

realize that they were measuring the hydrolysis of  $\text{ClSO}_3^-$  (eq 6) rather than the reaction between  $\text{HOCl}$  and  $\text{SO}_3^{2-}$  (eq 5).<sup>7</sup> Inoue and Sudo were able to use the heat of hydrolysis of  $\text{ISO}_3^-$  to measure this rate constant by a flow thermal method.

Our  $\Delta H^\ddagger$  value for the hydrolysis of  $\text{ISO}_3^-$  is  $65 \text{ kJ mol}^{-1}$ , which is larger than the value of  $49 \text{ kJ mol}^{-1}$  found for the hydrolysis of  $\text{ClSO}_3^-$ .<sup>8</sup> On the other hand the  $\Delta S^\ddagger$  value is  $+21 \text{ J mol}^{-1} \text{ K}^{-1}$  for the  $\text{ISO}_3^-$  hydrolysis compared to  $-32 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $\text{ClSO}_3^-$ .<sup>8</sup> The positive  $\Delta S^\ddagger$  value for  $\text{ISO}_3^-$  indicates that it does not take up a water molecule in attaining the transition state as was proposed for the reaction of  $\text{ClSO}_3^-$ . Instead, the reaction of  $\text{ISO}_3^-$  appears to be of a more dissociative nature followed by aquation. Steric hindrance may prevent the coordination of  $\text{H}_2\text{O}$  to sulfur in  $\text{ISO}_3^-$ .

### Conclusions

The PAF technique permits the very fast reactions between  $\text{I}_2/\text{I}_3^-$  and  $\text{SO}_3\text{H}^-/\text{SO}_3^{2-}$  to be resolved in terms of four rate constants. The rate constant for the reaction between  $\text{I}_2$  and  $\text{SO}_3^{2-}$  ( $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is even larger than the value for  $\text{HOCl}$  and

$\text{SO}_3^{2-}$  ( $7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>7</sup> In the latter case kinetic evidence exists for a reactive intermediate,  $\text{HOCISO}_3^{2-}$ , and the rate constant for the formation of this intermediate is  $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . We do not have direct kinetic evidence for  $\text{I}_2\text{SO}_3^{2-}$  as a reactive intermediate, but it may exist. In both the  $\text{HOCl}$  and the  $\text{I}_2$  reactions there is evidence for  $\text{XSO}_3^-$  intermediates that we propose have X-S bonds and hydrolyze with similar rate constants.

In the mixed Landolt chemical oscillator system,<sup>5,6</sup> the pH fluctuates from 3 to 8 and the  $\text{I}^-$  concentration also fluctuates. Hence, the assignment of a single rate constant for the reactions of  $\text{I}_2/\text{I}_3^-$  with  $\text{SO}_3\text{H}^-/\text{SO}_3^{2-}$  does not appear to be appropriate. The observed rate constants could change by 1-2 orders of magnitude as the pH changes. Even if the  $\text{I}^-$  concentration reaches  $0.01 \text{ M}$  in these reactions, the  $\text{I}_2$  path will predominate over the  $\text{I}_3^-$  path and the observed second-order rate constants will be greater than  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  at high pH. Furthermore, the initial product is  $\text{ISO}_3^-$  and its rate of hydrolysis may affect the regeneration of  $\text{I}^-$ . The simulated oscillations appear to fit satisfactorily,<sup>6</sup> but as more accurate kinetic information becomes available, it should be possible to refine the description of the oscillatory behavior.

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## Diphosphine-Bridged Heterobimetallic Hydride and Carbonyl Complexes of Rhodium and Iridium. Structure of $[\text{RhIr}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ , a Complex Containing an $\text{Ir}(-\text{I}) \rightarrow \text{Rh}(\text{I})$ Dative Bond

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The reaction of  $[\text{RhIrCl}_2(\text{CO})_2(\text{dppm})_2]$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with  $\text{NaBH}_4$  under CO gives  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  (1), while under  $\text{H}_2$  the product is  $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-H})(\text{dppm})_2]$  (2). The former is convertible to the latter via reaction with  $\text{H}_2$ , while the reverse process proceeds under CO atmosphere. Addition of 1 equiv of  $\text{HBF}_4 \cdot \text{OEt}_2$  to 1 yields  $[\text{RhIr}(\text{CO})_3(\mu\text{-H})(\text{dppm})_2][\text{BF}_4]$  (3) and addition of a second equivalent leads to  $[\text{RhIr}(\text{CO})_3(\mu\text{-H})_2(\text{dppm})_2][\text{BF}_4]_2$  (4); both protonations are reversible. Protonation of 2 produces  $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2][\text{BF}_4]$  (5). Like their neutral precursors, the protonated tricarbonyl and trihydride complexes may be interconverted via the appropriate hydrogenation or carbonylation processes. An X-ray structural determination of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  shows it to have a non-A-frame structure, with one of the two carbonyls attached to Ir oriented toward Rh in what might be considered a weakly semibridging manner; furthermore, the phosphine groups on Ir have a cis arrangement with a P-Ir-P angle of  $104.95 (7)^\circ$ . The rhodium center is square planar as expected for a Rh(I) formulation, while the geometry about iridium is a distorted tetrahedron (if the Rh-Ir bond is omitted) suggesting an Ir(-I) formulation. As such the  $\text{Ir}(\text{CO})_2\text{P}_2^-$  moiety can be considered as a pseudohalide, bound via a dative Ir→Rh bond. This compound crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 20.296 (4) \text{ \AA}$ ,  $b = 12.190 (7) \text{ \AA}$ ,  $c = 19.064 (7) \text{ \AA}$ ,  $\beta = 95.11 (2)^\circ$ , and  $Z = 4$ . The structure was refined to  $R = 0.047$  and  $R_w = 0.053$  on the basis of 5208 unique observed reflections and 559 parameters varied.

### Introduction

Hydride and carbonyl complexes of the group 8 metals have been implicated as intermediates in several catalytic processes, notably hydroformylation,<sup>1</sup> olefin hydrogenation,<sup>2</sup> and the water gas shift reaction.<sup>3</sup> However, to date most studies have concentrated on mononuclear complexes. As part of an ongoing effort to determine the effects of adjacent metal centers upon catalytic processes, we have been investigating the chemistry of binuclear diphosphine-bridged complexes of rhodium<sup>4-7</sup> and iridium.<sup>8-14</sup> In

a previous paper, we described a series of diiridium complexes that, aside from the diphosphine bridges, contained only hydride and carbonyl ligands.<sup>12</sup> A more limited series of analogous dirhodium species has also been described.<sup>15,16</sup> As an extension of our studies in this area, we set out to prepare and study similar heterobimetallic Rh/Ir complexes. In addition, previous work

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Table I. Spectral Data<sup>a</sup>

	IR, cm <sup>-1</sup>		NMR			
	solid <sup>b</sup>	solution <sup>c</sup>	$\delta(^{31}\text{P}\{^1\text{H}\})^d$	$^1J_{\text{Rh-P}}$ , Hz	$\delta(^1\text{H})^e$	
[RhIr(CO) <sub>2</sub> (dppm) <sub>2</sub> ] (1)	1958 (s), 1940 (vs), 1849 (s) <sup>h</sup>	1950 (s), 1934 (vs), 1861 (w, br) <sup>h</sup>	16.4 <sup>f</sup> , -16.3 <sup>g</sup>	129.6	8.05–6.90 (mult, 40 H), 4.84 (mult, 2 H), 2.93 (mult, 2 H)	
[RhIr(H)(CO) <sub>2</sub> (μ-H)(dppm) <sub>2</sub> ] (2)	1942 (s), 1924 (vs), <sup>h</sup> 2033 (w) <sup>i</sup>	1937 (vs), <sup>h</sup> 2033 (w) <sup>i</sup>	32.5 <sup>f</sup> , 9.9 <sup>g</sup>	118.2	7.79–7.02 (mult, 40 H), 4.22 (mult, 2 H), 2.51 (mult, 2 H), -11.00 (br, 1 H), -12.73 (br, 1 H)	
[RhIr(CO) <sub>3</sub> (μ-H)(dppm) <sub>2</sub> ][BF <sub>4</sub> ] (3)	2000 (s), 1974 (vs), 1899 (m) <sup>h</sup>	1986 (vs, br), 1960 (sh), 1893 (w) <sup>h</sup>	22.8 <sup>f</sup> , -5.5 <sup>g</sup>	112.2	7.54–7.30 (mult, 40 H), 4.38 (mult, 4 H), -10.19 (mult, 1 H, <sup>2</sup> J <sub>P(Ir)-H</sub> = 12.2 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> = 9.3 Hz, <sup>1</sup> J <sub>Rh-H</sub> = 19.0 Hz)	
[RhIr(CO) <sub>3</sub> (μ-H) <sub>2</sub> (dppm) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub> (4)	2141 (m), 2110 (m), 2001 (vs) <sup>h</sup>	2142 (s), 2110 (s), 2015 (vs) <sup>h</sup>	21.9 <sup>f</sup> , -10.2 <sup>g</sup>	102.7	7.57–7.33 (mult, 40 H), 4.63 (mult, 4 H), -11.18 (mult, 2 H, <sup>2</sup> J <sub>P(Ir)-H</sub> = 11.1 Hz, <sup>2</sup> J <sub>P(Rh)-H</sub> ≤ 7 Hz, <sup>1</sup> J <sub>Rh-H</sub> = 17.3 Hz)	
[RhIr(H)(CO) <sub>2</sub> (μ-H) <sub>2</sub> (dppm) <sub>2</sub> ][BF <sub>4</sub> ] (5)	2054 (m), 1971 (vs) <sup>h</sup>	2059 (s), 1986 (vs) <sup>h</sup>	27.1 <sup>f</sup> , -2.7 <sup>g</sup>	109.5	7.58–7.27 (mult, 40 H), 4.58 (br, 2 H), 3.90 (br, 2 H), -10.58 (br 1, H), -11.46 (br, 1 H), -11.76 (br, 1 H)	

