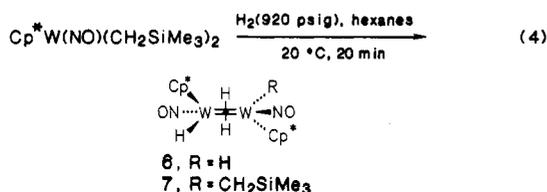


**Figure 2.** The 400-MHz  $^1\text{H}$  NMR spectrum of  $[\text{Cp}^*\text{W}(\text{NO})\text{H}](\mu\text{-H})_2[\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)]$  (7) in  $\text{CD}_3\text{NO}_2$ .

NMR), and the experimental conditions employed are considerably milder than those cited in two recent reports of *thermal* benzene C-H activation by monometallic complexes.<sup>12</sup> Regrettably, attempts to activate the C-H bonds of  $\text{CH}_4$ , *n*-hexane, or cyclohexane by 4 in an identical manner result only in the formation of low yields of  $\text{Cp}^*\text{W}(\text{NO})(\text{PMe}_3)_2$ <sup>13</sup> as the only identifiable product.

Hydrogenation at 80 psig of  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$  without the added Lewis base of eq 1 generates a mixture of at least eight products (by  $^1\text{H}$  NMR). When performed at 920 psig of  $\text{H}_2$ , however, the reaction is much cleaner, i.e., eq 4, the bimetallic products 6 and 7 being the prin-



cipal species formed. They may be separated by repeated fractional crystallizations from toluene/hexanes. The less soluble product 6 is the  $\text{Cp}^*$  analogue of  $[\text{CpW}(\text{NO})\text{H}]_2(\mu\text{-H})_2$ , a complex that we have described in great detail previously.<sup>14</sup> The other product 7 is novel and is isolable as a bright orange-red crystalline material whose solid and solution properties are similar to those of the mononuclear alkyl hydride complexes presented above. Its  $^1\text{H}$  NMR spectrum is shown in Figure 2. Particularly noteworthy features of this spectrum are the chemical shifts of the hydride resonances, the bridging hydrides resonating at  $\delta -6.36$  and  $+5.30$  and the terminal hydride resonating at  $\delta +6.57$  ppm (assigned on the basis of the intensities of the  $^{183}\text{W}$  satellites).<sup>14</sup> The spectroscopic properties of 6 and 7<sup>5</sup> are consistent with their having the molecular structures shown in eq 4, that of 7 having been confirmed in the solid state by a single-crystal X-ray crystallographic analysis.<sup>6</sup> Complex 7 is thus a new member of the extremely small family of thermally stable bimetallic alkyl hydride compounds, its closest relative probably being the unsymmetrical aryl complex  $\{[(\text{Et}_3\text{P})_2\text{PtPh}](\mu\text{-H})[\text{PtH}(\text{PEt}_3)_2]\}^+$ .<sup>15</sup> In a formal sense, 7 is an analogue of 4, the  $\text{PMe}_3$  ligand in the latter having been replaced by a  $\text{Cp}^*\text{W}(\text{NO})\text{H}_2$  group.

Further studies of these alkyl hydride complexes are currently in progress.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and to the University of British Columbia for the award of a graduate fellowship to J.T.M.

**Supplementary Material Available:** Elemental analysis and spectroscopic (IR and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR, mass spectral) data for complexes 1-7 and tables of fractional coordinates and isotropic and anisotropic thermal parameters for 4 (6 pages); a listing of structure factors for 4 (17 pages). Ordering information is given on any current masthead page.

### Folding and Unfolding of a Trirhodium Chain about an Isocyanide Ligand. The Structure of $[\text{Rh}_3\{\mu\text{-(Ph}_2\text{PCH}_2)_2\text{PPh}\}_2(\eta\text{-C}_4\text{H}_9\text{NC})_5\text{CO}]^{3+}$ as a Solid and in Solution

Alan L. Balch,\* L. Alan Fossett, and Marilyn M. Olmstead

Department of Chemistry, University of California Davis, California 95616

Received April 23, 1987

**Summary:** In the solid state,  $[\text{Rh}_3\{\mu\text{-(Ph}_2\text{PCH}_2)_2\text{PPh}\}_2(\eta\text{-BuNC})_5\text{CO}]^{3+}$  is a tan color and possesses a bent  $\text{Rh}_3$  chain with a triply bridging, four-electron-donating isocyanide and a bridging carbon monoxide, while in dichloromethane solution, it is blue with only terminal isocyanide ligands and a terminal carbon monoxide ligand.

