

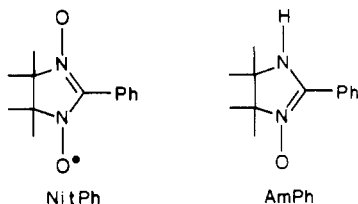
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### Dimeric Complex of a Reduced Nitroxyl Radical with Bis(hexafluoroacetylacetonato)manganese(II)

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The presence of di- and/or polynuclear manganese sites in enzyme systems has stimulated extensive recent interest in the chemistry of compounds containing two or more manganese ions.<sup>1</sup> Consequently, we are prompted to report the preparation and characterization of a dinuclear Mn(II) system obtained in low yield from the reaction of the nitronyl nitroxide NitPh with



bis(hexafluoroacetylacetonato)manganese(II) ( $\text{Mn}(\text{F}_6\text{acac})_2$ ).<sup>2</sup> The product, though not necessarily a model for any enzyme active site, is one of the simplest of the very few structurally characterized dimeric Mn(II)-Mn(II) species. An understanding of the structures and properties of these dinuclear systems will aid in interpreting the behavior of multinuclear manganese complexes.

#### Experimental Section

**Synthesis.** The starting materials  $\text{Mn}(\text{F}_6\text{acac})_2$ , NitPh, and AmPh were prepared by literature methods.<sup>3-5</sup> Solvents were dried prior to use and microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

In the reaction of NitPh with  $\text{Mn}(\text{F}_6\text{acac})_2$ , a mixture of 0.1 g of each reactant in 60 mL of heptane was refluxed for 15-20 min. After about 10 min, the solution developed a green color; with further heating it became brown-yellow. Cooling and/or evaporating yielded orange-yellow crystals, together with red and purple products that proved to be co-crystallized materials. Longer reflux times increased the proportion of dimer, and additional product was obtained when we attempted to re-crystallize either the purple product or a green material that was isolated after shorter reflux times.<sup>6</sup> A typical yield of dimer was 20%. Crystals of the dimer were slightly soluble in hydrocarbons, soluble in acetone and ethanol, and very soluble in chlorinated solvents. Mp (uncorrected): 201-202 °C; Anal. Calcd for  $\text{Mn}_2\text{C}_{46}\text{H}_{40}\text{F}_{24}\text{N}_4\text{O}_{10}$ : Mn, 8.0; C, 40.2; H, 2.9; N, 4.1. Found: Mn, 7.2; C, 40.4; H, 2.8; N, 4.4.

When AmPh was used in place of NitPh under the above conditions, the predominant product was the yellow bis adduct  $\text{Mn}(\text{F}_6\text{acac})_2$ - $(\text{AmPh})_2$ , which formed in 50% yield. Mp (uncorrected): 180 °C; Anal.

Table I. Crystallographic Data for  $[\text{Mn}(\text{F}_6\text{acac})_2\text{AmPh}]_2$

$\text{Mn}_2\text{C}_{46}\text{H}_{40}\text{F}_{24}\text{N}_4\text{O}_{10}$	fw = 1374.68
$a = 24.044$ (6) Å	space group: $C2/c$
$b = 13.688$ (3) Å	$T = 23$ °C
$c = 17.434$ (4) Å	$\rho_{\text{calcd}} = 1.593$ g cm <sup>-3</sup>
$\beta = 92.76$ (2)°	$\lambda(\text{Mo K}\alpha) = 0.71073$ Å
$V = 5731$ (2) Å <sup>3</sup>	$\mu = 5.50$ cm <sup>-1</sup>
$Z = 4$	$R(F_o) = 0.070$
	$R_w(F_o) = 0.095$