<sup>a</sup> Abbreviations used: w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder, mult = multiplet. <sup>b</sup> Nujol mull on KBr disk. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solution in KCl cells. <sup>d</sup> Versus 85% H<sub>3</sub>PO<sub>4</sub>, -40 °C, in CD<sub>2</sub>Cl<sub>2</sub> solvent. <sup>e</sup> Versus TMS, 25 °C, in CD<sub>2</sub>Cl<sub>2</sub> solvent. <sup>f</sup> Rh-P. <sup>g</sup> Ir-P. <sup>h</sup> μ(CO). <sup>i</sup> ν(Ir-H).

involving H<sub>2</sub><sup>14</sup> and alkyne<sup>17</sup> addition to mixed-metal rhodium-iridium species had demonstrated some rather interesting differences with respect to the chemistry of the homobimetallic analogues; thus, it was anticipated that the Rh/Ir hydrido carbonyls would themselves show some unique behavior not previously shown by their Rh<sub>2</sub> and Ir<sub>2</sub> counterparts.

### Experimental Section

**General Data.** All solvents were dried and distilled before use and were stored under N<sub>2</sub>. Reactions were carried out by using standard Schlenk procedures. Dinitrogen was passed through columns of Ridox and 4A molecular sieves to remove traces of oxygen and water, respectively. Carbon monoxide (Matheson) and dihydrogen were used as received. Hydrated rhodium(III) chloride was obtained from Johnson Matthey Ltd., hydrated iridium(III) chloride was purchased from Engelhard Scientific, and bis(diphenylphosphino)methane (dppm) was purchased from Organometallics Inc. The compound [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(dppm)<sub>2</sub>] was prepared as previously reported.<sup>18</sup> All other chemicals were used as received without further purification.

Variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at -40 °C on either a Bruker AM-400 spectrometer operating at 161.9 MHz or a Bruker HFX-90 spectrometer operating at 36.43 MHz. In the former case, an internal deuterated solvent lock was used, while in the latter an external acetone-*d*<sub>6</sub> lock was employed; chemical shifts are given with respect to 85% H<sub>3</sub>PO<sub>4</sub>. The <sup>1</sup>H and <sup>1</sup>H{<sup>31</sup>P} NMR spectra were recorded on a Bruker AM-400 spectrometer at room temperature, while variable-temperature <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker WH-200 spectrometer operating at 50.32 MHz; in these cases, chemical shifts are given with respect to external TMS, using solvent as an internal reference. Infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl cell windows, 0.5-mm path length). Spectral parameters for the compounds prepared are found in Table I. Conductivity measurements were carried out on a Yellow Springs Instruments Model 31 conductivity bridge, with solutions of approximately 10<sup>-3</sup> M concentration. Elemental analyses were performed by the microanalytical service within the department.

**Preparation of Compounds.** (a) [RhIr(CO)<sub>2</sub>(dppm)<sub>2</sub>] (1). An atmosphere of CO was placed over a mixture of [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(dppm)<sub>2</sub>] (300 mg, 0.252 mmol) and NaBH<sub>4</sub> (60 mg, 1.59 mmol) in THF (15 mL). Addition of methanol (5 mL) resulted in much effervescence and caused a slight deepening of the orange solution color. The mixture was allowed to stir for 2 h, after which 1 mL of degassed water was added to destroy the excess borohydride. The solution was taken to dryness in vacuo, producing an orange-brown residue, which was redissolved in THF (15 mL) and filtered. The filtrate volume was reduced to 5 mL and 40 mL of hexanes added, yielding **1** as an orange powder (258 mg, 89% yield). This complex proved to be a nonelectrolyte in CH<sub>2</sub>Cl<sub>2</sub> (Λ(10<sup>-3</sup> M) = 1.44 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).<sup>19</sup> Anal. Calcd for C<sub>53</sub>H<sub>44</sub>IrO<sub>3</sub>P<sub>4</sub>Rh: C, 55.45; H, 3.86. Found: C, 54.99; H, 4.03.

(b) [RhIr(H)(CO)<sub>2</sub>(μ-H)(dppm)<sub>2</sub>] (2). A slurry of [RhIrCl<sub>2</sub>(CO)<sub>2</sub>(dppm)<sub>2</sub>] (150 mg, 0.134 mmol) and NaBH<sub>4</sub> (60 mg, 1.59 mmol) in THF (5 mL) was placed under an atmosphere of H<sub>2</sub>. The reaction mixture changed from cloudy orange to cloudy yellow in color after 1 h and then to cloudy brown after 24 h. At this point, the solvent was evaporated under an H<sub>2</sub> stream, the brown residue extracted with toluene (5 mL) and filtered, and 20 mL of hexanes added, resulting in isolation of 107 mg (76% yield) of a medium brown powdery solid. Complex **2** was essentially nonconducting in CH<sub>2</sub>Cl<sub>2</sub> (Λ(10<sup>-3</sup> M) = 3.36 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).

(c) [RhIr(CO)<sub>3</sub>(μ-H)(dppm)<sub>2</sub>][BF<sub>4</sub>] (3). To a solution of **1** (130 mg, 0.113 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added 16.3 μL of HBF<sub>4</sub>·OEt<sub>2</sub> (18.3 mg, 0.113 mmol), resulting in a color change from deep orange to deep red-purple. The solution volume was reduced to 2 mL and 15 mL of ether added, causing the precipitation of a reddish solid. Recrystallization of this material from THF/ether yielded 118 mg (85%) of rust-colored solid. Compound **3** proved to be a 1:1 electrolyte in CH<sub>2</sub>Cl<sub>2</sub> (Λ(10<sup>-3</sup> M) = 56.4 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). Anal. Calcd for BC<sub>53</sub>F<sub>4</sub>H<sub>45</sub>IrO<sub>3</sub>P<sub>4</sub>Rh: C, 51.51; H, 3.67. Found: C, 50.87; H, 3.58.

(d) [RhIr(CO)<sub>3</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (4). To a solution of **1** (100 mg, 0.087 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added 30 μL of HBF<sub>4</sub>·OEt<sub>2</sub> (33.8 mg, 0.209 mmol), resulting in a change in color from orange to deep red-purple and then to pale yellow, accompanied by the precipitation of a light yellow solid. Ether (10 mL) was added to complete precipitation, the supernatant liquid drawn off, and the solid washed with ether and then dried under a stream of N<sub>2</sub>, affording 99 mg (84% yield) of light yellow product. Compound **4** behaved as a weak electrolyte in CH<sub>2</sub>Cl<sub>2</sub> (Λ(10<sup>-3</sup> M) = 24.9 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>), whereas it was found to be normal 2:1 electrolyte in nitromethane (Λ(10<sup>-3</sup> M) = 189.1 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). Anal. Calcd for B<sub>2</sub>C<sub>54</sub>Cl<sub>2</sub>F<sub>8</sub>H<sub>48</sub>IrO<sub>3</sub>P<sub>4</sub>Rh: C, 46.05; H, 3.50; Cl, 5.03. Found: C, 45.83; H, 3.44; Cl, 4.12. (Although this compound is prone to solvent loss, yielding variable results for chlorine analyses, the totally desolvated compound could not be obtained, and significant amounts (>1%) of Cl remained even after the compound was stored under vacuum.)

(e) [RhIr(H)(CO)<sub>2</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>] (5). A suspension of **3** (120 mg, 0.0971 mmol) in THF (5 mL) was stirred under an atmosphere of H<sub>2</sub> for 3 h, during which time the reaction mixture changed from cloudy and red-orange to clear and golden-yellow. After reduction of the solution volume to 2 mL, the product was precipitated by addition of 15 mL of ether. Recrystallization of this material from THF/ether produced 98 mg (83%) of golden-yellow powder. Compound **5** proved to be a 1:1 electrolyte in CH<sub>2</sub>Cl<sub>2</sub> (Λ(10<sup>-3</sup> M) = 57.0 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). Anal. Calcd for BC<sub>52</sub>F<sub>4</sub>H<sub>47</sub>IrO<sub>2</sub>P<sub>4</sub>Rh: C, 51.63; H, 3.92. Found: C, 51.51; H, 4.18.

