions of hydrogen sulfide with the homobimetallic  $\text{Rh}_2$  (**1**) and  $\text{Ir}_2$  (**2**) analogues but also to  $\text{H}_2\text{S}$  addition to the heterobimetallic analogue  $[\text{RhRe}(\text{CO})_4(\text{dppm})_2]$ , in which the hydrido sulphydryl intermediate  $[\text{RhRe}(\text{CO})_4(\text{SH})(\mu\text{-H})(\text{dppm})_2]$  underwent facile  $\text{H}_2$  loss to yield  $[\text{RhRe}(\text{CO})_4(\mu\text{-S})(\text{dppm})_2]$ .<sup>31</sup> It is noteworthy that although  $[\text{RhIr}(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  (theoretically the result of dehydrogenation of **7**) does react reversibly with  $\text{H}_2$  to form  $[\text{RhIr}(\text{H})_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$ ,<sup>29</sup> this product does not undergo a hydride migration process as observed for its diiridium analogue; instead, both hydrides remain attached to iridium and remain oriented cis to each other. For the diiridium complex, the mechanism proposed<sup>29</sup> for rearrangement of the hydride ligands involves a swinging of the sulfido group in and out of the bridging position on and off each metal in turn. This transformation yields species having terminal hydrides on *both* metals and results in an alternation of each metal center between 16- and 18-electron configurations. It appears that the tendency for rhodium and iridium, in these mixed Rh/Ir complexes, to retain their respective 16- and 18-electron configurations,<sup>15,29</sup> and the greater tendency to have Ir-H rather than Rh-H bonds inhibits the aforementioned rearrangements which in turn inhibits the subsequent reductive elimination of  $\text{H}_2$ .

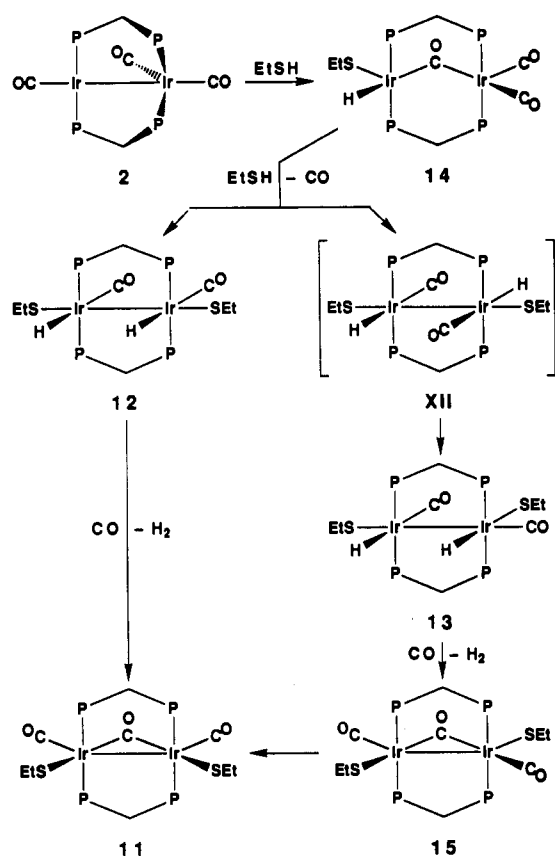
Hydrogen selenide was also found to react with complexes **1** and **2**. The addition of  $\text{H}_2\text{Se}$  to  $[\text{Rh}_2(\text{CO})_3(\text{dppm})_2]$  (**1**) yields several products, but their characterization via NMR techniques was not possible due to the broadened and overlapping nature of the resonances. However, the previously-described selenide A-frame  $[\text{Rh}_2(\text{CO})_2(\mu\text{-Se})(\text{dppm})_2]$ <sup>17a</sup> was not obtained, even after refluxing the mixture, purging it with  $\text{N}_2$ , or leaving it under

$\text{N}_2$  for several days. Such a product might have been expected based on the ease of formation of  $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$  from **1** and  $\text{H}_2\text{S}$ .