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors

atom	x	y	z	$U(\text{eq}), \text{Å}^2$
Mn	0.18056 (4)	0.22358 (8)	0.51292 (1)	46 (0.6)
O(1)	0.2379 (2)	0.2645 (3)	0.4267 (2)	45 (2)
O(2)	0.1087 (2)	0.2387 (4)	0.4336 (3)	58 (3)
O(3)	0.1476 (2)	0.3600 (3)	0.5536 (3)	58 (3)
O(4)	0.1748 (2)	0.0701 (4)	0.4821 (3)	62 (3)
O(5)	0.1323 (2)	0.1681 (4)	0.6056 (3)	78 (4)
N(1)	0.2209 (2)	0.2807 (4)	0.3519 (3)	47 (3)
N(2)	0.1759 (3)	0.3377 (5)	0.2514 (3)	72 (4)
C(1)	0.2329 (3)	0.2081 (6)	0.2892 (4)	63 (5)
C(2)	0.1916 (5)	0.2422 (8)	0.2262 (5)	102 (8)
C(3)	0.1906 (3)	0.3514 (5)	0.3259 (4)	52 (4)
C(4)	0.2917 (5)	0.2375 (11)	0.2617 (7)	141 (10)
C(5)	0.2379 (6)	0.1081 (8)	0.3159 (5)	137 (10)
C(6)	0.1982 (6)	0.2278 (10)	0.1464 (5)	130 (9)
C(7)	0.1356 (5)	0.1747 (11)	0.2428 (8)	150 (11)
C(8)	0.1736 (3)	0.4390 (5)	0.3678 (4)	59 (5)
C(9)	0.1225 (4)	0.4824 (7)	0.3489 (5)	78 (6)
C(10)	0.1076 (4)	0.5653 (8)	0.3837 (7)	93 (8)
C(11)	0.1417 (5)	0.6104 (8)	0.4367 (7)	110 (9)
C(12)	0.1926 (5)	0.5683 (7)	0.4571 (6)	97 (8)
C(13)	0.2082 (4)	0.4850 (6)	0.4215 (5)	74 (6)
C(14)	0.0638 (3)	0.2793 (6)	0.4488 (4)	56 (4)
C(15)	0.0544 (3)	0.3447 (6)	0.5061 (5)	62 (5)
C(16)	0.0979 (3)	0.3806 (5)	0.5529 (4)	58 (5)
C(17)	0.1361 (4)	0.0123 (6)	0.4974 (5)	69 (6)
C(18)	0.0985 (4)	0.0204 (7)	0.5529 (6)	83 (7)
C(19)	0.0991 (4)	0.0959 (8)	0.6039 (5)	81 (7)
C(20)	0.0150 (4)	0.2472 (8)	0.3972 (6)	82 (7)
C(21)	0.0836 (5)	0.4579 (8)	0.6136 (6)	93 (8)
C(22)	0.1321 (5)	-0.0775 (9)	0.4465 (7)	99 (9)
C(23)	0.0583 (6)	0.1060 (13)	0.6671 (9)	124 (11)
F(1)	-0.0343 (2)	0.2695 (6)	0.4222 (4)	141 (6)
F(2)	0.0148 (3)	0.2911 (7)	0.3316 (4)	167 (7)
F(3)	0.0140 (3)	0.1561 (6)	0.3824 (6)	196 (8)
F(4)	0.0367 (3)	0.5006 (6)	0.6013 (5)	190 (8)
F(5)	0.1198 (3)	0.5223 (6)	0.6266 (5)	163 (7)
F(6)	0.0782 (5)	0.4167 (7)	0.6788 (5)	206 (9)
F(7)	0.0942 (4)	-0.1380 (5)	0.4596 (5)	186 (8)
F(8)	0.1781 (4)	-0.1293 (6)	0.4527 (6)	193 (9)
F(9)	0.1272 (5)	-0.0584 (5)	0.3761 (4)	203 (9)
F(10)	0.0335 (6)	0.0267 (9)	0.6788 (8)	295 (15)
F(11)	0.0235 (5)	0.1657 (12)	0.6557 (7)	257 (14)
F(12)	0.0792 (5)	0.1262 (14)	0.7315 (6)	272 (13)

<sup>a</sup>  $U(\text{eq})$  = one-third of the trace of the orthogonalized U matrix ( $\times 10^3$ ).

Calcd for  $\text{Mn}_2\text{C}_{36}\text{H}_{38}\text{F}_{12}\text{N}_4\text{O}_6$ : Mn, 6.1; C, 47.8; H, 4.2; N, 6.2. Found: Mn, 6.0; C, 47.6; H, 4.4; N, 5.7.