**Reaction of 2 with CO.** A solution of **2** in THF (50 mg in 2 mL) was stirred under an atmosphere of CO for 2 h, after which time **1** was the only species observed in the IR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the solution.

**Reaction of 2 with HBF<sub>4</sub>·OEt<sub>2</sub>.** To a solution of **2** in CH<sub>2</sub>Cl<sub>2</sub> (20 mg in 2 mL) was added 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> (2.6 μL), causing a slight deepening of the yellow color of solution. The product of the reaction was found by <sup>31</sup>P{<sup>1</sup>H} NMR and solution IR spectroscopy to be compound **5**.

**Reaction of 3 with HBF<sub>4</sub>·OEt<sub>2</sub>.** To a solution of **3** in CH<sub>2</sub>Cl<sub>2</sub> (40 mg in 2 mL) was added 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> (5.0 μL), causing a color change from deep orange-red to light brown. The <sup>31</sup>P{<sup>1</sup>H} NMR and solution IR spectra showed **4** to be the only species present after reaction.

**Reactions of 3 with KOC(CH<sub>3</sub>)<sub>3</sub> and NaBH<sub>4</sub>.** Solid potassium tert-butoxide (5 mg) was added to a solution of **3** in CH<sub>2</sub>Cl<sub>2</sub> (15 mg in 2 mL)

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(19) A typical 1:1 electrolyte such as [Rh<sub>2</sub>(CO)<sub>2</sub>(μ-Cl)(μ-CO)(dppm)<sub>2</sub>][BF<sub>4</sub>] will give a conductivity of ca. 45 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. See also: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

**Table II.** Crystallographic Data for  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  (**1**)

formula	$\text{C}_{53}\text{H}_{44}\text{IrO}_3\text{P}_4\text{Rh}$
fw	1147.94
space group	$P2_1/c$ (No. 14)
temp, °C	22
radiation ( $\lambda$ , Å)	graphite-monochromated Mo $K\alpha$ (0.71069)
unit cell params	
$a$ , Å	20.296 (4)
$b$ , Å	12.190 (7)
$c$ , Å	19.064 (7)
$\beta$ , deg	95.11 (2)
$V$ , Å <sup>3</sup>	4697.9
$Z$	4
$\rho$ (calcd), g cm <sup>-3</sup>	1.623
linear abs coeff ( $\mu$ ), cm <sup>-1</sup>	33.403
range of transm factors	0.791–1.354
$R^a$	0.047
$R_w^b$	0.053

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

and the mixture stirred for 1 h, during which time the color changed from red-orange to light orange. The  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectra of the solution showed complete conversion of the starting material to species **1**. Similarly, reaction of a THF solution of **3** (25 mg in 3 mL) with  $\text{NaBH}_4$  (5 mg) resulted in the formation of the same product.

**Reaction of 4 with  $\text{NEt}_3$ .** To a solution of **4** in  $\text{CH}_2\text{Cl}_2$  (40 mg in 2 mL) was added  $\text{NEt}_3$  (10  $\mu\text{L}$ ,  $\sim 2$  equiv), causing an immediate color change from light brown to deep red-orange. The  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectra showed **3** to be the product formed.

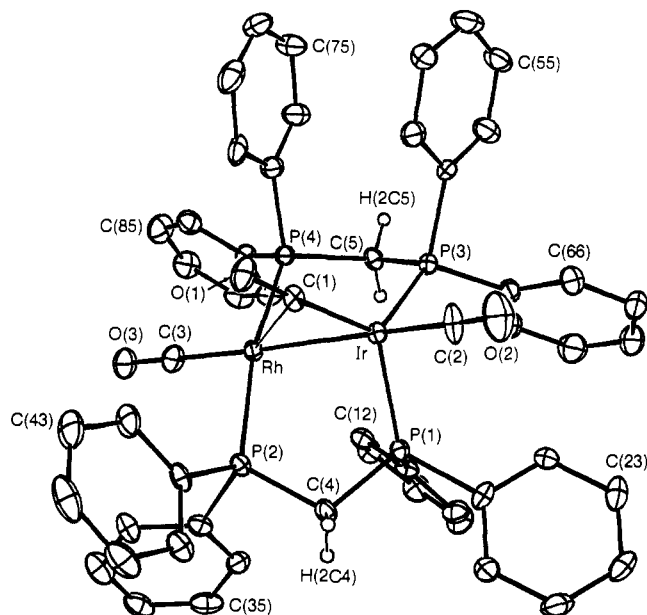
**Reaction of 5 with CO.** A solution of **5** in  $\text{CH}_2\text{Cl}_2$  (50 mg in 2 mL) was stirred under an atmosphere of CO for 18 h, resulting in a color change from golden yellow to red-orange. The  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectra of the solution showed **3** to be the only species present.

**Reactions of 5 with  $\text{KOC}(\text{CH}_3)_3$  and  $\text{NaBH}_4$ .** To a solution of **5** in THF (20 mg in 2 mL) was added solid potassium *tert*-butoxide (5 mg). After being stirred for 18 h, the mixture was found by  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectroscopy to contain only compound **2**. The reaction of **5** (40 mg in 4 mL THF) with  $\text{NaBH}_4$  (5 mg) similarly gave **2** as the sole product after 1 h of reaction time.

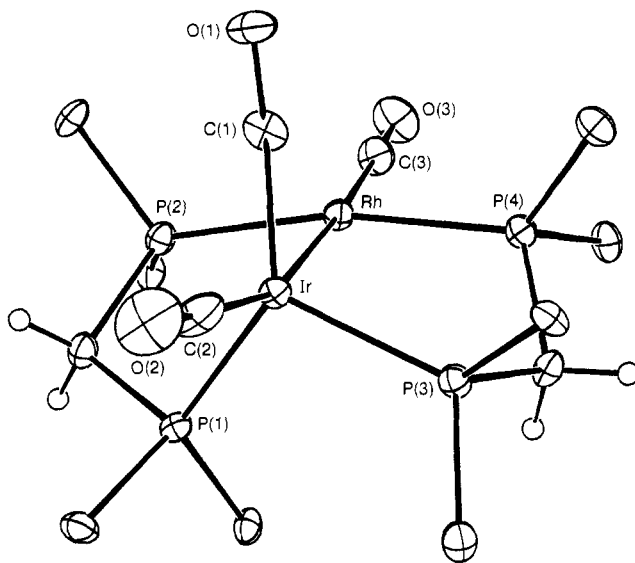
**X-ray Data Collection.** Red-orange crystals of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  were obtained by slow diffusion of ether into a concentrated  $\text{CH}_2\text{Cl}_2$  solution of the compound. Several suitable crystals were mounted and flame-sealed in glass capillaries under  $\text{N}_2$  to minimize decomposition. 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  $20.0^\circ \leq 2\theta \leq 24.0^\circ$ . The monoclinic diffraction symmetry and the systematic absences ( $h0l$ ,  $l = \text{odd}$ ;  $0k0$ ,  $k = \text{odd}$ ) were consistent with the space group  $P2_1/c$ .

Intensity data were collected at 22 °C by using the  $\theta/2\theta$  scan technique to a maximum  $2\theta = 50.0^\circ$ . 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 at 120-min intervals of X-ray exposure time. There was no significant systematic decrease in the intensities of these standards; thus, no decomposition correction was applied. A total of 8686 unique reflections were measured and processed in the usual way, using a value of 0.04 for  $p$ ;<sup>20</sup> 5208 of these were considered to be observed and were used in subsequent calculations. Absorption corrections were applied to the data by using the method of Walker and Stuart.<sup>21,22</sup> See Table II for crystal data and more information on the X-ray data collection.

**Structure Solution and Refinement.** The structure was solved in the space group  $P2_1/c$  with standard Patterson and Fourier techniques. All non-hydrogen atoms were ultimately located. Atomic scattering factors<sup>23,24</sup> and anomalous dispersion terms<sup>25</sup> were taken from the usual tabulations. All hydrogen atoms were included as fixed contributions and not refined. Their idealized positions were calculated from the geometries



**Figure 1.** Perspective view of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  (**1**) showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens, which are shown artificially small for the methylene groups but are not shown at all for the phenyl groups.



**Figure 2.** View of complex **1** approximately along the Rh–Ir bond, omitting the phenyl carbon atoms except those bound to phosphorus.

about the attached carbon atoms, and they were assigned thermal parameters 20% greater than the equivalent isotropic  $B$ 's of their attached C atoms.

The final model, with 559 parameters refined, converged as shown in Table II. In the final difference Fourier map the 10 highest residuals (1.3–0.7  $e/\text{Å}^3$ ) were found to be in the vicinity of the Ir and Rh atoms (a typical carbon atom in an earlier synthesis had an electron density of 4.9  $e/\text{Å}^3$ ). The positional parameters of all non-hydrogen atoms are given in Table III. Selected distances and angles are given in Tables IV and V, respectively. Additional information is available as supplementary material.