Treatment of  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$  (**2**) with  $\text{H}_2\text{Se}$  yields several species in the initial reaction mixture that can be identified and tentatively characterized using  $^{31}\text{P}\{\text{H}\}$ ,  $^1\text{H}$ , and  $^1\text{H}\{^{31}\text{P}\}$  NMR spectroscopy. The spectroscopic results and tentative structures (with the bridging diphosphine ligands omitted for clarity) are shown in Table VII. Complexes **9a-e** and **10** are observed when the reaction is carried out at room temperature, while complex **9f** is observed only at temperatures below  $-30^\circ\text{C}$ . Species **9a-9c** and **9f** are assigned structures similar to complexes **4a-c** and **5**, respectively, based upon the similarities in their NMR spectra. Like **4c**,<sup>18</sup> compound **9c** is proposed to be fluxional, with both hydride ligands migrating rapidly from metal to metal. Compound **9d** is proposed to be another selenide-bridged dihydride isomer, no analogue of which was observed in the  $\text{H}_2\text{S}$  chemistry. The  $^1\text{H}$  NMR spectrum of **9d**, with selective  $^{31}\text{P}$  decoupling, shows that both hydride resonances collapse to doublets ( $^2J_{\text{HH}} = 5.6$  Hz) upon irradiation of the  $^{31}\text{P}$  signal at  $\delta -4.81$ , but are unaffected by irradiation of the  $^{31}\text{P}$  resonance at  $\delta -12.04$ . This clearly establishes that these hydrides are terminally bound to one iridium center. The H-H coupling constant is also consistent with the cis arrangement shown. Compounds **9e** and **9f** both have selenohydril and hydride resonances. On the basis of the close similarities in the  $^{31}\text{P}\{\text{H}\}$  NMR spectra, and on the similar hydride resonances of compounds **9f** and **5**, compound **9f** is proposed to be a selenohydril-bridged species analogous to **5**. Compound **9e** is proposed to have terminal SeH and H groups based on the selective  $^{31}\text{P}$ -decoupled  $^1\text{H}$  NMR experiments. In addition the SeH resonance in **9e** is a triplet displaying coupling to only one set of phosphorus nuclei, whereas the analogous resonance in **9f** is broad, presumably due to coupling to both chemically inequivalent  $^{31}\text{P}$  nuclei. Unfortunately the number of carbonyls in these samples could not be established owing to the number of species present, although all resonances appear to correspond to terminal carbonyls. It is proposed that **9e** is the tricarbonyl precursor of **9f**, in which carbonyl loss from one metal is replaced by a dative  $\text{Se} \rightarrow \text{Ir}$  interaction. Compound **10** shows no hydride or selenohydril resonances in its  $^1\text{H}$  NMR spectrum

(34) Vaartstra, B. A.; Xiao, J.; Jenkins, J. A.; Verhagen, R.; Cowie, M. *Organometallics* **1991**, *10*, 2708.

Scheme II



so on the basis of its symmetrical appearance in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is proposed to be the selenide-bridged A-frame  $[\text{Ir}_2(\text{CO})_2(\mu\text{-Se})(\text{dppm})_2]$  (**10**), exactly analogous to the known sulfide-bridged species. Despite the formation of small quantities of **10**,  $\text{H}_2$  loss from the dihydride precursors is not facile. With time or heating, conversion of these dihydrides to **10** is not observed to any significant extent; instead decomposition occurs.

As can be seen above, the reactions of **1** and **2** with both S-H bonds of  $\text{H}_2\text{S}$  (and of **2** with the Se-H bonds of  $\text{H}_2\text{Se}$ ) are quite facile under ambient conditions. Although intermediate **5** could be assigned the structure indicated with reasonable confidence, the isolation of homobinuclear complexes modeling this first-bond addition product that would be stable at room temperature remained a goal. The instability of **5** is presumably due to the availability of the second S-H bond for oxidative addition to the second low-valent metal center. Thus thiols and selenols, possessing only one S-H or Se-H bond, were considered to be well suited for the preparation of stable first-bond-addition analogues.

