

Figure 1. Phosphotriester method of deoxyoligonucleotide synthesis.

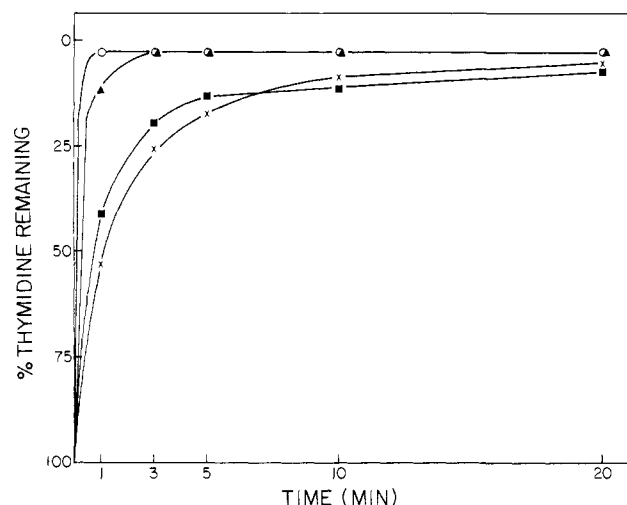


Figure 2. Relative reactivities of 3'-phosphate phenyl diesters of 5'-(dimethoxytrityl)thymidine: (A) (O) 50 mM *o*-(1-methylimidazolyl) (1c), (B), (▲) 5 mM *o*-(1-methylimidazolyl) (1c), (C) (■) 50 mM *p*-(1-methylimidazolyl) (1d), (D), (×) 50 mM *p*-chloro (1b).

1-Methyl-2-(2-hydroxyphenyl)imidazole was synthesized from methyl salicylate (Aldrich) and *N*-methylethylenediamine (Aldrich).<sup>8</sup> The corresponding 3'-phosphate phenyl diester of 5'-(dimethoxytrityl)thymidine (1c, Figure 1) was initially synthesized as a 2,4-dichlorophenyl triester<sup>9</sup> which was then hydrolyzed to the diester (concentrated  $\text{NH}_4\text{OH}$ /dioxane, 1/1, 60 °C, 12 h). The product diester was purified on silica gel ( $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ , 9/1, v/v) then converted to the triethylammonium salt by evaporation from 5%  $\text{Et}_3\text{N}/\text{CH}_3\text{CN}$  and washing of a  $\text{CH}_2\text{Cl}_2$  solution of this salt with 0.1 M aqueous triethylammonium bicarbonate (pH 8.5).

Relative reactivities of the different diesters toward an immobilized nucleoside 5'-hydroxyl were measured by reaction of diester (0.05 or 0.005 M), mesitylenesulfonyl chloride (0.15 M) and 1-methylimidazole (0.45 M) in pyridine with silica gel bearing a 3'-ester linked thymidine (2, Figure 1). The polymer support was loaded to approximately 30  $\mu\text{mol}$  of thymidine per g of silica gel,<sup>10</sup> and a large excess (100 equiv) of the diester was used relative to immobilized thymidine. Reactions were quenched at various times with  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9/1, v/v), and the dimethoxytrityl group was removed (0.1 M *p*-TSA/ $\text{CH}_3\text{CN}$ ).<sup>10</sup> After extensive washings and 2 h concentrated  $\text{NH}_4\text{OH}$  cleavage of the product from the silica gel, unreacted starting thymidine was quantitated by reverse-phase HPLC. A comparison of curves A and D in Figure 2 demonstrates that 1-methyl-2-(2-hydroxyphenyl)imidazole diester (1c, Figure 1) is significantly more reactive than

the known *p*-chlorophenyl derivative (1b, Figure 1). When the experiment is repeated using 5 mM 1-methyl-2-(2-hydroxyphenyl)imidazole diester (curve B, Figure 2) a rate increase of approximately 5-10-fold over 50 mM *p*-chlorophenyl diester (curve D, Figure 2) is observed.