The bridge/terminal interchange for two-electron-donating isocyanide (and carbon monoxide) ligands has received considerable attention.<sup>1</sup> However, little is known about transformations involving the other bridging modes for isocyanide ligands.<sup>2,3</sup> Herein we report on a novel reaction in which a triply bridging isocyanide ligand converts into a terminal isocyanide upon dissolution. The structural chemistry involved demonstrates the remarkable flexibility found in trinuclear complexes bridged by bis((diphenylphosphino)methyl)phenylphosphine (dpmp) ligands.<sup>4</sup>

Addition of 5 equiv of *n*-butyl isocyanide to a dichloromethane solution of  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CO})_3(\mu\text{-Cl})\text{Cl}]\text{-BPh}_4^{4a}$  produces a deep blue solution from which tan crystals of  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CO})(\eta\text{-BuNC})_5][\text{PF}_6]_3$  (1)<sup>5</sup> are obtained (in 50% yield) by precipitation through the addition of a methanol solution of ammonium hexafluorophosphate. In the solid state, 1 shows infrared absorptions due to terminal isocyanides at  $2160 \text{ cm}^{-1}$ , to a bridging

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(2) Yamamoto, Y. *Coord. Chem. Rev.* 1980, 32, 193.

(3) Exchange of four-electron, doubly bridging isocyanides with terminal isocyanides in  $\text{Ni}_4(\text{CN-}t\text{-Bu})_7$  has been reported: Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* 1977, 99, 743.

(4) (a) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* 1983, 105, 1677. (b) Olmstead, M. M.; Guimerans, R. R.; Balch, A. L. *Inorg. Chem.* 1983, 22, 2473. (c) Balch, A. L.; Guimerans, R. R.; Olmstead, M. M. *J. Organomet. Chem.* 1984, 268, C38. (d) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M. *Organometallics* 1985, 4, 781.

(5) Anal. Calcd for  $\text{C}_{90}\text{H}_{103}\text{F}_{18}\text{N}_5\text{O}_5\text{P}_6\text{Rh}_3$ : C, 49.12; H, 4.72; N, 3.18. Found: C, 48.51; H, 4.62; N, 3.07.

(12) (a) Chetcuti, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1987, 109, 942. (b) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 1090.

(13) For Cp analogues, see: Christensen, N. J.; Hunter, A. D.; Legzdins, P.; Sánchez, L. *Inorg. Chem.*, in press.

(14) (a) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* 1986, 108, 7971. (b) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* 1985, 4, 1263.

(15) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 778.

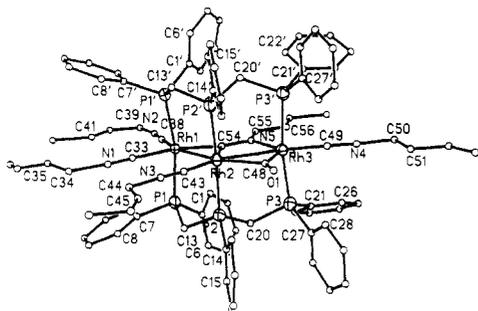


Figure 1. A perspective view of  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNC}_4\text{H}_9)_5(\text{CO})]^{3+}$ .

isocyanide at  $1635\text{ cm}^{-1}$ , and to a bridging carbon monoxide ligand at  $1832\text{ cm}^{-1}$  (identified by the shift in this band to  $1793\text{ cm}^{-1}$  upon  $^{13}\text{C}$  labeling). The electronic absorption spectrum of **1** as a mull in Nujol shows a series of shoulders at 645, 550, 430, and 380 nm on a gradually rising absorption. No intense band at ca. 666 nm, corresponding to the solution spectrum, is seen. These tan crystals of **1** dissolve to give deep blue solutions (which remain blue at  $-50\text{ }^\circ\text{C}$ ) with spectroscopic properties that are markedly different from those obtained from the solid. The dissolution process is completely reversible. Blue dichloromethane solutions of **1** give tan crystals upon addition of methanol. The infrared spectrum of a blue dichloromethane solution shows a terminal isocyanide stretching vibration at  $2154\text{ cm}^{-1}$  and a terminal carbon monoxide stretching band at  $1985\text{ cm}^{-1}$ , which shifts to  $1939\text{ cm}^{-1}$  on substitution with  $^{13}\text{C}$ . No bands due to bridging isocyanide or bridging carbon monoxide are observed in the  $1900\text{--}1600\text{ cm}^{-1}$  region. The electronic absorption spectrum of **1** in dichloromethane shows an intense band at 666 nm ( $\epsilon\ 15000$ ) and other features at 542 and 384 nm. The electrical conductivity of **1** in acetone solution indicates that it is a 1:3 electrolyte ( $\Lambda_M = 320\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$ ). The  $^{31}\text{P}$  NMR spectrum shows that three distinct phosphorus environments are present at 24.8 ( $^1J(\text{Rh},\text{P}) = 100\text{ Hz}$ ), 18.7 ( $^1J(\text{Rh},\text{P}) = 115\text{ Hz}$ ), and 16.7 ppm ( $^1J(\text{Rh},\text{P}) \approx 115\text{ Hz}$ ) with additional, but unanalyzed, spin-spin splitting due to P-P coupling.