**Crystal Structure.** All crystallographic data were collected on a Nicolet R3m/V diffractometer from a crystal fragment of dimensions 0.45  $\times$  0.40  $\times$  0.22 mm. General procedures used in the structure analysis have been described.<sup>7,8</sup> Crystallographic data are given in Table I; further details are included with the supplementary material. Refined unit cell parameters were based upon the setting angles of 25 reflections with  $25^\circ \leq 2\theta \leq 30^\circ$ . A total of 5461 intensity data with  $2\theta \leq 50^\circ$  were collected; of these, 2920 reflections with  $F_o^2 > 3\sigma(F_o^2)$  were used in the structure refinement. Solution of the structure was accomplished by a combination of direct and heavy-atom methods. Final least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in fixed, idealized positions. As is frequently

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- Abbreviations used:  $\text{F}_6\text{acac}$  = hexafluoroacetylacetonato; NitPh = 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide; AmPh = 2-phenyl-4,4,5,5-tetramethylimidazoline 3-oxide.
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- The initial green material we observe is presumably the previously reported cyclic hexamer: Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795-2799. The red and purple products were characterized independently in our laboratory and by Gatteschi et al., who will report full details of their preparation and characterization: Gatteschi, D. Personal Communication.

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Table III. Selected Bond Distances and Angles

(a) Distances (Å)			
Mn-O(1)	2.161 (4)	O(1)-N(1)	1.366 (6)
Mn-O(1)'	2.186 (4)	N(1)-C(1)	1.515 (8)
Mn-O(2)	2.171 (5)	C(1)-C(2)	1.518 (10)
Mn-O(3)	2.162 (5)	C(2)-N(2)	1.435 (11)
Mn-O(4)	2.171 (5)	N(2)-C(3)	1.343 (8)
Mn-O(5)	2.172 (5)	C(3)-N(1)	1.281 (8)
Mn...Mn'	3.465 (2)		
(b) Angles (deg)			
O(1)-Mn-O(1)'	74.3 (2)	O(2)-Mn-O(5)	94.0 (2)
O(1)-Mn-O(2)	92.7 (2)	O(3)-Mn-O(1)'	96.4 (2)
O(1)-Mn-O(3)	105.1 (2)	O(3)-Mn-O(4)	153.7 (2)
O(1)-Mn-O(4)	96.6 (2)	O(3)-Mn-O(5)	80.8 (2)
O(1)-Mn-O(5)	171.8 (2)	O(4)-Mn-O(1)'	103.7 (2)
O(2)-Mn-O(1)'	165.4 (2)	O(4)-Mn-O(5)	79.4 (2)
O(2)-Mn-O(3)	80.4 (2)	O(5)-Mn-O(1)'	99.6 (2)
O(2)-Mn-O(4)	84.0 (2)		
Mn-O(1)-Mn'	105.7 (2)	C(1)-N(1)-C(3)	111.4 (5)
Mn-O(1)-N(1)	122.3 (3)	N(1)-C(1)-C(2)	100.4 (6)
Mn'-O(1)-N(1)	131.9 (3)	C(1)-C(2)-N(2)	103.4 (6)
O(1)-N(1)-C(1)	121.6 (5)	C(2)-N(2)-C(3)	111.2 (6)
O(1)-N(1)-C(3)	126.8 (5)	N(2)-C(3)-N(1)	110.8 (6)

found in crystal structures of compounds containing  $\text{CF}_3$  groups, the fluorine thermal ellipsoids are large and highly anisotropic. Most of the large peaks on the final difference Fourier map were in the vicinity of the  $\text{CF}_3$  groups, but no convincing disorder model could be constructed. Anisotropy of the thermal ellipsoids of C(2) and N(2) indicates some conformational flexibility of the five-membered ring, again a common observation. These problems are presumably a major part of the reason for the somewhat high final  $R$  factors; however, they do not seriously compromise the chemically significant structure parameters. Computer programs utilized included a local version of the UCLA Crystallographic Computing Package,<sup>9</sup> MITHRIL,<sup>10</sup> and the graphics portions of the SHELXTL package.<sup>11</sup>

Final atomic parameters for the non-hydrogen atoms are listed in Table II, and selected bond distances and angles are tabulated in Table III. Full tables of all crystallographic results are included with the supplementary material.

**Magnetic Susceptibility Measurements.** Magnetic data were obtained for  $T = 2\text{--}300\text{ K}$  at 10 T by use of an SHE Corp. SQUID magnetometer located at the University of Southern California. Data were corrected for magnetization of the sample holder and for ligand diamagnetism, estimated from Pascal's constants. The observed susceptibilities were fit by least squares methods to the spin-only equation<sup>12</sup> for the magnetic susceptibility of an interacting pair of  $S = 5/2$  ions. A table of observed and calculated susceptibility values is included with the supplementary material.