## Results

The spectral parameters of the new products are presented in the Discussion section and are tabulated in Table I. The results of the transformations observed are summarized in Scheme I.

## Discussion

**(a) Description of the Structure.** The title complex,  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$ , has the structure shown in Figure 1 in which both diphosphine ligands bridge the metal nuclei in an atypical, non-A-frame manner. This geometry, having the phosphorus atoms

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**Table III.** Positional and Thermal Parameters for the Atoms of  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]^a$ 

atom	x	y	z	B, Å <sup>2</sup>
Ir	0.22767 (2)	0.18475 (3)	0.20696 (2)	2.43 (1)
Rh	0.29649 (4)	0.01816 (6)	0.14660 (4)	2.47 (2)
P(1)	0.3071 (1)	0.2972 (2)	0.1655 (1)	2.6 (1)
P(2)	0.3935 (1)	0.1003 (2)	0.1928 (1)	2.8 (1)
P(3)	0.1413 (1)	0.1843 (2)	0.1186 (1)	2.6 (1)
P(4)	0.1993 (1)	-0.0319 (2)	0.0841 (1)	2.7 (1)
O(1)	0.2495 (4)	-0.0071 (6)	0.3079 (4)	4.8 (2)
O(2)	0.1733 (5)	0.3389 (7)	0.3123 (5)	8.2 (3)
O(3)	0.3699 (4)	-0.1729 (6)	0.0928 (5)	5.6 (2)
C(1)	0.2427 (4)	0.0629 (8)	0.2647 (5)	3.2 (2)
C(2)	0.1927 (6)	0.2849 (9)	0.2716 (6)	4.9 (3)
C(3)	0.3419 (5)	-0.0999 (8)	0.1120 (5)	3.9 (2)
C(4)	0.3891 (5)	0.2505 (8)	0.2027 (5)	3.0 (2)
C(5)	0.1549 (5)	0.0894 (8)	0.0468 (5)	2.9 (2)
C(11)	0.3164 (4)	0.3118 (8)	0.0701 (5)	2.9 (2)
C(12)	0.3121 (5)	0.2197 (9)	0.0276 (5)	3.3 (2)
C(13)	0.3180 (5)	0.2299 (9)	-0.0446 (5)	3.9 (3)
C(14)	0.3260 (6)	0.329 (1)	-0.0746 (5)	4.8 (3)
C(15)	0.3311 (6)	0.423 (1)	-0.0329 (6)	5.2 (3)
C(16)	0.3274 (5)	0.4132 (9)	0.0390 (6)	4.2 (3)
C(21)	0.3043 (5)	0.4418 (8)	0.1919 (5)	3.5 (2)
C(22)	0.2463 (5)	0.4961 (9)	0.1781 (6)	3.8 (2)
C(23)	0.2421 (6)	0.6100 (9)	0.1891 (6)	4.9 (3)
C(24)	0.2955 (6)	0.6671 (8)	0.2150 (6)	4.6 (3)
C(25)	0.3536 (6)	0.6135 (9)	0.2323 (6)	5.0 (3)
C(26)	0.3588 (5)	0.5015 (9)	0.2188 (6)	4.3 (3)
C(31)	0.4642 (5)	0.0796 (9)	0.1401 (5)	3.3 (2)
C(32)	0.5013 (5)	-0.0167 (9)	0.1500 (6)	4.3 (3)
C(33)	0.5528 (6)	-0.035 (1)	0.1095 (6)	5.6 (3)
C(34)	0.5691 (5)	0.039 (1)	0.0596 (6)	5.1 (3)
C(35)	0.5327 (6)	0.133 (1)	0.0487 (6)	5.3 (3)
C(36)	0.4786 (5)	0.1531 (8)	0.0878 (5)	3.6 (2)
C(41)	0.4282 (5)	0.0512 (8)	0.2787 (5)	3.3 (2)
C(42)	0.4089 (6)	-0.0504 (9)	0.3021 (6)	4.6 (3)
C(43)	0.4384 (6)	-0.095 (1)	0.3636 (6)	5.7 (3)
C(44)	0.4860 (6)	-0.037 (1)	0.4029 (6)	6.5 (3)
C(45)	0.5059 (6)	0.065 (1)	0.3812 (6)	5.6 (3)
C(46)	0.4764 (5)	0.111 (1)	0.3194 (6)	4.3 (3)
C(51)	0.0603 (5)	0.1406 (8)	0.1437 (5)	3.0 (2)
C(52)	0.0571 (5)	0.0818 (8)	0.2059 (6)	4.2 (3)
C(53)	-0.0044 (6)	0.0414 (9)	0.2229 (6)	4.9 (3)
C(54)	-0.0608 (6)	0.061 (1)	0.1783 (7)	5.9 (3)
C(55)	-0.0573 (5)	0.120 (1)	0.1183 (7)	5.2 (3)
C(56)	0.0022 (5)	0.157 (1)	0.1004 (6)	4.7 (3)
C(61)	0.1195 (5)	0.3130 (8)	0.0729 (5)	3.3 (2)
C(62)	0.1407 (6)	0.3371 (9)	0.0071 (7)	4.9 (3)
C(63)	0.1256 (7)	0.444 (1)	-0.0213 (7)	6.7 (4)
C(64)	0.0942 (6)	0.521 (1)	0.0128 (8)	6.9 (4)
C(65)	0.0734 (6)	0.4968 (9)	0.0782 (8)	5.9 (3)
C(66)	0.0865 (6)	0.392 (1)	0.1072 (6)	4.8 (3)
C(71)	0.1358 (5)	-0.1091 (8)	0.1233 (5)	3.6 (2)
C(72)	0.1461 (6)	-0.1468 (8)	0.1918 (6)	4.3 (3)
C(73)	0.0948 (7)	-0.2025 (9)	0.2208 (7)	6.1 (3)
C(74)	0.0345 (6)	-0.222 (1)	0.1818 (8)	6.5 (4)
C(75)	0.0241 (6)	-0.185 (1)	0.1145 (8)	6.3 (3)
C(76)	0.0750 (5)	-0.131 (1)	0.0845 (6)	4.6 (3)
C(81)	0.2131 (5)	-0.1129 (8)	0.0058 (5)	3.4 (2)
C(82)	0.2313 (5)	-0.0612 (9)	-0.0557 (6)	4.3 (3)
C(83)	0.2462 (6)	-0.124 (1)	-0.1126 (6)	5.1 (3)
C(84)	0.2455 (6)	-0.236 (1)	-0.1083 (6)	5.8 (3)
C(85)	0.2300 (7)	-0.289 (1)	-0.0476 (7)	5.8 (3)
C(86)	0.2129 (5)	-0.228 (1)	0.0090 (6)	4.5 (3)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

on one metal mutually trans and on the other metal mutually cis, is similar to those reported for the closely related, formally Rh(0) complexes,  $[\text{Rh}_2(\text{CO})_3(\text{dppm})_2]^{26}$  and  $[\text{Rh}_2(\text{CO})_3(\text{PhO})_2\text{PN}(\text{Et})\text{P}(\text{OPh})_2]^{27}$  and to that presumed for the iridium analogue  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]^{28}$ . Figure 2 shows a view approximately along

**Table IV.** Selected Distances (Å) in  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]^a$ 

(a) Bonded Atoms		
Ir-Rh	2.7722 (7)	P(2)-C(31) 1.840 (8)
Ir-P(1)	2.309 (2)	P(2)-C(41) 1.825 (8)
Ir-P(3)	2.321 (2)	P(3)-C(5) 1.833 (8)
Ir-C(1)	1.857 (9)	P(3)-C(51) 1.833 (8)
Ir-C(2)	1.916 (9)	P(3)-C(61) 1.829 (9)
Rh-P(2)	2.312 (2)	P(4)-C(5) 1.842 (8)
Rh-P(4)	2.295 (2)	P(4)-C(71) 1.811 (8)
Rh-C(3)	1.861 (9)	P(4)-C(81) 1.831 (8)
P(1)-C(4)	1.841 (8)	O(1)-C(1) 1.186 (9)
P(1)-C(11)	1.853 (8)	O(2)-C(2) 1.12 (1)
P(1)-C(21)	1.835 (8)	O(3)-C(3) 1.134 (9)
P(2)-C(4)	1.843 (8)	
(b) Nonbonded Atoms		
Rh-C(1)	2.644 (7)	P(3)-P(4) 2.983 (4)
P(1)-P(2)	2.991 (3)	

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. Additional distances are given in the supplementary material.