The structure of  $[\text{Rh}_3(\mu\text{-dpmp})_2(n\text{-BuNC})_5(\text{CO})]^{3+}$  in the solid state has been determined by X-ray crystallography.<sup>6</sup> A view of the cation, which has crystallographic  $C_s$  symmetry, is shown in Figure 1. A section through the mirror plane which contains the  $\text{Rh}_3(n\text{-BuNC})_5(\text{CO})$  unit with some important dimensions is presented in Figure 2. The most significant feature is the presence of the triply bridging isocyanide that bonds Rh(1) and Rh(2) through its terminal carbon atom and uses the nitrogen atom to bind to Rh(3). The Rh(3)-N(5) distance is longer than the Rh(1)-C(54) and Rh(2)-C(54) distances, but it is consistent with the presence of a single bond between rhodium and nitrogen. As a result of accommodating this triply bridging isocyanide, the Rh-Rh-Rh angle ( $112.3(1)^\circ$ ) is sharply bent. Two other examples of triply bridging isocyanides similar to that in **1** are known:  $\text{Pt}_7(2,6\text{-xylyl isocyanide})_{12}$ <sup>7</sup> and  $\text{Os}_6(\text{CO})_{18}(\text{CNC}_6\text{H}_4\text{CH}_3)_2$ .<sup>8</sup> In the latter, the Os-N distance, 2.16 (3) Å, is appreciably shorter than the Rh-N distance in **1**, but the constraints

(6) Tan prisms of  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNC}_4\text{H}_9)_5(\text{CO})][\text{PF}_6]_2\cdot 2\text{CH}_3\text{OH}$  were obtained with difficulty by diffusion of methanol into an acetone solution of **1**. They belong to the orthorhombic space group  $Pcmn$  ( $zba$  of  $Pnma$ , No. 62) with  $a = 15.509(5)$ ,  $b = 23.421(6)$ , and  $c = 28.507(8)$  Å at 130 K. Refinement of 3032 reflections with  $I > 3\sigma(I)$  using 298 parameters yielded  $R = 0.106$ .

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(8) Orpen, A. G.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1978, B34, 1989.

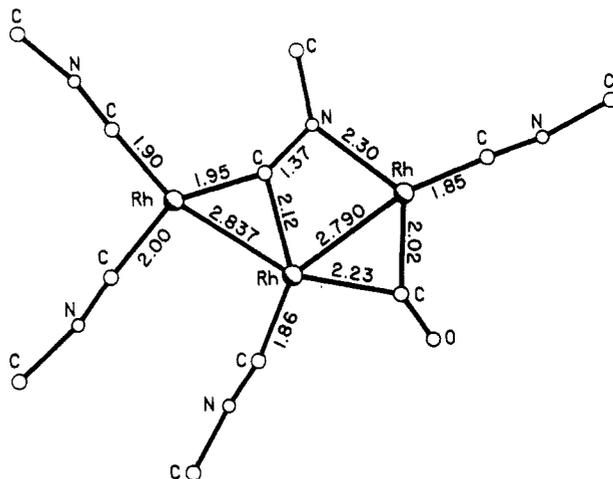
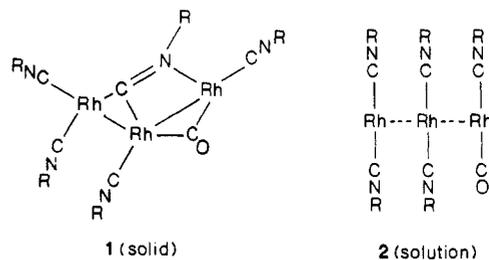