## Results and Discussion

A view of the molecular structure of  $[\text{Mn}(\text{F}_6\text{acac})_2\text{AmPh}]_2$  is shown in Figure 1. The centrosymmetric structure is comprised of two *cis*- $\text{Mn}(\text{F}_6\text{acac})_2$  units doubly bridged by oxygen atoms of the AmPh ligands. The core of the molecule may thus be regarded as derived from two distorted  $\text{MnO}_6$  octahedra sharing a common edge. The angular distortions from ideal octahedral symmetry are substantial; however, the Mn-O distances span only the small range 2.161 (4)–2.186 (4) Å. These are typical bond distance values for six-coordinate Mn(II). The Mn-Mn distance is 3.465 (2) Å.

In the course of the formation of the dimeric product, the nitronyl nitroxyl NitPh has undergone deoxygenation and reduction to the amidine oxide AmPh. There is precedent for these reactions for the free ligand under a variety of conditions.<sup>5</sup> The AmPh ligand could, in principle, exist in two tautomeric forms,

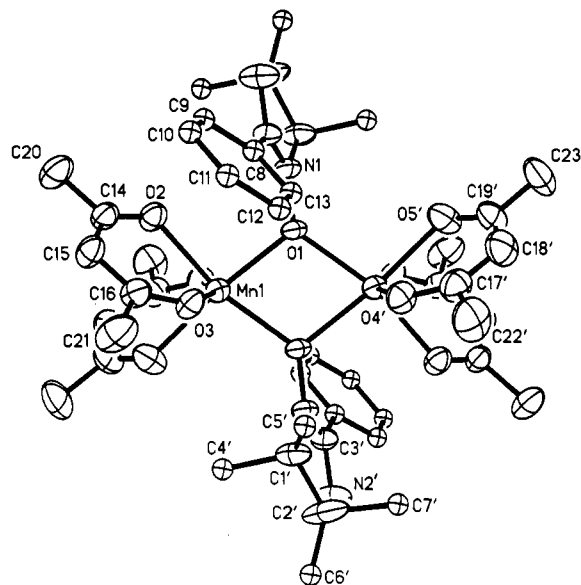


Figure 1. Perspective view of the molecular structure. Primes denote atoms related to their counterparts in the asymmetric unit by the crystallographic center of symmetry. For clarity, fluorine atoms have been omitted and carbon atoms of the methyl and phenyl substituents on the AmPh ligand have been given artificially small isotropic thermal parameters.

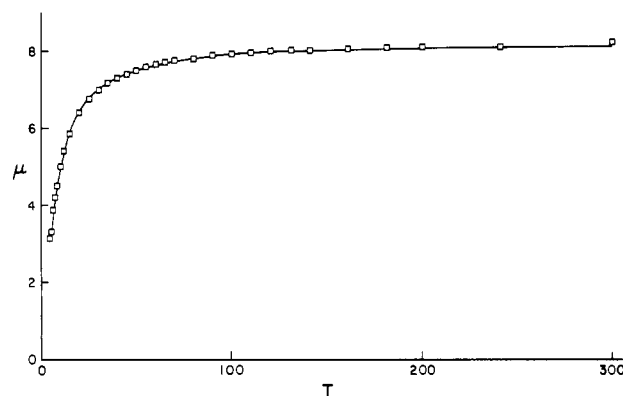


Figure 2. Plot of effective magnetic moment vs  $T$ . The solid line represents values calculated from the best fit parameters  $g = 1.97$  and  $J = -1.99\text{ cm}^{-1}$ .

with protonation either at O(1) or at N(2). The ligand geometry suggests protonation at N(2); examination of a final difference Fourier map showed a residual peak at the expected position (0.90 Å from N; bond angles of 116 and 125°) near N(2). This peak was more prominent on difference maps with smaller  $(\sin \theta)/\lambda$  cutoffs, though larger peaks around the  $\text{CF}_3$  groups precluded definitive assignment of this feature. The overall picture, however, is consistent. Other details of the ligand structure are as expected; in particular, the N(1)-O(1) distance of 1.366 (6) Å and the stereochemistry about N(1) are characteristic of a reduced species rather than a nitroxyl radical. Coordination of reduced nitroxyls has previously been observed in two Pd(II) complexes.<sup>13,14</sup>