Omission of 1-methylimidazole from the above condensation reaction results in a large decrease (90-fold) in rate of diester coupling with the *p*-chlorophenyl diester (1b, Figure 1), while a negligible effect is observed with the catalytic protecting group diester (1c, Figure 1) (data not shown). Curve C in Figure 2 demonstrates that 1-methyl-2-(4-hydroxyphenyl)imidazole diester (1d, Figure 1) shows no rate enhancement over the *p*-chlorophenyl diester. This diester has the 1-methylimidazolyl moiety positioned para to the phosphate, thereby precluding neighboring-group participation. These results strongly suggest the rate enhancement in curves A and B (Figure 2) is due to the ortho positioning of 1-methylimidazole and its participation in the rate-limiting step.

1-Methyl-2-(2-hydroxyphenyl)imidazole protecting group is removed from a phosphate triester by treatment with concentrated ammonium hydroxide (12 h, 60 °C) or by treatment with tetramethylguanidinium 2-pyridinedoximate in dioxane/water (12 h, 60 °C).<sup>11</sup> The potential synthetic utility of this protecting group for the rapid synthesis of deoxyoligonucleotides was assessed by the synthesis of pentadecathymidylic acid ( $\text{T}_{15}$ ) using short condensation times (5 min). HPLC analysis of the fully deprotected crude products confirmed a high-yield synthesis of  $\text{T}_{15}$ . This result and those shown above clearly demonstrate that catalytic protecting groups can effect a dramatic improvement of phosphorylation kinetics in the chemical synthesis of deoxyoligonucleotides.

**Acknowledgment.** We thank Dr. Bob Lazarus for helpful discussions and Peter Ng for technical assistance.

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## A Novel Metal-Metal Bonded Iridium(II) Dimer

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As part of an investigation of the ligand tetracyanobidimidazole ( $\text{H}_2\text{Tcbiim}$ )<sup>1</sup> we report the synthesis and structure of a novel dimer of iridium(II) containing the first example of an iridium-iridium bond without bridging ligands. Although such dimers are well-known in rhodium chemistry<sup>2</sup> the number of iridium(II) dimers previously reported is very small, and all have bridging ligands.<sup>3</sup>

The precursors to the iridium(II) dimer are salts of general formula  $\text{M}[\text{Ir}(\text{CO})_2\text{Tcbiim}]$  which have planar anions. The colors of the solids vary with the cation, e.g., when  $\text{M}' = \text{N}(\text{Et})_4^+$ , red,  $\text{N}(\text{Me})_4^+$ , green, and  $\text{C}(\text{NH}_2)_3^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ , blue-black. In dilute solutions of acetonitrile all the salts are yellow, implicating an intermolecular association. We have studied this by the methods of charge-transfer spectroscopy and find  $\Delta H = -27$  kJ/mol and

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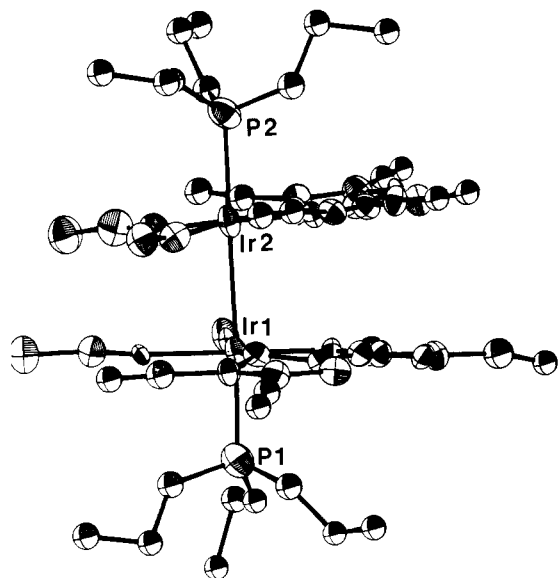


Figure 1.