Figure 2. A drawing of the planar core of  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNC}_4\text{H}_9)_5(\text{CO})]^{3+}$  showing some important distances (esd's on Rh-Rh distances, 0.004, and on Rh-C or Rh-N distances, 0.04). Only the  $\alpha$ -carbon atom of each  $n$ -butyl group is shown.

on the geometry of the bridging isocyanides are much less in these larger clusters. In addition to this triply bridging isocyanide, the cation contains four terminal isocyanide ligands, one conventional doubly bridging carbon monoxide ligand, and the two trans triphosphine groups. The Rh-Rh separations are similar to those found in related complexes with bridging carbon monoxide or isocyanide ligands.<sup>4b,d</sup> With the unique bridging isocyanide acting as a four-electron donor, each rhodium in the cation has 18 valence electrons.

The markedly different properties of this complex in solution are indicative of a major structural change upon dissolution. The spectroscopic data are consistent with structure **2** (which shows only the in-plane ligands, the



$\text{dpmp}$  ligands lie above and below this plane) for the cation in solution. This structure has only terminal isocyanide and carbon monoxide ligands as the infrared data require and three distinct phosphorus environments as the  $^{31}\text{P}$  NMR data dictate. Structure **2** is readily obtained from the bridged form shown in Figure 1 by rupture of three bonds, Rh(1)-C(54), Rh(2)-C(48) and Rh(3)-N(5), unfolding of the  $\text{Rh}_3$  angle, and elongation of the Rh-Rh distances. A cation similar to **2**,  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNCH}_3)_6]^{3+}$  ( $\lambda_{\text{max}}\ 674\text{ nm}$  ( $\epsilon\ 33000$ )) with only terminal isocyanides, has been isolated from the reaction of methyl isocyanide with  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CO})_3(\mu\text{-Cl})\text{Cl}][\text{BPh}_4]$  and characterized by X-ray crystallography.<sup>9,10</sup> However,  $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNCH}_3)_6]^{3+}$  shows no evidence for forming

(9) Balch, A. L.; Fossett, L. A.; Olmstead, M. M., to be submitted for publication. The Rh-Rh distances are 3.090 (1) and 3.106 (1) Å, and the Rh-Rh-Rh angle is  $160.2(1)^\circ$ .

(10) An alternative, closed triangular cluster structure analogous to that of  $\text{Ru}_3(\text{CO})_{12}$  for the solution form of this 48e complex appears unlikely. The similarity of the electronic spectra of  $[\text{Rh}_3(\mu\text{-dpmp})_2(n\text{-BuNC})_5(\text{CO})]^{3+}$  and  $\text{Rh}_3(\mu\text{-dpmp})_2(\text{CNCH}_3)_6^{3+}$ , which clearly have similar ligand sets, makes for a compelling argument in favor of structure **2** for the solution form of  $[\text{Rh}_3(\mu\text{-dpmp})_2(n\text{-BuNC})_5(\text{CO})]^{3+}$ .

bridging isocyanides in solution or in the solid state. Clearly a delicate balance of factors allows for the interconversion between ligand arrangements 1 and 2, but the formation of the bridged form 1 clearly demonstrates the ability of all of the rhodium atoms in dpmp-bridged complexes to bind to a single substrate.

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**Supplementary Material Available:** Tables summarizing the data collection and refinement, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (14 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

### A General Route to Anionic ( $\eta^4$ -Diene)manganese Tricarbonyl Complexes. Reactions with Electrophiles

Maurice Brookhart,\* Seok K. Noh, and Francis J. Timmers

Department of Chemistry, University of North Carolina  
Chapel Hill, North Carolina 27514

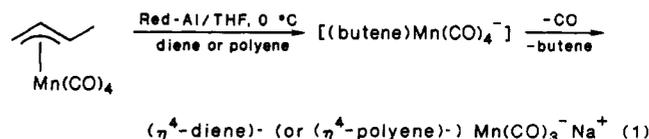
Received April 6, 1987

**Summary:** Reduction of (methallyl)Mn(CO)<sub>4</sub> with Red-Al in the presence of substrates containing a conjugated 1,3-diene unit leads to formation of ( $\eta^4$ -diene)Mn(CO)<sub>3</sub><sup>-</sup> complexes that can be isolated as stable PPN<sup>+</sup> salts. Substrates examined include 1,3-butadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cycloheptatriene, and cyclooctatetraene. These nucleophilic complexes react readily with electrophiles including H<sup>+</sup>, (CH<sub>3</sub>)<sub>3</sub>SiOTf, (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup>, and CO<sub>2</sub> to yield a variety of new manganese tricarbonyl complexes.