**Table V.** Selected Angles (deg) in  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]^a$ 

Rh-Ir-P(1)	84.25 (5)	Rh-P(2)-C(4)	114.9 (3)
Rh-Ir-P(3)	94.17 (5)	Rh-P(2)-C(31)	114.3 (3)
Rh-Ir-C(1)	66.3 (2)	Rh-P(2)-C(41)	116.6 (3)
Rh-Ir-C(2)	164.5 (3)	C(4)-P(2)-C(31)	103.9 (4)
P(1)-Ir-P(3)	104.95 (7)	C(4)-P(2)-C(41)	104.6 (4)
P(1)-Ir-C(1)	126.6 (3)	C(31)-P(2)-C(41)	100.8 (4)
P(1)-Ir-C(2)	98.7 (3)	Ir-P(3)-C(5)	113.0 (3)
P(3)-Ir-C(1)	120.1 (3)	Ir-P(3)-C(51)	116.7 (3)
P(3)-Ir-C(2)	99.8 (3)	Ir-P(3)-C(61)	118.6 (3)
C(1)-Ir-C(2)	100.3 (4)	C(5)-P(3)-C(51)	102.1 (4)
Ir-Rh-P(2)	88.18 (6)	C(5)-P(3)-C(61)	103.5 (4)
Ir-Rh-P(4)	88.22 (6)	C(51)-P(3)-C(61)	100.9 (4)
Ir-Rh-C(3)	175.7 (3)	Rh-P(4)-C(5)	110.9 (3)
P(2)-Rh-P(4)	167.56 (8)	Rh-P(4)-C(71)	122.4 (3)
P(2)-Rh-C(3)	92.2 (3)	Rh-P(4)-C(81)	112.3 (3)
P(4)-Rh-C(3)	92.3 (3)	C(5)-P(4)-C(71)	103.6 (4)
Ir-P(1)-C(4)	108.6 (3)	C(5)-P(4)-C(81)	102.9 (4)
Ir-P(1)-C(11)	121.9 (3)	C(71)-P(4)-C(81)	102.8 (4)
Ir-P(1)-C(21)	115.9 (3)	Ir-C(1)-O(1)	171.9 (6)
C(4)-P(1)-C(11)	103.9 (4)	Ir-C(2)-O(2)	176.0 (9)
C(4)-P(1)-C(21)	103.9 (4)	Rh-C(3)-O(3)	178.2 (8)
C(11)-P(1)-C(21)	100.8 (4)	P(1)-C(4)-P(2)	108.6 (4)
P(3)-C(5)-P(4)	108.7 (4)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. Additional angles are given in the supplementary material.

the metal-metal axis, in which all phenyl carbons except those bound to phosphorus are omitted.

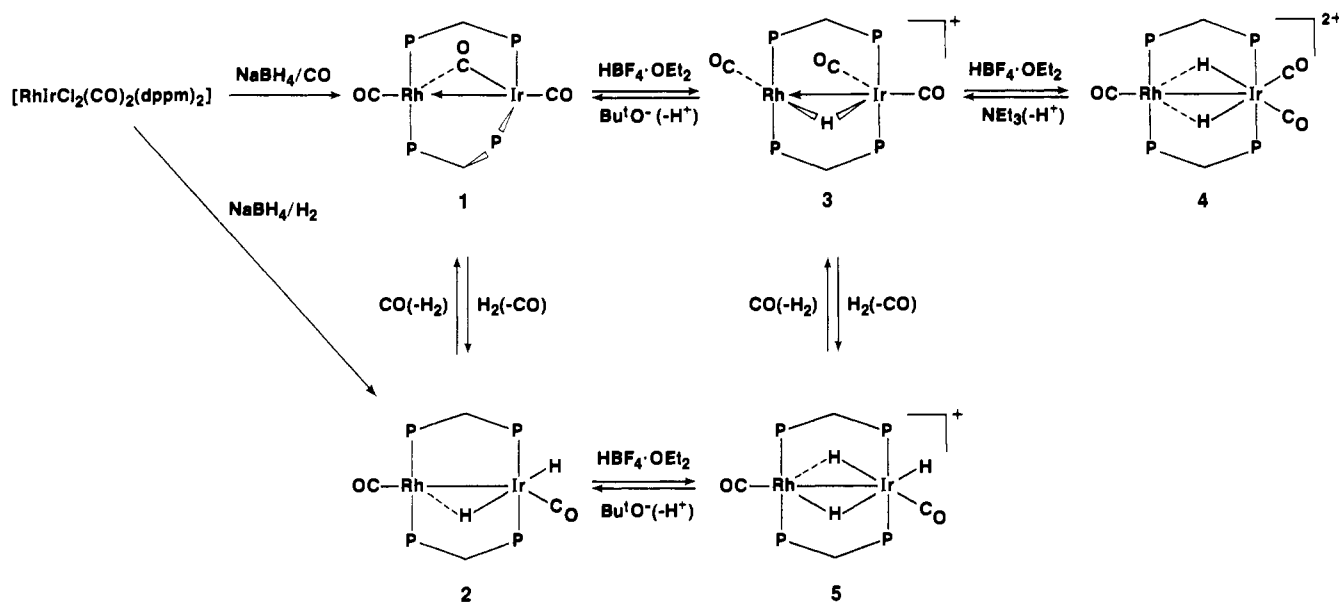
The coordination spheres about the two metals are quite different, the Rh atom having a coordination number of 4 (excluding the weak interaction with C(1)), while the Ir atom is bound to five other atoms (including Rh). This appears to be the general structural form for the complexes  $[\text{MM}'(\text{CO})_3(\text{dppm})_2]$  (M, M' = Rh, Ir), even though the homobimetallic species are potentially symmetrical, and also appears to be the structure adopted by  $[\text{RhCo}(\text{CO})_3(\text{dppm})_2]^{28}$ . We suggest that instead of viewing these complexes as containing formally zerovalent metal atoms, as would be implied by a symmetrical formulation, it is more appropriate to regard them as mixed-valence M(I)/M(-I) species, in which the M(-I) atom functions as a pseudohalide that bonds to the other metal via a dative metal-metal bond. This view is consistent with the asymmetric structure observed and the coordination environments about each metal (vide infra). The present compound may therefore be considered as containing an Ir(-I)→Rh(I) dative bond. This formulation is supported by the square-planar ligand configuration at Rh, an arrangement typical of d<sup>8</sup> systems. The phosphine atoms P(2) and P(4) are approximately trans to each other about Rh (P(2)-Rh-P(4) = 167.66 (8)°) as are the carbonyl group C(3)O(3) and the Ir center (Ir-Rh-C(3) = 175.7 (3)°).

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Scheme I



The geometry about Ir, on the other hand, may be described as roughly trigonal bipyramidal, with Rh and C(2) in the axial sites and P(1), P(3), and C(1) in the equatorial positions. However, it must be pointed out that the distortions from this geometry are not negligible. In particular, the Rh–Ir–C(1) angle, at  $66.3 (2)^\circ$ , is rather acute, and all three equatorial substituents are bent away from C(2) by approximately  $100^\circ$ , such that the Ir center is raised  $0.355 \text{ \AA}$  above the plane defined by P(1), P(3), and C(1). Alternately, if the Ir→Rh bond is not included in the above description, the coordination geometry about Ir in the isolated  $\text{Ir}(\text{CO})_2\text{P}_2$  unit may be described as approximately tetrahedral. Such a view is consistent with Ir being in the  $-1$  oxidation state, having a  $d^{10}$  configuration (cf.  $\text{Ir}(\text{CO})_4^-$ ) and suggests a pseudohalide formulation for this group. The largest distortions from an idealized tetrahedral geometry again appear to result from the formation of the Ir→Rh dative bond and a possible weak interaction between the carbonyl group, C(1)O(1), and Rh (vide infra). The Ir(–1) formulation is supported by the analogous coordination geometries observed for the  $d^{10}$  Ni(0) centers in the closely related complexes  $[\text{Ni}_2(\text{CO})_2(\mu\text{-CO})(\text{dppm})_2]^{29}$  and  $[\text{Ni}_2(\text{CO})_2(\mu\text{-CO})((\text{CF}_3)_2\text{PSP}(\text{CF}_3)_2)_2]^{30,31}$ . The structure of **1** is also very similar to that determined for the related species  $[(\text{PEt}_3)_2\text{RhCo}(\text{CO})_5]^{32}$  and to that proposed for  $[\text{RhCo}(\text{CO})_7]^{33}$  and it is noteworthy that a mixed-valence formulation and a labile  $\text{Co}(-1) \rightarrow \text{Rh}(1)$  dative bond were also proposed for the former. A forthcoming paper,<sup>28</sup> in which facile cleavage of the  $\text{Co} \rightarrow \text{Rh}$  bond in the closely related species  $[\text{RhCo}(\text{CO})_3(\text{dppm})_2]$  (yielding  $[\text{Rh}(\text{CO})(\text{dppm})_2]^+$  and  $[\text{Co}(\text{CO})_4]^-$ ) is demonstrated, offers further support for our mixed-valence formulations for these dppm-bridged species. Compound **1** and the related Rh<sub>2</sub> and Ir<sub>2</sub> analogues are thus members of a growing class of complexes containing dative M→M' bonds.<sup>28,32,34</sup>