The reaction of compound **2** with ethanethiol under an atmosphere of  $\text{N}_2$  did not give the expected hydride thiolate product and instead yields  $[\text{Ir}_2(\text{SEt})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$  (**11**), the net result of addition of 2 equiv of thiol and loss of  $\text{H}_2$ , as shown in Scheme II. One bridging and two terminal carbonyl groups are indicated by the infrared and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **11**, in distinct contrast to the dicarbonyl products formed in the reactions of **2** with  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{SiRR}'$  ( $\text{R} = \text{R}' = \text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ ;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Ph}$ ).<sup>28</sup> The  $^1\text{H}$  NMR spectrum of **11** shows no resonances due to hydride ligands, indicating that, in contrast to the reaction of **2** with  $\text{H}_2\text{S}$ ,  $\text{H}_2$  loss from any hydridic intermediates formed as precursors to **11** is quite facile. Unlike the results for the reactions of  $[\text{RhRe}(\text{CO})_4(\text{dppm})_2]$  with thiols, where products of the form  $[\text{RhRe}(\text{CO})_3(\mu\text{-H})(\mu\text{-SR})(\text{dppm})_2]$  ( $\text{R} = \text{Et}$ ,  $\text{Ph}$ ) have been characterized,<sup>31</sup> adducts formed by addition of only 1 equiv of EtSH to **2** cannot be isolated at room temperature. Complex **11** is the only product initially observed

at ambient temperature even if conditions of high dilution of reaction mixture or slow addition of thiol are employed. Additional decomposition products, presumably resulting from CO loss, are observed with time. Therefore, solutions of **11** under  $\text{N}_2$  turn from yellow to deep red-orange within a few hours, with loss of intensity of the infrared band due to the bridging carbonyl group. The deep red solid isolated from such solutions, shows several broad unresolved resonances in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, indicating a mixture of products.

Although no hydride species were observed at ambient temperatures, they can be observed at lower temperatures. The intermediates observed at low temperature, and the likely course of the reaction are summarized in Scheme II. Starting at  $-80^\circ\text{C}$ , the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a mixture of **2** and EtSH in  $\text{CD}_2\text{Cl}_2$  shows the presence of only **2** until the solution temperature has been raised to  $-20^\circ\text{C}$ . At this point, additional signals due to  $[\text{Ir}_2(\text{CO})_4(\text{dppm})_2]$  (formed by CO uptake by **2**), a small amount of **11**, and phosphorus resonances at  $\delta -6.1$  (singlet) and  $\delta -8.4, -12.8$  (multiplets) due to one symmetric (**12**) and one asymmetric species (**13**), respectively, are observed. The corresponding  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR data (see Table II) indicate that both **12** and **13** are dicarbonyl dihydride species. The presence of two resonances, at  $\delta 5.42$  and  $4.20$ , for the dppm methylene protons of **12** rules out a formulation such as structure **XII**, in which both sides of the  $\text{Ir}_2\text{P}_4$  plane are equivalent (although, as noted later, such a species cannot be ruled out as a short-lived intermediate). It is also less likely that the hydride ligands of **12** are disposed along the Ir-Ir bond, since the elimination of  $\text{H}_2$  from such a structure would be much more difficult. Species **12** is believed to possess a structure similar to those assigned to complexes **18** and **22** (vide infra), despite its instability at elevated temperatures relative to these thiophenolate- and benzeneselenolate-containing analogues.

Selective heteronuclear decoupling experiments ( $^{13}\text{C}\{^{31}\text{P}\}$  and  $^1\text{H}\{^{31}\text{P}\}$ ) for species **13** establish that one hydride and one carbonyl ligand are attached to each of the iridium centers of this intermediate. The structure proposed for **13** is similar to that for  $[\text{Ir}_2(\text{H})_2\text{Cl}_2(\text{CO})_2(\text{dppm})_2]$ <sup>30</sup> and differs from that for **12** in that the ethanethiolate and carbonyl groups on one iridium have been transposed. Formation of such a structure, containing an EtS group trans to a hydride, may not be entirely straightforward, and may involve the intermediacy of a species such as **XII**. Rearrangement of **XII** to **13** may occur via "burrowing"<sup>35</sup> of a hydride ligand through the Ir-Ir bond, from one side of the  $\text{Ir}_2\text{P}_4$  plane to the other, as has been previously proposed in related species.<sup>15,18,29,30,33d,36</sup>