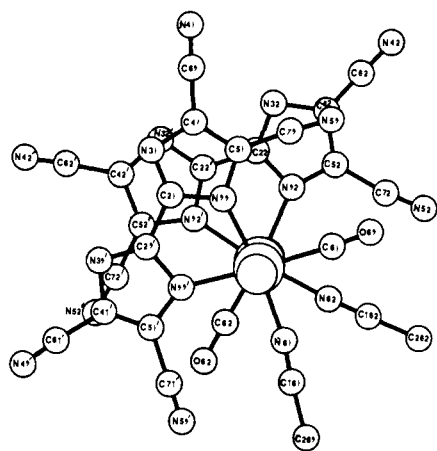


Figure 2.

$K = 10 \text{ M}^{-1}$  for the formation of an iridium(I) dimer in solution. This dimer absorbs at 472 nm with an extinction coefficient  $\epsilon = 15000 \text{ M}^{-1} \text{ cm}^{-1}$ , and there are also bands due to higher degrees of oligomerization. These results suggested tendencies toward extended stack formation which were confirmed by solving the X-ray crystal structure of  $\text{N}(\text{Et})_4[\text{Ir}(\text{CO})_2\text{Tcbiim}]$ .<sup>4</sup> Similar association oligomers are known in rhodium and platinum chemistry.<sup>5</sup>

The Ir(II) dimer  $\text{Ir}_2(\text{Tcbiim})_2(\text{CO})_4(\text{CH}_3\text{CN})_2$ <sup>6</sup> precipitates during the electrolysis of an acetonitrile solution of the Ir(I) precursor at a platinum anode, in the absence of other electrolyte. The structure of this dimer is not known, but the low solubility suggests some type of intermolecular interaction. If triethyl phosphite is added to a suspension of this compound in acetonitrile, a solution forms. On cooling, crystals form of an Ir(II) compound containing triethyl phosphite.

The crystal structure of  $\text{Ir}_2(\text{Tcbiim})_2(\text{CO})_2(\text{CH}_3\text{CN})_2[\text{P}(\text{OEt})_3]_2\text{CH}_3\text{CN}$ , which has the composition  $\text{Ir}_2\text{C}_{40}\text{N}_{19}\text{H}_{39}\text{O}_8\text{P}_2$ , was solved in the orthorhombic space group  $P2_12_12_1$  with  $a = 14.26 \text{ \AA}$ ,  $b = 17.14 \text{ \AA}$ ,  $c = 21.55 \text{ \AA}$ , and  $Z = 4$ . A final agreement of  $R = 5.5\%$  and  $R_w = 4.6\%$  was obtained for 2106 observed reflections. The ORTEP view of the dimer without the solvent of

Table I. Bond Angles and Bond Distances

| Bond Angles    |            |              |            |
|----------------|------------|--------------|------------|
| N11-Ir1-N11'   | 78.5 (9)   | N12-Ir2-N12' | 77.1 (9)   |
| N11-Ir1-P1     | 90.7 (7)   | N12-Ir2-P2   | 88.9 (7)   |
| N11'-Ir1-P1    | 87.2 (7)   | N12'-Ir2-P2  | 84.6 (7)   |
| N11-Ir1-C81    | 96 (1)     | N12-Ir2-C82  | 98 (1)     |
| P1-Ir1-C81     | 100 (1)    | P2-Ir2-C82   | 99 (1)     |
| N11'-Ir1-N61   | 95.8 (9)   | N12'-Ir2-N62 | 95 (1)     |
| P1-Ir1-N61     | 88.8 (7)   | P2-Ir2-N62   | 92.0 (9)   |
| C81-Ir1-N61    | 89 (1)     | C82-Ir2-N62  | 90 (1)     |
| P1-Ir1-Ir2     | 176.8 (3)  | P2-Ir2-Ir1   | 179.0 (3)  |
| Bond Distances |            |              |            |
| Ir1-Ir2        | 2.826 (02) | Ir2-N12      | 2.061 (22) |
| Ir1-N11        | 2.030 (23) | Ir2-N12'     | 2.081 (22) |
| Ir1-N11'       | 2.145 (23) | Ir2-P2       | 2.343 (12) |
| Ir1-P1         | 2.341 (11) | Ir2-C82      | 1.981 (31) |
| Ir1-C81        | 1.830 (29) | Ir2-N62      | 2.022 (26) |
| Ir1-N61        | 2.067 (23) |              |            |

crystallization is shown in Figure 1; a view down the metal-metal axis is shown in Figure 2. Selected values of interatomic distances and angles are given in Table I.