The Ir–Rh distance of  $2.7722 (7) \text{ \AA}$  falls within the range typically observed for Rh–Rh ( $2.533\text{--}2.813 \text{ \AA}$ )<sup>4,6,15,26,27,35</sup> and Ir–Ir ( $2.7661\text{--}2.8933 \text{ \AA}$ )<sup>10,12,17,36</sup> single bonds in related systems. Compression along the Ir–Rh axis, through mutual attraction of the metals, is borne out through comparison of the Ir–Rh distance with the intraligand P...P separations ( $2.991 (3)$ ,  $2.983 (3) \text{ \AA}$ ). The Ir→Rh dative bond is accompanied by what may be a weakly semibridging carbonyl group, C(1)O(1), bonded primarily to Ir (Ir–C(1) =  $1.857 (1) \text{ \AA}$ ) and interacting weakly with Rh (Rh...C(1) =  $2.644 (7) \text{ \AA}$ ). This group is nearly linear with respect to Ir (Ir–C(1)–O(1) =  $171.9 (6)^\circ$ ) and is rather strongly bound to this metal, as evidenced by the short Ir–C(1) distance. The C(1)–O(1) distance is longer than those for the other carbonyl groups, possibly resulting from a slight decrease in the C–O bond order due to donation of electron density from Rh into the  $\pi^*$  orbital of C(1)–O(1), in order to alleviate charge buildup at the Rh center due to the dative Ir→Rh bond. The Rh–C(1) distance is longer than the corresponding metal–semibridging-carbonyl distance in the dirhodium analogue ( $2.533 (3) \text{ \AA}$ ), indicating a weaker interaction in the present case. The structural parameters for this carbonyl group do not adequately fit the trends described previously for known classes of semibridging carbonyls.<sup>37</sup> We suggest therefore that the interaction of C(1)O(1) with Rh is rather weak. This would seem to agree with the lack of coupling between rhodium and either of the Ir-bound carbonyl ligands in the <sup>13</sup>C NMR spectrum.

Other parameters in the molecule are essentially as expected. The Ir–P distances are very similar to the Rh–P distances, despite the dissimilar coordination geometries about the metals.

#### (b) Preparation and Characterization of Compounds. Although

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the chemistries of dirhodium and diiridium systems can differ appreciably, they frequently do so in a complementary manner. As an example, we have shown in several studies<sup>8,9,12-14,17,38</sup> that the more stable and less kinetically labile iridium complexes can frequently serve as models for unstable or labile intermediates in analogous rhodium chemistry. It therefore appeared an obvious extension to investigate the related heterobimetallic Rh/Ir compounds in order to attempt to bridge the gaps between dirhodium and diiridium chemistry.

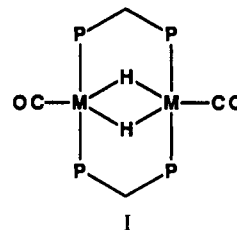
For the preparation of the Rh/Ir complexes of interest, the complex  $[\text{RhIrCl}_2(\text{CO})_2(\text{dppm})_2]$ , first prepared by Shaw and co-workers,<sup>18</sup> is a useful precursor. The reaction of this mixed-metal starting material with  $\text{NaBH}_4$  under CO gives rise to the formally zerovalent binuclear species  $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$  (**1**), which is the mixed-metal analogue of the previously observed dirhodium<sup>15b,26</sup> and diiridium<sup>8</sup> compounds. Its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is characteristic of those observed for such a mixed-metal dppm-bridged complex, displaying a pattern consistent with an AA'BB'X spin system. The Rh-bound phosphorus resonance appears as a doublet of multiplets ( $\delta$  16.4), with each multiplet resembling the Ir-P signal ( $\delta$  -16.3). No resonance is observed in the high-field region of the  $^1\text{H}$  NMR spectrum, indicating that **1** is not a hydrido species. The infrared spectrum of **1** displays bands at 1958, 1940, and 1849  $\text{cm}^{-1}$  (Nujol) and is similar to those of the above-mentioned homobimetallic tricarbonyls, suggesting a similar structure, in which one metal is 5-coordinate and the other 4-coordinate. The X-ray structure confirms the non-A-frame structure of the complex and indicates that the "third" CO ligand and the related distortions at the metal center are associated with iridium. That the Ir atom should have the M(-I) formulation instead of Rh is consistent with the greater electronegativity of the former.<sup>39</sup>

Like its homobimetallic counterparts, species **1** is fluxional in solution. The room-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows resonances at  $\delta$  188.7 (triplet,  $^2J_{\text{P}(\text{Ir})-\text{C}} = 18.1$  Hz) and 185.1 (doublet of triplets,  $^1J_{\text{Rh}-\text{C}} = 67.9$  Hz and  $^2J_{\text{P}(\text{Rh})-\text{C}} = 13.7$  Hz) with relative intensities of 2:1, whereas at  $-80^\circ\text{C}$  three signals of equal intensity appear at  $\delta$  191.9 (triplet,  $^2J_{\text{P}(\text{Ir})-\text{C}} = 41.7$  Hz), 185.0 (broad singlet), and 183.8 (doublet of triplets,  $^1J_{\text{Rh}-\text{C}} = 69.7$  Hz and  $^2J_{\text{P}(\text{Rh})-\text{C}} = 13.4$  Hz). Similar results were obtained in the case of  $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$ ,<sup>8</sup> indicating that the carbonyl ligands are not exchanging between metal centers in either complex. In the present case, the fluxionality at ambient temperature appears to involve interchange between the terminal and semi-bridging carbonyls attached to iridium, with the rhodium carbonyl remaining unaffected and therefore uninvolved in the process. It should also be noted that the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** remains essentially invariant throughout the temperature range studied ( $+25$  to  $-80^\circ\text{C}$ ), which would indicate that, in addition to the mechanism for carbonyl interchange, an exchange pathway is involved (such as a "wagging" of the P-Ir-P unit about the Rh-Ir bond) that allows the phosphorus atoms attached to iridium to appear equivalent within the NMR time scale.

Although complex **1** does not appear to undergo CO scrambling over both metals under  $\text{N}_2$  atmosphere, ligand exchange under  $^{13}\text{CO}$  is facile and results in enrichment of all three positions within  $1/2$  h. It would appear that a labile tetracarbonyl species,  $[\text{RhIr}(\text{CO})_4(\text{dppm})_2]$  (**6**), analogous to the labile diiridium species  $[\text{Ir}_2(\text{CO})_4(\text{dppm})_2]$ <sup>8</sup> may be involved as an intermediate in the scrambling process. However, its identification is not unambiguous. The infrared spectrum of a solution of **1** under an atmosphere of CO shows two new carbonyl stretches at 1955 and 1926  $\text{cm}^{-1}$ , while the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows the two signals due to **1**, with no apparent evidence of an additional species. However, as the temperature is lowered, two additional resonances appear at  $\delta$  3.1 and  $-12.3$ . At  $-60^\circ\text{C}$  these resonances appear as an unresolved multiplet and a pseudotriplet, respectively, and account for ca. 40% of the total intensity. At the same temperature, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a  $^{13}\text{CO}$ -enriched sample of **1** under

an atmosphere of  $^{13}\text{CO}$  shows new broad resonances at  $\delta$  188 and 197 as well as one that falls under the  $\delta$  192 resonance due to **1**; unfortunately, the very poor signal-to-noise ratio for these signals does not allow their unambiguous assignment. Flushing the solution with  $\text{N}_2$  results in the disappearance of all new resonances, leaving only those due to **1**. We suggest that this labile species is the tetracarbonyl, **6**. Although the NMR studies indicate that this species is fluxional it does not appear to be interconverting with **1** on the NMR time scale since the resonances due to **1** and **6** appear to behave independently as the temperature is varied.