Species **12** and **13** are also observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy when the reaction of **2** with EtSH is carried out at low temperature in THF-*d*<sub>5</sub>; in addition, intermediates **14** and **15** are also seen in this solvent. Proton NMR experiments with selective  $^{31}\text{P}$  decoupling show that species **14** also gives rise to one highfield resonance at  $\delta -10.20$  (triplet,  $^2J_{\text{P-H}} = 14.0$  Hz), corresponding to a terminal hydride attached to iridium. Although  $^{13}\text{C}\{^1\text{H}\}$  NMR data for this reaction mixture were not acquired, **14** is assigned the structure shown based on the similarities between its  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  spectroscopic parameters and those for the analogous thiophenolate-containing species, **19**, for which  $^{13}\text{C}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$  data have been obtained (vide infra). The nonhydridic intermediate **15** shows  $^{31}\text{P}\{^1\text{H}\}$  spectroscopic parameters similar to the more fully characterized thiophenolate analogue, **16**, and thus is believed to possess a similar structure. When the reaction mixture is warmed to room temperature, signals

(35) The term "burrowing" refers to movement of a bridging hydride ligand from one face of a binuclear complex to the other, presumably via a linear M-H-M intermediate.

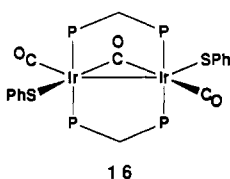
(36) (a) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642. (b) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818.



due to all of these intermediates disappear, being replaced by those due to the final product, **11**.

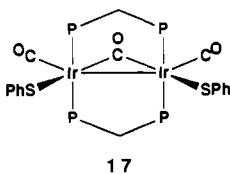
It is notable that although both the starting material, **2**, and the final product, **11**, are tricarbonyl complexes, intermediates **12** and **13** possess only two CO groups each, implying that, like the addition of the second S–H bond of H<sub>2</sub>S to **2**, the reaction of **14** with another equivalent of EtSH is accompanied by CO loss. It is likely that the CO evolved in this step, which would then be present in solution either uncoordinated or bound to the labile [Ir<sub>2</sub>(CO)<sub>4</sub>(dppm)<sub>2</sub>], is readily scavenged by the products of H<sub>2</sub> loss from **12** and **13**, leading to formation of **11** and **15**. The isomerization of the asymmetric **15** to the symmetrical **11** may occur via reversible CO loss and recoordination, which is consistent with the tendency of **11** to decompose via loss of CO (vide supra).

Under ambient conditions, thiophenol also reacts with complex **2** in a 2:1 ratio yielding compound **16**, containing three carbonyl groups and two thiolate residues. Like those of **11**, the infrared spectra of **16** are consistent with a structure containing one bridging and two terminal carbonyl groups, and no resonances are seen in the high-field region of the <sup>1</sup>H NMR spectrum, showing that H<sub>2</sub> loss has taken place. Compound **16** shows two phosphorus resonances and is analogous to the unsymmetrical product **15** observed only at low temperature in the ethanethiol reaction. Its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows resonances due to one bridging and two different terminal carbonyl ligands, and decoupling experiments (<sup>13</sup>C{<sup>31</sup>P}) show that the terminal CO groups are bound to different iridium centers, with a <sup>2</sup>J<sub>C–C</sub> coupling of 24.9 Hz between the higher-field terminal carbonyl and the bridging CO, which is comparable to values previously observed for similar systems containing carbonyl groups oriented trans across a metal center.<sup>33</sup> Besides being an isomeric form of the structurally characterized compound **17** (vide infra), complex **16** is reminiscent