The molecular unit has two chiral metal centers. Our structure is of one of the enantiomers of the chiral diastereoisomer. The geometry about the Ir(II) centers is distorted octahedral. The Ir centers are very similar, but small differences are observed. The bond angles and bond distances for the Ir-Tcbiim<sup>2-</sup> unit compare well with previous structures.<sup>4,7</sup> The bond axis, defined as P1-Ir1-Ir2-P2, is slightly bent, as shown by the P1-Ir1-Ir2 bond angle of 177° and the P2-Ir2-Ir1 bond angle of 179°. The Ir, Tcbiim<sup>2-</sup>, CO, and CCN of the coordinated acetonitrile form an approximate plane for each Ir unit, the largest perpendicular distance from planarity is less than 0.35 Å. The twist angle between the two planes containing the bond axis CO(1) and the bond axis and CO(2) is 44.4°. The Ir-Tcbiim planes bend away from each other with a dihedral angle of 9.6°, relieving the strain imposed by the metal-metal bond.

The iridium-iridium distance of 2.83 Å is a full 0.3 Å shorter than that found in the association dimer of Ir(I). The disposition of ligands about the metals does not suggest any  $\delta$  bonding as has sometimes been suggested in rhodium isonitrile complexes where eclipsed geometries are observed even when ligand structure does not demand it.<sup>2</sup> It is likely that the  $\pi$  accepting properties of Tcbiim<sup>2-</sup> play an important role in stabilizing this dimer, a point we will pursue elsewhere. The Ir-Ir distance is in the range of reported bridged Ir(II) dimers of 2.6 Å<sup>8,9</sup> up to 2.83 Å.<sup>10</sup>

The UV-vis spectrum of the triethyl phosphite adduct has three bands, at 342 ( $\epsilon = 30000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 275 ( $\epsilon = 48000 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 225 nm ( $\epsilon = 55000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The tail of the band at 342 nm falls into the visible range, accounting for the pale yellow color.

The observation of planar stacked iridium(I) species<sup>4</sup> suggested the possibility of an oxidized stack. The dimers reported here confirm that possibility and show that a planar Ir(Tcbiim)<sub>2</sub> unit can be maintained even with full oxidation to Ir(II) as the metal-metal bond order increases to unity. The likely stability of intermediate oxidation, if Coulombic balance of the stack changes can be controlled, is evident. We will describe that situation in a separate report.

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**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes, fractional atomic coordinates, and thermal parameters (13 pages). Ordering information is given on any current masthead page.

**Interconversion of Tetrahedral and  $\Pi$ -CO Containing Butterfly Clusters:**  $[\text{Fe}_4(\text{MPR}_3)(\text{CO})_{12}(\eta^2\text{-CO})]^- \rightleftharpoons [\text{Fe}_4(\text{MPR}_3)(\text{CO})_{13}]^-$  ( $\text{M} = \text{Au}$ ,  $\text{R} = \text{Et}$ ;  $\text{M} = \text{Cu}$ ,  $\text{R} = \text{Ph}$ ) and  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\eta^2\text{-COMe})$

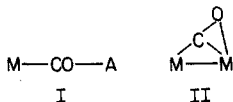
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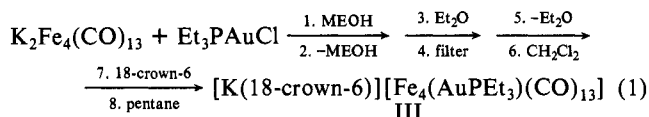
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The interaction of both C and O of a carbon monoxide molecule is known to facilitate a wide range of CO chemistry, such as CO insertion and CO cleavage.<sup>2</sup> Systematic routes are available for the synthesis of  $\Sigma$ -CO complexes I; however, the designed synthesis of  $\Pi$ -CO complexes II containing three<sup>3</sup> or more<sup>4-10</sup> metal