The reaction of  $[\text{RhIrCl}_2(\text{CO})_2(\text{dppm})_2]$  with sodium borohydride under an atmosphere of  $\text{H}_2$  gives rise to complex **2**,  $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-H})(\text{dppm})_2]$ . Its solution infrared spectrum shows only one carbonyl stretch (1937  $\text{cm}^{-1}$ ), suggestive of a symmetrical structure similar to that of the previously reported  $[\text{M}_2(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2]$  ( $\text{M} = \text{Rh},^{16} \text{Ir}^{12}$ ); however, the presence of two carbonyl bands in the solid-state IR spectrum (1942, 1924  $\text{cm}^{-1}$ ) suggests a less symmetrical structure, and a weak stretch at 2033  $\text{cm}^{-1}$  suggests at least one terminal hydride ligand in the complex. Furthermore, the high-field region of the  $^1\text{H}$  NMR spectrum of **2** shows two different resonances ( $\delta$  -11.00 and -12.73). Both of these are broad at ambient temperature, but at  $-40^\circ\text{C}$  the latter hydride peak (now at  $\delta$  -12.84) appears as a triplet. This high-field signal is due to a hydride ligand terminally bound to iridium ( $^2J_{\text{P}(\text{Ir})-\text{H}} = 17.6$  Hz), as selective heteronuclear decoupling of the iridium-bound phosphorus resonance causes this signal to collapse into a singlet. At this temperature, it is also observed that the lower field hydride signal (now at  $\delta$  -11.15) also resolves into a broad doublet when either the iridium-bound or the rhodium-bound phosphorus resonance is selectively irradiated; although the poor resolution makes it impossible to determine the phosphorus-hydride couplings, the rhodium-hydride coupling may be estimated as approximately 14 Hz. Clearly this lower field resonance is due to a hydride ligand that bridges the two metals. The value of  $^1J_{\text{Rh}-\text{H}}$  involving this hydride suggests that the rhodium-hydride interaction is weaker than in similar dirhodium complexes that contain symmetrically bridging hydride ligands ( $^1J_{\text{Rh}-\text{H}} = 20$  Hz for  $[\text{Rh}_2(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2]$ ,<sup>16</sup> and  $^1J_{\text{Rh}-\text{H}} = \text{ca. } 20$  Hz for the series  $[\text{Rh}_2\text{Cl}_2\text{X}(\mu\text{-H})(\mu\text{-CO})(\text{dppm})_2]$  ( $\text{X} = \text{Cl}, \text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3, \text{FBF}_3$ )<sup>35d</sup>), indicating that compound **2** contains an unsymmetrical Rh-Ir bridge in which the hydride interacts more strongly with Ir. Couplings of this magnitude have been noted in other mixed binuclear and trinuclear Rh/Ir complexes containing asymmetrically bridging hydrides,<sup>14,40</sup> while a  $^1J_{\text{Rh}-\text{H}}$  coupling of 24.4 Hz has been reported for  $[(\eta^4\text{-C}_8\text{H}_{12})\text{Rh}(\mu\text{-H})(\mu\text{-Cl})\text{IrH}_2(\text{PPh}_3)_2]$ , a species containing a more symmetrical hydride bridge.<sup>41</sup> The structure proposed for **2** (Scheme I) thus differs from that shown for the homobimetallic dihydrides, in which both hydrides bridge the metals symmetrically (structure I;  $\text{M} = \text{Rh},^{16} \text{Ir}^{12}$ ). In Scheme



I, dashed lines between Rh and H are employed to denote this weaker bonding. A trans arrangement of the hydride ligands across the iridium center in **2** would explain the reluctance of this species to reductively eliminate  $\text{H}_2$ ; however, we cannot unambiguously rule out a cis disposition of hydrides, since even for **5**, for which two hydrides are mutually cis, reductive elimination is slow (vide infra). Although it is possibly not surprising that

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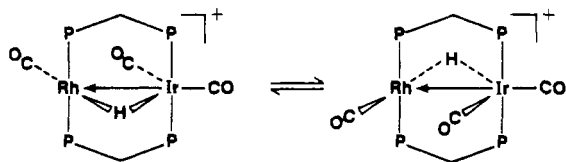
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**2** is thermally more stable than the dirhodium analogue, it is surprisingly also more stable than the diiridium species; both homobimetallic complexes decompose within several hours at 20 °C whereas **2** is stable for several days at room temperature.

Compound **1** may be converted to **2** via reaction with H<sub>2</sub> over a 24-h period, whereas conversion of **2** to **1** by reaction with CO is complete within approximately 2 h.

Compound **1** reacts with 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub>, yielding [RhIr(CO)<sub>3</sub>(μ-H)(dppm)<sub>2</sub>][BF<sub>4</sub>] (**3**). This compound has the same stoichiometry as the dirhodium<sup>15</sup> and diiridium<sup>8,10</sup> analogues, but possesses a significantly different structure. Whereas the homobimetallic species have A-frame structures in which a hydride and a carbonyl ligand bridge the metals, compound **3** has no bridging carbonyl group. The lowest CO stretch in the infrared spectrum (1899 cm<sup>-1</sup>) is significantly higher than those due to the bridging carbonyls in the homobimetallic analogues (1870 cm<sup>-1</sup> (Rh<sub>2</sub>);<sup>15</sup> 1850 cm<sup>-1</sup> (Ir<sub>2</sub>)<sup>8</sup>). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at room temperature shows signals at δ 186.2 (doublet of triplets, <sup>1</sup>J<sub>Rh-C</sub> = 73.9 Hz and <sup>2</sup>J<sub>P(Rh)-C</sub> = 15.0 Hz) and 179.5 (broad) with relative intensities of 1:2, indicating that two carbonyls are located on the iridium center while one is coordinated to rhodium; the <sup>1</sup>H NMR spectrum shows one high-field resonance, a complex multiplet at δ -10.19 due to the bridging hydride, and one resonance at δ 4.38 (quintet) for the methylene protons of the dppm groups. At -80 °C the carbon NMR spectrum shows that the Rh-bound carbonyl resonance remains unchanged while the broad Ir-carbonyl signal splits into two unresolved ones of equal intensity at δ 184.1 and 176.9. In the proton NMR spectrum, the hydride resonance is broad at this temperature while the methylene resonance has resolved into two signals at δ 4.54 and 4.07, integrating as two protons each. It appears that a fluxional process such as



equilibrates the iridium-bound carbonyl groups at higher temperatures. We propose that this occurs via tunneling of the hydride ligand between the metals, resulting in a twisting of the HIr(CO)<sub>2</sub> unit about the P-Ir-P axis, bringing the hydride from one face of the dimer to the other and interchanging the carbonyls on Ir. An analogous structure and fluxionality has been proposed for the isoelectronic species [RhFeH(CO)<sub>3</sub>(dppm)<sub>2</sub>].<sup>28</sup> Selective decoupling of the two phosphorus environments while observing the <sup>1</sup>H NMR spectrum at 22 °C enables the magnitudes of the Rh-H and P-H couplings to be determined (<sup>1</sup>J<sub>Rh-H</sub> = 19.0 Hz, <sup>2</sup>J<sub>P(Rh)-H</sub> = 9.3 Hz, <sup>2</sup>J<sub>P(Ir)-H</sub> = 12.2 Hz). The values for the phosphorus-hydrogen couplings might suggest that this hydride is more strongly bound to iridium than rhodium; however, the Rh-H coupling, although somewhat smaller, is comparable to those quoted above for hydrido-bridged dirhodium compounds and other symmetrically bridged species and thus is more in line with a close-to-symmetrical bridge. Compound **3** may be converted back to **1** via reaction with the strong base potassium *tert*-butoxide, but this transformation does not occur when a weaker base such as triethylamine is used.

Reaction of **1** with 2 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> (or reaction of **3** with 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub>) yields the dicationic species [RhIr(CO)<sub>3</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**4**). This product appears to resemble the iridium carbonyl hydrides [Ir<sub>2</sub>(H)<sub>2</sub>(CO)<sub>3</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and [Ir<sub>2</sub>(CO)<sub>4</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>,<sup>8</sup> in that movement of the hydride ligands of **4** from bridging to terminal sites (one on each metal) would make this complex structurally comparable to the diiridium tricarbonyl species, while addition of one CO ligand at the coordinatively unsaturated Rh center would produce a form parallel to the diiridium tetracarbonyl. These changes would involve the formation of terminal Rh-H and Rh-CO bonds, which are less favored than the equivalent Ir-H and Ir-CO bonds, providing a rationale for the nonobservance of the exact mixed-metal analogues of these Ir<sub>2</sub> systems. Only one hydride signal

is seen in the <sup>1</sup>H NMR spectrum of **4**, appearing as a complex multiplet at δ -11.18 and integrating as two protons. Selective irradiation of the resonance due to the Rh-bound phosphorus nuclei causes the hydride signal to collapse to an overlapping doublet of triplets (<sup>1</sup>J<sub>Rh-H</sub> = 17.3 Hz, <sup>2</sup>J<sub>P(Ir)-H</sub> = 11.1 Hz). Irradiation of the Ir-P signal resolves the hydride multiplet into a broadened doublet, from which <sup>2</sup>J<sub>P(Rh)-H</sub> may be estimated as ≤ 7 Hz (the half-width at half-height of either peak of the doublet); broad-band phosphorus decoupling further sharpens this doublet, but the resonance is not resolved to the base line and the peaks are still 7 Hz wide at half-height, thus explaining our inability to accurately determine <sup>2</sup>J<sub>P(Rh)-H</sub>. The Rh-H coupling constant suggests a somewhat weaker interaction of the hydride ligands with Rh, which is supported by the failure to resolve coupling to the Rh-bound phosphines; however, bonding appears to be more symmetric than in species **2**. The infrared spectra of this complex indicate that all carbonyl groups are terminally bound. Species **4** may be deprotonated easily by NEt<sub>3</sub>, regenerating compound **3**.