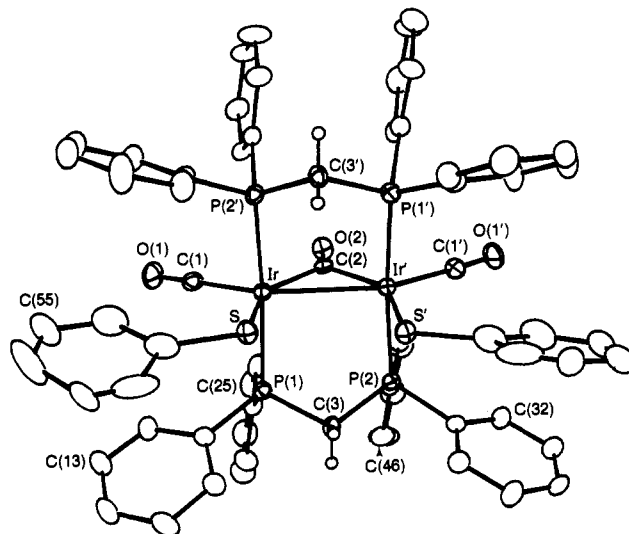


of the anti isomer of [Ir<sub>2</sub>Cl<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>],<sup>37</sup> and shows a similar bridging CO stretching frequency (1720 cm<sup>-1</sup> vs 1728 cm<sup>-1</sup> for this dichloro analogue). Compound **16** is also obtained as the immediate and sole product of the reaction of **2** with diphenyl disulfide. Although we would have expected the syn product, based on a concerted oxidative addition, the transannular oxidative addition of trifluoromethyl disulfide to [Rh<sub>2</sub>(CNMe)<sub>4</sub>(dppm)<sub>2</sub>]<sup>2+</sup> has been noted by Balch and co-workers,<sup>10</sup> so the structure proposed for **16**, in which the thiolate groups are *not* mutually cis, is not unprecedented.

If compound **16** is allowed to stir in CH<sub>2</sub>Cl<sub>2</sub> solution for several hours, a new symmetrical product, [Ir<sub>2</sub>(SPh)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>] (**17**), analogous to the final ethanethiol product **11**, can



be observed spectroscopically. The IR spectrum shows new bands at 1663, 1951, and 1700 cm<sup>-1</sup>, indicative of retention of the three carbonyl ligands. All spectroscopic data (IR and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR) are consistent with the structure shown. The isomerization process is not quantitative, so equilibrium mixtures are usually formed in which **16** is present in significant quantities



**Figure 1.** Perspective view of [Ir<sub>2</sub>(SPh)<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(dppm)<sub>2</sub>] (**17**) showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for hydrogens, which are shown artificially small for the dppm methylene groups and are not shown for the phenyl groups. Primed atoms are related to unprimed atoms by the crystallographic 2-fold axis passing through C(2)O(2) and the center of the Ir–Ir' bond.

(~40% of total concentration). From such mixtures single crystals of complex **17** have been isolated, allowing its characterization by X-ray crystallography, indicating that the solid-state structure is consistent with the spectroscopic properties of this species in solution and with the formulation for the ethanethiolate-containing analogue, **11**.

The structure of complex **17** is shown in Figure 1. The molecule possesses a 2-fold axis of symmetry passing through the center of the metal–metal bond and the atoms C(2) and O(2). The metal nuclei are bridged by the dppm ligands and a carbonyl group, and one carbonyl and one thiophenolate ligand are coordinated terminally to each metal. As is typical of most other binuclear dppm-bridged systems, the diphosphine groups are oriented trans to each other about the iridium centers (P(1)–Ir–P(2') = 170.10(8)°). The coordination geometry about Ir can be described as distorted trigonal bipyramidal (neglecting the Ir–Ir' bond), with P(1) and P(2') occupying axial sites and S, C(1), and C(2) in equatorial positions. Distortions from this model arise from the presence of the metal–metal bond, the bridging nature of the carbonyl group C(2)O(2), and the mutual repulsion between the sulfur atoms S and S'. The latter feature appears to be exerting the largest effect, as reflected in the large S...S' separation (3.378(4) Å), which, although less than the sum of the van der Waals radii of these atoms (3.60 Å),<sup>38</sup> is substantially larger than the intraligand P(1)–P(2) separation (3.003(3) Å). This interaction results in an expanded S–Ir–C(2) angle (142.6(2)°), whereas the compressed C(1)–Ir–C(2) angle (104.9(4)°) appears to be due to greater repulsion between the thiophenolate group and the terminal carbonyl C(1)O(1) (S–Ir–C(1) = 112.5(3)°) than between the terminal and bridging CO ligands. The geometry about the bridging carbonyl group is comparable in Ir–C(2) distance (2.049(9) Å) and Ir–C(2)–Ir' angle (87.4(5)°) to that of other dppm-bridged diiridium compounds containing the same unit.<sup>17b,26,37,39</sup> Despite the interactions between the sulfur atoms, no significant twisting of the complex about the Ir–Ir' bond occurs, as seen from the small S–Ir–Ir'–S and P(1)–Ir–Ir'–P(2) torsion angles (3.59(9) and 5.3(1)°, respectively).