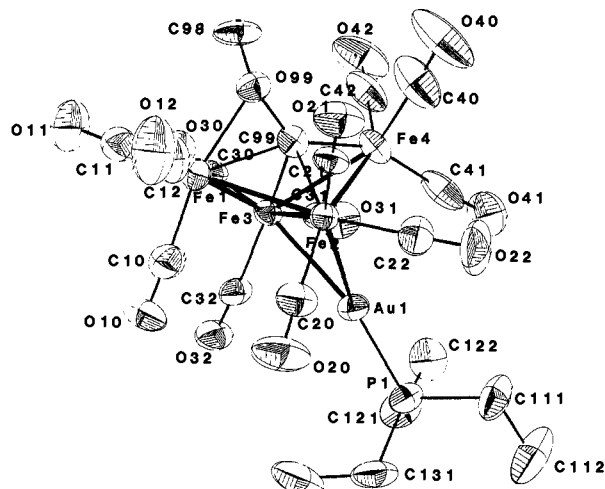


atoms has not been achieved. Previously, we attempted to induce  $\Pi$ -CO formation via the synthesis of highly crowded tetrahedral metal clusters, but the strain energy was relieved by a distortion of the clusters which did not yield a  $\Pi$ -CO.<sup>11</sup> In the present report we describe a systematic route to new  $\Pi$ -CO compounds,  $[\text{K}(18\text{-crown-6})][\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{13}]$  (III),  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COMe})$  (IV), and their relation to some copper analogues.

Complex III was prepared according to eq 1.<sup>12</sup> Dissolution



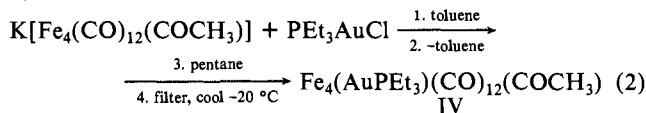
of the solid at  $-78^\circ\text{C}$  followed by  $^{13}\text{C}$  NMR spectroscopy at this temperature yields a spectrum which has seven peaks in the terminal CO region ( $\delta$  224.0–212.4) as well as a downfield resonance at 284.6 ppm.<sup>13</sup> The intensity pattern and peak positions



**Figure 1.** ORTEP diagram of  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COCH}_3)$  showing thermal ellipsoids at the 50% probability level. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{C99-Fe1} = 2.14$  (2),  $\text{C99-Fe4} = 1.86$  (2),  $\text{C99-O99} = 1.37$  (2),  $\text{O99-Fe1} = 2.029$  (9),  $\text{Au1-Fe2} = 2.666$  (2),  $\text{Au1-Fe3} = 2.675$  (3) [ $\text{Fe-Fe}$  bonding distances range 2.606 (3)–2.687 (4)];  $\text{C99-O99-C98} = 119$  ( $2^\circ$ ).

are similar to those for the butterfly form of  $[\text{HFe}_4(\text{CO})_{13}]^-$ .<sup>14</sup> Warming the solution to room temperature and then recooling to  $-80^\circ\text{C}$  affords a  $^{13}\text{C}$  NMR spectrum in which an additional resonance is at 222.4 ppm. The  $^{31}\text{P}$  NMR spectrum of solutions which were prepared and run at  $-80^\circ\text{C}$  has two resonances at  $\delta$  62.5 and 57.7 (positive values are downfield of external  $\text{H}_3\text{PO}_4$ ) in the intensity ratio 1:14. The downfield resonance gains intensity as the solution is warmed to room temperature and dominates the spectrum (10:1) when the solution is recooled to  $-80^\circ\text{C}$ . Thus, as in the case of  $[\text{HFe}_4(\text{CO})_{13}]^-$ , there are two isomers of this cluster in solution: a  $\text{Fe}_4$  butterfly with a  $\Pi$ -CO<sup>4</sup> and a  $\text{Fe}_4$  tetrahedron containing only conventional C-bonded carbonyls.<sup>14,15</sup> Formation of a  $\Pi$ -CO in the crystalline state is also indicated by the appearance of a low-frequency CO stretch,  $1412\text{ cm}^{-1}$ , in the IR spectrum of the solid. The vibrational frequency of the  $\Pi$ -CO in the  $[\text{PPN}]^+$  and  $\text{K}^+$  salts of  $[\text{HFe}_4(\text{CO})_{13}]^-$  occurs at 1415 and  $1382\text{ cm}^{-1}$ , respectively.<sup>16</sup>