Reaction of **2** with 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> leads to the cationic trihydride **5**, [RhIr(H)(CO)<sub>2</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>], similar to the result of the protonation of the analogous iridium dihydride<sup>12</sup> but quite unlike the product reported in the rhodium chemistry, where H<sub>2</sub> loss apparently occurs, yielding [Rh<sub>2</sub>(CO)<sub>2</sub>(μ-H)(dppm)<sub>2</sub>]<sup>+</sup>.<sup>15,16</sup> The <sup>1</sup>H NMR spectrum of **5** shows three hydride resonances (δ -10.58, -11.46, and -11.76), all of which are broadened at room temperature. Cooling the sample to -40 °C results in the resolution of the middle signal into a triplet, which was shown by selective heteronuclear decoupling of the phosphorus resonances to be a terminal hydride attached to iridium (<sup>2</sup>J<sub>P(Ir)-H</sub> = 11.8 Hz). The other hydride resonances remained broad, even with selective <sup>31</sup>P decoupling; broad-band irradiation resolved these into doublets, with <sup>1</sup>J<sub>Rh-H</sub> = 10.4 Hz for the former and <sup>1</sup>J<sub>Rh-H</sub> = 23.2 Hz for the latter bridging hydride, with no apparent H-H coupling observed. The magnitudes of the rhodium-hydride couplings indicate that, unlike complex **4**, the bridging hydrides in **5** are disposed in two different manners: the one with the larger coupling to Rh probably approximates a symmetrical bridge; the other interacts much less strongly with Rh (and therefore is more strongly bound to Ir). Although, on the basis of the spectral study, it is not clear which bridging hydride ligand is more symmetrically bound, we propose that it is the one opposite the terminal hydride, as shown in Scheme I. Such a proposal is consistent with the high trans influence of the terminal hydride, resulting in a weakening of the opposite Ir-H bond and a concomitant strengthening of the associated Rh-H bond. The infrared spectra of **5** are quite similar to those observed for [Ir<sub>2</sub>(H)(CO)<sub>2</sub>(μ-H)<sub>2</sub>(dppm)<sub>2</sub>][BF<sub>4</sub>].<sup>12</sup> Whereas exchange between the terminal and one bridging hydride ligand was observed in the diiridium species, none was observed for **5**. This is not surprising since, according to the mechanism previously proposed,<sup>12</sup> a species with a terminal hydride on Rh (instead of Ir) would be one of the limiting forms, which should be significantly less stable than that observed owing to the differences between the Ir-H and Rh-H bond energies. Compound **5** may be converted back to **2** by reaction with BH<sub>4</sub><sup>-</sup> or Bu<sup>-</sup>O<sup>-</sup>. Attempts to further protonate **5** to yield a dicationic tetrahydride failed. In fact, no species containing more than three hydrides was observed in this study, in contrast to the diiridium chemistry where several tetrahydride complexes were found.

As described in the Experimental Section, we have found that conversion of complex **3** to **5** via reaction with H<sub>2</sub> is the superior synthetic route (vs protonation of **2**), going to completion in 3 h. The reverse process (**5** + CO → **3**) requires 24 h.

### Summary

The title complex (**1**) is the mixed-metal analogue of the previously synthesized dirhodium and diiridium tricarbonyl complexes, and appears best formulated as a mixed-valence species containing an Ir(-I)→Rh(I) dative bond. The hydridic species (**2-5**) appear to more strongly resemble those reported in the diiridium chemistry than the dirhodium forms. However, the structures reported herein differ significantly from the homobimetallic complexes via the inherent asymmetry imparted by the

presence of two different metal centers, which manifests itself most prominently in the metal-hydride bonding, a result of the greater strength of Ir-H vs Rh-H bonds. Although species with close-to-symmetric Rh-H-Ir bridges have been observed, in several complexes relatively weak Rh-H interactions appear to be present as evidenced by the smaller NMR couplings between rhodium and hydride ligand as well as between the hydride and rhodium-bound phosphorus nuclei. It is also significant that the cationic species **3** differs appreciably from the Rh<sub>2</sub> and Ir<sub>2</sub> analogues in that it has no bridging carbonyl group. Clearly the mixed-metal complexes will not always have properties intermediate between those of the homobimetallic analogues but will show some unique characteristics by virtue of the polarity induced in a heterobinuclear system. These are the first mixed-metal rhodium-iridium complexes prepared that contain only carbonyl and hydride ligands besides the bridging diphosphines. The interconversions via simple

hydrogenation, carbonylation, protonation, and deprotonation steps illustrate their potential utility for modeling catalytic processes, studies of which are presently underway in this group.

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**Supplementary Material Available:** Tables of thermal parameters for the anisotropic atoms, idealized hydrogen parameters, bond distances and angles within the phenyl rings, and a summary of crystal data and the details of the intensity collection (10 pages); a listing of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

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## A New Three-Dimensionally Nonmolecular Cd-S Lattice in Crystalline Cd<sub>7</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-2)<sub>14</sub>(DMF)<sub>2</sub>

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Bis(2-methylbenzenethiolato)cadmium crystallizes from DMF as Cd<sub>7</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-2)<sub>14</sub>(DMF)<sub>2</sub> (**5**) and has a three-dimensionally nonmolecular crystal structure quite different from those of Cd(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and 4-substituted Cd(SC<sub>6</sub>H<sub>4</sub>X)<sub>2</sub>. The crystals (tetragonal, P<sub>4</sub>32<sub>1</sub>2, *a* = *b* = 14.028 (1) Å, *c* = 55.295 (8) Å, *V* = 10 880.7 (1.9) Å<sup>3</sup>, *Z* = 8 (× Cd<sub>3.5</sub>S<sub>7</sub>C<sub>49</sub>H<sub>49</sub>C<sub>3</sub>H<sub>7</sub>NO), 4311 independent observed (*I*/σ(*I*) > 3) data (Mo Kα), *R* = 0.034) contain {Cd<sub>3</sub>(μ-SAr)<sub>3</sub>(DMF)} cycles, in which the DMF carbonyl oxygen atom has asymmetric secondary coordination (Cd-O = 2.72, 2.95, 2.99 Å) to the three Cd atoms with tetrahedral Cd(μ-SAr)<sub>4/2</sub> primary coordination. The Cd<sub>3</sub> cycles are linked by (μ-SAr) ligands and spiro Cd atoms. The unique structural feature of these three-dimensionally nonmolecular linkages is the occurrence of large open elongated macrocycles, ca. 28 Å long and 14 Å wide, around which the pathway with the smallest number of connections involves 24 Cd atoms and 24 bridging thiolate ligands. Adamantanoid cages are absent.

### Introduction

We are investigating the structures and reactions of the class of compounds Cd(SR)<sub>2</sub> and recently reported the crystal structures of the aryl derivatives Cd(SPh)<sub>2</sub> (**1**), Cd(SC<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub> (**2**), Cd(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub> (**3**), and Cd<sub>8</sub>(SC<sub>6</sub>H<sub>4</sub>Br-4)<sub>16</sub>(DMF)<sub>3</sub> (**4**), all crystallized from DMF.<sup>1-3</sup> Crystalline **1-3** are three-dimensionally nonmolecular. They comprise adamantanoid cages, each with an {octahedro-(μ-SAr)<sub>6</sub>-tetrahedro-Cd<sub>4</sub>} core and with four intercage linkages through shared SAr ligands at the vertices of the tetrahedral adamantanoid units: the general formula is thus  $\frac{3}{8}[(\mu\text{-SAr})_6\text{Cd}_4(\mu\text{-SAr})_{4/2}]$ .

Alternatively, these structures can be considered as three-dimensional Cd-S lattices, adorned with substituents. In this view, the Cd(SAr)<sub>2</sub> structures are comparable with the lattices of silicates, aluminosilicates, and aluminophosphates.<sup>4</sup> The topological correspondence is between the tetrahedral adamantanoid cage [(μ-SAr)<sub>6</sub>Cd<sub>4</sub>(μ-SAr)<sub>4/2</sub>] and the tetrahedral TO<sub>4</sub> unit (T = Al, Si, P), which is much smaller. Indeed, the lattice adopted by **1** and **2** is isostructural with that of α-cristobalite, and **3** is analogous to a zeolite with cavities and channels, but with much larger dimensions. The stoichiometries of the metal sulfide lattice in Cd(SAr)<sub>2</sub> compounds and of the metal oxide lattices are the same, namely MX<sub>2</sub> (X = O, S). Further, just as the microporous oxide

lattices have spatially differentiated regions of MO<sub>2</sub> framework and of cavity and/or channel, so there is in crystalline **1-3** clear spatial segregation of the CdS<sub>2</sub> framework and the regions occupied only by Ar substituents. The volumes occupied by the Ar substituents are larger, both in actuality and as a proportion of the lattice volume, than the void volumes of the microporous oxides. There is a nice complementarity between these nonmolecular Cd-S lattices with internal Ar substituents and molecular CdS clusters coated with Ar substituents, such as [S<sub>4</sub>Cd<sub>10</sub>(SPh)<sub>16</sub>]<sup>4-</sup>,<sup>5</sup> [S<sub>4</sub>Cd<sub>17</sub>(SPh)<sub>28</sub>]<sup>2-</sup>,<sup>6</sup> and stabilized colloidal CdS.<sup>7-10</sup>

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