The pathway of the ligand reduction has not been established, but it is probably not a simple process. Other species are present in the reaction mixture and the dimer is obtained only in low yields. When the reduced ligand AmPh is allowed to react with  $\text{Mn}(\text{F}_6\text{acac})_2$  under similar conditions, the predominant product is the mononuclear bis adduct  $\text{Mn}(\text{F}_6\text{acac})_2(\text{AmPh})_2$ .

The magnetic susceptibility data (Figure 2) are readily interpreted on the basis of a weakly interacting pair of high-spin  $\text{Mn}^{2+}$  ions. The  $\chi_m$  vs  $T$  curve shows a maximum at approximately 7

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K, indicative of weak antiferromagnetic coupling. A least-squares fit of the data for  $T = 4-300$  K to the spin-only expression for two  $S = 5/2$  ions<sup>12</sup> yields best fit parameters  $g = 1.97$  and  $J = -1.99$  cm<sup>-1</sup>. These values yield a mean discrepancy of 1.4% between observed and calculated  $\chi$  values. The  $J$  value is very close to that previously reported for an O-bridged Mn(II) dimer with a Schiff base ligand.<sup>15</sup> The core of this latter dimer has a shorter Mn-Mn distance (3.300 vs 3.465 (2) Å) and corresponding smaller bridging Mn-O-Mn angles (101.2 (1) and 101.3 (1) vs 105.7 (2)°) than those we observe. Clearly, the small  $J$  values in these systems are not highly sensitive to variations in bridging geometry.

Only a few other structurally characterized examples of O-bridged Mn(II)-Mn(II) dimers exist. In the Schiff-base complex mentioned above, the bridging atoms are part of a larger chelating ligand. As in the present case, the Mn atoms are six-coordinate, but a number of the structure parameters differ significantly from those we observe.<sup>15</sup> A dinuclear O-bridged system in which the Mn(II) ions have a tetrahedral coordination geometry and are somewhat more strongly coupled ( $J = -5.0$  cm<sup>-1</sup>) than in the two six-coordinate dimers has recently been reported.<sup>16</sup> A bridging arrangement similar to that we observe is found in a polymeric Mn(II) complex derived from a substituted picolinic acid, but no magnetic data have been reported for this system.<sup>17</sup>

**Acknowledgment.** The X-ray diffractometer and the MicroVAX II computer were purchased with the assistance of NSF Grant CHE-85-14495. The SQUID magnetometer at the University of Southern California was also purchased with the aid of an NSF grant. We also thank Deborah Glover, an NSF-REU program participant, for experimental assistance.

**Supplementary Material Available:** Experimental details of the crystallographic study and listings of anisotropic temperature factors, hydrogen atomic positional parameters, bond distances, bond angles, and observed and calculated magnetic susceptibilities (9 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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**"Electron-Deficient" Trigonal-Planar Tin- and Lead-Containing Iron Carbonyl Complexes: [Et<sub>4</sub>N]<sub>2</sub>[E{Fe(CO)<sub>4</sub>]<sub>3</sub>] (E = Sn, Pb)**

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Three-coordinate lead and tin complexes are rare. When the group IV atom is bonded to nonmetallic elements, pyramidal compounds are formed, among which are [Li(THF)<sub>2</sub>][E(PBu<sup>t</sup>)<sub>3</sub>] (E = Sn, Pb; THF = tetrahydrofuran)<sup>1</sup> and E[η<sup>1</sup>-CH-(PPh<sub>2</sub>)<sub>2</sub>][η<sup>2</sup>-CH(PPh<sub>2</sub>)<sub>2</sub>] (E = Sn, Pb).<sup>2</sup> Planar arrays have been observed for Ge(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>(=C[C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>)<sub>3</sub><sup>3</sup> and metalated lead and tin atoms. Not long ago it was believed that the metalated species