(38) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983: (a) pp 258–259 and references therein. (b) pp 312–315 and references therein.

(39) Vaartstra, B. A.; Cowie, M. *Organometallics* **1989**, *8*, 2388.

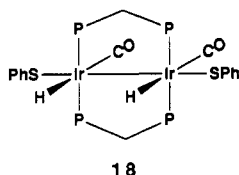
(37) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324.



This complex is similar to the syn isomer of  $[\text{Ir}_2\text{Cl}_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$ <sup>37</sup> (which cocrystallized with the major [anti] isomer in 1:3 ratio), in which the SPh units of **17** have been replaced by Cl ligands. One interesting difference is the shortness of the Ir-S bond (2.480(2) Å) with respect to the Ir-Cl bonds (average 2.504 Å) in the former species, despite the fact that sulfur has a larger covalent radius than chlorine.<sup>38a</sup> The same trend has also been noted by Cotton and co-workers in their determinations of the structures of  $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ <sup>40</sup> and  $[\text{Ir}(\mu\text{-SPh})(\text{COD})]_2$ <sup>11</sup> and has been ascribed to the higher degree of  $\pi$ -overlap in Ir-S bonds compared to Ir-Cl bonds; another contributor might be the more favorable interaction between the soft-acid Ir center and the soft-base PhS ligand than between Ir and the harder base Cl.<sup>38b</sup> The difference between the Ir-S and Ir-Cl bond lengths was found to be 3 times as great for the  $[\text{Ir}(\mu\text{-X})(\text{COD})]_2$  dimers as for the  $[\text{Ir}_2\text{X}_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$  systems, which would be consistent with the relative electron deficiency of the 16-electron iridium centers of the former vs the 18-electron nuclei in the dppm-containing complexes. The iridium-sulfur distance in **17** is within the rather broad range observed for other sulfur-containing iridium complexes (2.33–2.53 Å);<sup>3a,d,8b,11,41,42</sup> however, a more meaningful comparison may be made to the range of distances observed when sulfur is terminally bound to iridium (2.41–2.51 Å).<sup>3a,8b,42</sup>

Other parameters in this compound appear normal. The Ir-Ir' distance (2.8286(6) Å) is within the range observed in similar systems containing an Ir-Ir bond (2.77–2.89 Å).<sup>17b,26-28,30,37,39,43</sup> This distance is significantly longer than that observed in the dichloro analogue (2.779(1) Å),<sup>37</sup> possibly reflecting the greater steric requirements of the SPh vs Cl ligands in forcing the metal centers apart; however, it is still less than the intraligand P(1)–P(2) separation (vide supra). The Ir-P distances (2.339(2), 2.333(2) Å) are also typical for these systems.

Reaction of hydrogen with compound **16** or **17** leads to loss of CO and uptake of 1 equiv of H<sub>2</sub> to form  $[\text{Ir}_2(\text{H})_2(\text{SPh})_2(\text{CO})_2(\text{dppm})_2]$  (**18**). Loss of the bridging carbonyl ligand is indicated by the infrared spectrum ( $\nu(\text{CO})$ : 2044, 1932 cm<sup>-1</sup>), specifically by the disappearance of bands near 1700 cm<sup>-1</sup>. The high-field region of the <sup>1</sup>H NMR spectrum shows an apparent quintet resonance at  $\delta$  –11.58 corresponding to two hydrides. Although the appearance of this resonance suggests that complex **18** contains hydrides that are bridging the metal centers, this