( $\eta^4$ -Diene)iron tricarbonyl complexes have been known for many years and used extensively in synthetic applications.<sup>1</sup> Isoelectronic ( $\eta^4$ -diene)Mn(CO)<sub>3</sub> anions have only recently been reported,<sup>2</sup> but the methods of preparation described are not general. We report here a general, convenient synthetic route to ( $\eta^4$ -diene)Mn(CO)<sub>3</sub><sup>-</sup> complexes, including the parent complex ( $\eta^4$ -butadiene)Mn(CO)<sub>3</sub><sup>-</sup> (1), and selected reactions of these nucleophilic species with electrophiles.

The anionic diene complexes were prepared as shown in eq 1. Reduction of (methallyl)Mn(CO)<sub>4</sub> in THF with a 3.4 M solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (1 equiv) at 0 °C in the presence of 2 equiv of the diene or polyene leads to formation of the ( $\eta^4$ -diene)- (or ( $\eta^4$ -polyene)-) Mn(CO)<sub>3</sub><sup>-</sup>Na<sup>+</sup> complexes. Loss of CO and butene occurs; ( $\eta^2$ -butene)Mn(CO)<sub>4</sub><sup>-</sup> is a

likely intermediate but was not detected.



Scheme I shows the complexes formed from butadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cycloheptatriene, and cyclooctatetraene. IR spectra of the THF solutions<sup>3</sup> after hydride addition indicate clean conversion to the sodium salts 1a-5a; treatment of these solutions with PPN<sup>+</sup>Cl<sup>-</sup> results in conversion to the PPN<sup>+</sup> salts 1b-5b which can be precipitated (often as microcrystalline material) by addition of diethyl ether (yields based on C<sub>4</sub>H<sub>6</sub>Mn(CO)<sub>4</sub>: 1b (65%), 2b (70%), 3b (40%), 4b (35%), 5b (70%).<sup>4</sup>

All anionic complexes 1b-5b are cleanly protonated by HBF<sub>4</sub>-Me<sub>2</sub>O (-78 °C, CH<sub>2</sub>Cl<sub>2</sub>); weaker acids such as NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup> also suffice. Complex 1b yields the neutral butenyl species 6 (95%, orange oil) characterized by an agostic three-center, two-electron Mn-H-C interaction (*J*<sub>C-H</sub> = 89 Hz).<sup>5</sup> Complex 6 is stable to temperatures of 120 °C. Two degenerate modes of isomerization can be detected by variable-temperature NMR spectroscopy.<sup>6</sup> These two processes, together with measured  $\Delta G^\ddagger$ 's, are shown in Scheme I; both processes have close analogies.<sup>7</sup> The low-energy process involves "methyl" rotation and averaging of the agostic hydrogen with H<sub>1S</sub> and H<sub>1A</sub> while the high-energy process involves end-to-end averaging via the classical diene hydride. The latter process averages the H<sub>ag</sub>, H<sub>1S</sub>, H<sub>1A</sub> set with H<sub>4A</sub>, H<sub>5A</sub>; H<sub>3</sub> with H<sub>4</sub>; C<sub>1</sub> with C<sub>4</sub>; and C<sub>2</sub> with C<sub>3</sub>. Protonation of 2b and 3b yields the agostic species 7 and 8 which also display degenerate

(3) 1a-3a: IR ( $\nu_{\text{CO}}$ , THF) 1940 (s), 1840 (s), 1815 (s), 1785 (s) cm<sup>-1</sup>. 4a: IR ( $\nu_{\text{CO}}$ , THF) 1940 (s), 1845 (s), 1815 (s), 1790 (m) cm<sup>-1</sup>. 5a: IR ( $\nu_{\text{CO}}$ , THF) 1952 (s), 1865 (s), 1840 (s), 1790 (w) cm<sup>-1</sup>.