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**Table I.** Crystal, Data Collection, and Refinement Parameters for 1 and 2

empirical formula	C <sub>28</sub> H <sub>40</sub> Fe <sub>3</sub> O <sub>12</sub> N <sub>2</sub> Pb (2)	C <sub>28</sub> H <sub>40</sub> Fe <sub>3</sub> O <sub>12</sub> N <sub>2</sub> Sn (1)
fw	971.37	882.86
space group	P2 <sub>1</sub> /c (No. 14)	
λ, Å	0.710 69	
temp, °C	23	
lattice params		
a, Å	10.959 (2)	10.910 (4)
b, Å	40.60 (1)	40.45 (1)
c, Å	17.455 (4)	17.461 (5)
β, deg	97.99 (2)	98.00 (2)
V, Å <sup>3</sup>	7692 (4)	7630 (4)
Z	8	
D <sub>calc</sub> , g·cm <sup>-3</sup>	1.68	1.54
μ(Mo Kα), cm <sup>-1</sup>	54.94	18.21
transmission coeff	0.4075-1.0000	0.7912-1.0000
residuals: R; R <sub>w</sub>	0.065; 0.078	0.059; 0.071

were only isolable as four-coordinate solvent-stabilized products,<sup>4</sup> but more recently several planar three-coordinate complexes have been structurally characterized, all showing evidence for a localized π-interaction between the group 14 element and a transition metal. Examples of this type of structure include [(μ<sub>3</sub>-E){W(CO)<sub>5</sub>]<sub>3</sub>] (E = Ge, Sn),<sup>5</sup> [(μ<sub>3</sub>-E){(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Mn(CO)<sub>2</sub>]<sub>3</sub>] (E = Ge,<sup>6</sup> Sn,<sup>7</sup> Pb<sup>8</sup>), [R<sub>3</sub>SnM(CO)<sub>5</sub>] (R = C<sub>2</sub>H<sub>5</sub>, M = Cr, Mo, W; R = MeC<sub>2</sub>H<sub>5</sub>, M = Cr, W),<sup>9</sup> and [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>EM(CO)<sub>5</sub> (E = Sn, M = Cr, Mo, W; E = Pb, M = Mo).<sup>10</sup> Lead also adopts a trigonal-planar coordination environment in the polymeric solid-state structure of Cp<sub>2</sub>Pb.<sup>11</sup> We wish to report here the X-ray analyses of [Et<sub>4</sub>N]<sub>2</sub>[E{Fe(CO)<sub>4</sub>]<sub>3</sub>] (E = Sn (1), Pb (2)), trigonal-planar main-group/transition-metal compounds.

**Experimental Section**

Compounds 1 and 2 were prepared simply by addition of SnCl<sub>2</sub> or PbCl<sub>2</sub> to Fe(CO)<sub>5</sub> dissolved in KOH/MeOH or from the reaction of [Et<sub>4</sub>N]<sub>2</sub>[EFe<sub>3</sub>(CO)<sub>16</sub>] with CO as previously described.<sup>12,13</sup> Ir (ν<sub>CO</sub> in cm<sup>-1</sup>; CH<sub>2</sub>Cl<sub>2</sub>): 1, 2021 w, 2002 w, 1977 s, 1904 s; 2, 1973 s, 1895 s. The products are sparingly soluble in dichloromethane and methanol but insoluble in water, hexane, and diethyl ether.

**X-ray Structural Analyses.** X-ray-quality red, needlelike crystals of 1 (0.10 × 0.10 × 0.30 mm<sup>3</sup>) were grown from a concentrated methanol solution, while black, needlelike crystals of 2 (0.50 × 0.20 × 0.20 mm<sup>3</sup>) were obtained by cooling a concentrated methanol solution containing 2,2'-bipyridine and water. The data collection and refinement parameters for 1 and 2 are given in Table I. Reflections were collected for octants +h,+k,±l for both 1 and 2. For 1, 10 500 reflections were measured, of which 9869 were independent and 4007 were observed ( $I > 3.00$  (σ(I))). For 2, 10 741 reflections were measured, with 10 119 independent and 4343 observed reflections. Data were corrected for absorption and Lorentz/polarization effects. The analytical form of the scattering factors for the appropriate neutral atoms was corrected for both the real (Δf') and imaginary (iΔf'') components of anomalous dispersion.<sup>14</sup> All programs employed were part of the Molecular Structure Corp. data reduction and refinement programs (TEXSAN, version 2.0). Heavy-atom positions were determined by the program Mithril<sup>15</sup> and subsequent

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