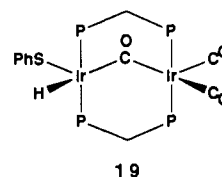


species is believed to have the structure shown, in which terminal

- (40) Cotton, F. A.; Lahuerta, P.; Sanaú, M.; Schwotzer, W. *Inorg. Chim. Acta* **1986**, *120*, 153.
- (41) (a) Bonnet, J.-J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940. (b) Devillers, J.; Bonnet, J.-J.; de Montauzon, D.; Galy, J.; Poilblanc, R. *Inorg. Chem.* **1980**, *19*, 154. (c) Kalck, P.; Bonnet, J.-J. *Organometallics* **1982**, *1*, 1211. (d) Devillers, J.; de Montauzon, D.; Poilblanc, R. *Nouv. J. Chim.* **1983**, *7*, 545. (e) El Amane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773. (f) Sielisch, T.; Cowie, M. *Organometallics* **1988**, *7*, 707. (g) Balch, A. L.; Waggoner, K. M.; Olmstead, M. M. *Inorg. Chem.* **1988**, *27*, 4511. (h) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1759.
- (42) (a) Kalck, P.; Bonnet, J.-J.; Poilblanc, R. *J. Am. Chem. Soc.* **1982**, *104*, 3069. (b) Stephan, D. W. *Inorg. Chem.* **1984**, *23*, 2207. (c) Del Zotto, A.; Mezzetti, A.; Dolcetti, G.; Rigo, P.; Pahor, N. B. *J. Chem. Soc., Dalton Trans.* **1989**, 607.
- (43) (a) Mague, J. T.; Klein, C. L.; Majeste, R. J.; Stevens, E. D. *Organometallics* **1984**, *3*, 1860. (b) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869. (c) Wu, J.; Reinking, M. K.; Fanwick, P. E.; Kubiak, C. P. *Inorg. Chem.* **1987**, *26*, 247. (d) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *6*, 1805.

Ir-H groups are present. The five-line multiplet could be produced by the second-order coupling effects inherent in an AA'XX'X''X''' spin system, or by rapid exchange of these hydrides between the metal centers, producing a time-averaged A<sub>2</sub>X<sub>4</sub> spin system. The latter view is supported by the broadening of the resonance that occurs as the temperature is lowered, possibly due to slowing of the exchange process. However, a totally decoalesced spectrum could not be observed, even at –80 °C. Complex **18** appears to be a thiophenolate-containing analogue of species **12**, the symmetrical dihydridic intermediate in the reaction of **2** with EtSH, but differs from **12** in being stable at room temperature and unreactive toward CO. No reductive elimination of thiophenol from **18** is observed.

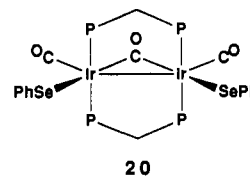
The reaction of thiophenol with **2** in CD<sub>2</sub>Cl<sub>2</sub> was also monitored by NMR at lower temperatures. At –20 °C compound **19**, having a structure like that of **14**, is observed. This species has a high-



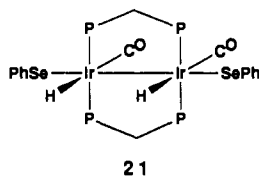
field triplet in the <sup>1</sup>H spectrum at  $\delta$  –9.98 (<sup>2</sup>J<sub>P-H</sub> = 10.0 Hz), and one bridging and two terminal carbonyl resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. Selective <sup>13</sup>C{<sup>31</sup>P} decoupling experiments indicate that both terminal carbonyls are coordinated to the same metal center. A small amount of the dicarbonyl dihydride, **18**, is also observed under these conditions, but unlike the reaction between ethanethiol and **2**, it appears to be a byproduct, and not an intermediate, since no conversion of **18** to either of the tricarbonyls, **16** or **17**, is observed under CO. Furthermore, under conditions that would minimize the amount of free (dissociated) CO in solution, such as the slow addition of 1 equiv of thiophenol to a dilute THF solution of **2**, stirred under a rapid N<sub>2</sub> stream, the tricarbonyl product **16** is the only product detected. A bis(thiophenolate) analogue of species **13** is not observed in the course of this reaction. When the sample is warmed to room temperature, the monohydridic intermediate disappears, with the major species produced being **16** and **17**. Roughly the same amount of **18** as was earlier observed remains in the final mixture.

The reaction of compound **2** with benzeneselenol also follows a 2:1 stoichiometry. Spectroscopic evidence, particularly the infrared and <sup>13</sup>C{<sup>1</sup>H} NMR data, suggests that the major product,  $[\text{Ir}_2(\text{SePh})_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]$  (**20**), has the same structure as the structurally-characterized species **17**, with selenium atoms replacing the sulfurs. This symmetrical complex has been more directly prepared via the reaction of diphenyl diselenide with **2**, a result in marked contrast to the reaction of **2** with (PhS)<sub>2</sub>, where the product is the asymmetric species **16**.