(4) Spectral properties of PPN<sup>+</sup> salts. 1b: IR ( $\nu_{\text{CO}}$ , THF) 1935 (s), 1838 (s), 1815 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -0.89 (d, *J* = 8 Hz, H<sub>1A,4A</sub>), 0.87 (d, *J* = 7 Hz, H<sub>1B,4B</sub>), 4.68 (m, H<sub>2,3</sub>), 7.3-7.8 (m, PPN<sup>+</sup>); <sup>13</sup>C NMR (THF-*d*<sub>6</sub>)  $\delta$  34.0 (td, *J* = 152, 6 Hz, C<sub>1,4</sub>), 78.9 (dd, *J* = 161, 9 Hz, C<sub>2,3</sub>), 130-140 (m, PPN<sup>+</sup>), 233.8 (s, CO<sup>'</sup>s). 2a: IR ( $\nu_{\text{CO}}$ , THF) 1935 (s), 1938 (s), 1815 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.0-1.3 (m, H<sub>5,6,7</sub>), 1.5-1.9 (m, H<sub>5,7</sub>), 2.19 (ddd, H<sub>1,4</sub>), 4.69 (m, H<sub>2,3</sub>), 7.3-7.8 (m, PPN<sup>+</sup>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  27.9 (t, *J* = 123 Hz, C<sub>6</sub>), 28.9 (t, *J* = 123 Hz, C<sub>5,7</sub>), 52.2 (d, *J* = 156 Hz, C<sub>1,4</sub>), 84.0 (d, *J* = 159 Hz, C<sub>2,3</sub>), 130-140 (m, PPN<sup>+</sup>), 232.7 (s, CO<sup>'</sup>s). 3b: IR ( $\nu_{\text{CO}}$ , THF) 1935 (s), 1838 (s), 1815 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.0-1.4 (m, H<sub>5,6,7,7a,7b</sub>), 1.88-2.1 (m, H<sub>5,5a,5b,8,8a,8b</sub>), 2.45 (m, H<sub>1,4</sub>), 4.75 (m, H<sub>2,3</sub>), 7.3-7.8 (m, PPN<sup>+</sup>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  26.6 (t, C<sub>6,7</sub>), 29.7 (t, C<sub>5,6</sub>), 54.7 (d, C<sub>1,4</sub>), 87.2 (d, C<sub>2,3</sub>), 130-140 (m, PPN<sup>+</sup>). 4b: IR ( $\nu_{\text{CO}}$ , THF) 1935 (s), 1840 (s), 1820 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  2.2 (m, H<sub>1,7,7a,1</sub>), 2.53 (m, H<sub>4</sub>), 4.5-4.9 (m, H<sub>2,3</sub>), 5.9 (m, H<sub>5</sub>), 7.3-7.8 (m, PPN<sup>+</sup>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  32.0 (t, *J* = 126.5 Hz, C<sub>7</sub>), 49.2 (d, *J* = 147 Hz, C<sub>1</sub>), 52.7 (d, *J* = 146 Hz, C<sub>4</sub>), 83.6 (d, *J* = 161 Hz, C<sub>2</sub>), 91.0 (d, *J* = 160 Hz, C<sub>3</sub>), 118.4 (d, *J* = 152 Hz, C<sub>6</sub>), 133.9 (C<sub>5</sub>), 130-140 (m, PPN<sup>+</sup>), 231.2 (s, CO<sup>'</sup>s). 5a: IR ( $\nu_{\text{CO}}$ , THF) 1950 (s), 1865 (s), 1840 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (THF-*d*<sub>6</sub>)  $\delta$  4.84 (s, H<sub>1-3</sub>), 7.3-7.8 (m, PPN<sup>+</sup>); <sup>13</sup>C NMR (THF-*d*<sub>6</sub>)  $\delta$  94.1 (d, *J* = 149.5 Hz, C<sub>1-3</sub>), 130-140 (m, PPN<sup>+</sup>), 232.1 (s, CO<sup>'</sup>s). Complex 5a is fluxional, and all ring hydrogens and ring carbons appear equivalent by NMR down to temperatures of -100 °C. This fluxional behavior is similar to the (C<sub>8</sub>H<sub>8</sub>)Fe(CO)<sub>3</sub> analogue: Kreiter, C. G.; Maasbol, A.; Anet, F. A. L.; Kaesz, H. D.; Winstein, S. *J. Am. Chem. Soc.* 1966, 88, 3444. Cotton, F. A.; Davison, A.; Faller, J. W. *Ibid.* 1966, 88, 4507. Keller, C. E.; Shaulders, B. A.; Pettit, R. *Ibid.* 1966, 88, 4760. Anet, F. A. L.; Kaesz, H. D.; Maasbol, A.; Winstein, S. *Ibid.* 1967, 89, 2489. Complexes 1b, 2b, 3b, and 5b are very air-sensitive in solution. The solids are only moderately air-sensitive and can be handled briefly in air. Complex 4b is thermally unstable and undergoes slow decomposition even at -10 °C both in solution and as a solid.

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(6) For spectroscopic characterization and analytical data see supplementary material.

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