Complex **20** is not the sole product of the reaction between benzeneselenol and **2**, as a dihydridic product of formula  $[\text{Ir}_2(\text{H})_2(\text{SePh})_2(\text{CO})_2(\text{dppm})_2]$  (**21**) is also observed. The <sup>1</sup>H,



<sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic parameters (Table II) for this compound are quite similar to those observed for species **18**, and suggest that complex **21** is also a dicarbonyl dihydride. Rapid exchange between the metal centers may also be implicated, as broadening of the hydride resonance occurs as the temperature is lowered, possibly due to slowing of the exchange process; again, as for **18**, a totally decoalesced spectrum could not be observed,



even at  $-80\text{ }^{\circ}\text{C}$ . Species **21** can also be formed when a solution of **20** is allowed to react with  $\text{H}_2$ , but attempts to prepare this material in pure form were unsuccessful, as complex **21** decomposes over time at room temperature.

### Conclusions

The reactivities of  $[\text{MM}'(\text{CO})_3(\text{dppm})_2]$  ( $\text{MM}' = \text{Rh}_2$  (**1**),  $\text{Ir}_2$  (**2**),  $\text{RhIr}$  (**3**)) toward substrates containing sulfur–hydrogen and selenium–hydrogen bonds have been investigated. For the dirhodium species the reactions are extremely facile, precluding the observation of intermediates. In contrast the diiridium compound has demonstrated a rich chemistry in which a variety of intermediates can be characterized, either at ambient temperature or below. The reactivity of **2** is characterized by its preference to react with *two* S–H or Se–H bonds. This is not surprising for substrates containing two such bonds, such as  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ , since a similar facile, “double-activation” process was previously observed for primary and secondary silanes.<sup>28</sup> However the oxidative addition of 2 equiv of thiols or selenols to yield bis(thiolate) or bis(selenolate) products is unexpected, based on a comparison with the closely related complexes,  $[\text{RhM}(\text{CO})_4(\text{dppm})_2]^{n+}$  ( $\text{M} = \text{Mn},^{44} \text{Re},^{31} n = 0; \text{M} = \text{Ru}, \text{Os}, n = 1^{45}$ ), which added only 1 equiv of thiol. Clearly the diiridium complex

**2** has a strong tendency to utilize both metals in the oxidative-addition reactions. The mixed Rh/Ir species **3** is unusual in its reactivity with  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  and resembles neither the  $\text{Rh}_2$  nor  $\text{Ir}_2$  analogues. This is the first of the dppm-bridged species studied to stop at the first oxidative-addition step, yielding  $[\text{RhIrH}(\text{CO})_2(\mu\text{-XH})(\text{dppm})_2]$  ( $\text{X} = \text{S}, \text{Se}$ ).

Although the different substrates give rise to products and intermediates which are not always analogous, we assume that all proceed by initial oxidative addition of one S–H or Se–H bond at the unsaturated metal. Whether the first intermediate observed is that anticipated, having formal  $\text{M}^{+2}$  and  $\text{M}^0$  centers, or one in which both metals are in a +1 oxidation state, depends on the rate of rearrangement to the more stable  $\text{M}^+/ \text{M}^+$  species. Differences in chemistry between  $\text{H}_2\text{X}$  and  $\text{HXR}$  ( $\text{X} = \text{S}, \text{Se}$ ) are not unexpected keeping in mind that the  $\text{H}_2\text{X}$  molecules have an additional X–H bond which can oxidatively add to the metals in an intramolecular “double-activation” process.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for support of this work and the NSERC for partial support of the diffractometer.

**Supplementary Material Available:** Tables of crystallographic data, parameters for the phenyl and solvent atoms, thermal parameters for anisotropic atoms, idealized hydrogen parameters, and bond distances and angles within the phenyl rings (7 pages). Ordering information is given on any current masthead page.

(44) Wang, L. S.; McDonald, R.; Cowie, M. Manuscript in preparation.  
 (45) Hiltz, R. W.; Mao, T.; Cowie, M. Manuscript in preparation.