Preparation of  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COCH}_3)$  (IV) is achieved by reaction 2. Both the IR and low-temperature  $^{13}\text{C}$  NMR



spectra<sup>17</sup> ( $-78^\circ\text{C}$ ) are similar to those for  $\text{HFe}_4(\text{CO})_{12}(\text{COCH}_3)$ <sup>18</sup> (V), suggesting similar structures.<sup>10</sup> Figure 1 depicts the result of the single-crystal X-ray structure determination for compound IV.<sup>19</sup> As with its protonated analogue, IV provides an example of a CO ligand formally acting as an overall six-electron donor ( $4e^-$  to the cluster framework and  $2e^-$  to the  $\text{CH}_3^+$  group). Only one resonance in the  $^{31}\text{P}$  NMR spectrum is observed,  $-80$  to  $+20$

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(13) IR ( $\text{CH}_2\text{Cl}_2$ ) 2038 (m), 2004 (m, sh), 1972 (vs), 1920 (br, sh)  $\text{cm}^{-1}$ .

$^{13}\text{C}$  NMR (22.49 MHz,  $(\text{CD}_3)_2\text{CO}$ , external  $\text{Me}_4\text{Si}$ ),  $-80^\circ\text{C}$   $\delta$  284.6 ( $\Pi$ -CO), 224.0, 223.1, 220.6, 217.8, 216.1, 213.5, 212.1 ( $I = 1:2:1:2:1:2:2:2$ ); 18-crown-6,  $\delta$  70.5;  $\text{PCH}_2\text{CH}_3$ ,  $\delta$  19.4 (d,  $J_{\text{PC}} = 29.3$  Hz);  $\text{PCH}_2\text{CH}_3$ ,  $\delta$  8.8. Anal. Calcd (Found) for  $\text{C}_{31}\text{H}_{39}\text{PF}_4\text{O}_9\text{K Au}$ : Fe, 18.53 (15.06); Au, 16.34 (17.09).

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(15) Initial observation of the absorption in the  $^{31}\text{P}$  NMR due to the tetrahedral form at  $-78^\circ\text{C}$  might be precluded at lower temperatures.

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(17) IR ( $\text{CH}_2\text{Cl}_2$ ) 2072 (w), 2048 (sh), 2037 (vs), 2011 (vs), 1988 (br, m), 1920 (vw)  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR (22.49 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ,  $-80^\circ\text{C}$ )  $\delta$  304.5 (COC-H<sub>3</sub>), 219.7, 216.8, 214.8, 213.2, 213.0, 212.0, 208.5, 207.6 ( $I = 1:2:2:1:1:1:1:2:2$ );  $^{31}\text{P}$  NMR (36.19 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  58.1. Anal. Calcd (Found) for  $\text{C}_{20}\text{H}_{18}\text{Fe}_4\text{AuO}_{13}\text{P}$ : Fe, 24.34 (24.38); Au, 21.46 (28.55).

(18) IR (hexane) 2085 (vw), 2046 (vs), 2020 (s), 1998 (s), 1990 (m), 1890 (s)  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR (90 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-90^\circ\text{C}$ )  $\delta$  301 (COC-H<sub>3</sub>).

(19) Crystal data for  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COCH}_3)$ :  $a = 14.764$  (3)  $\text{\AA}$ ,  $b = 9.574$  (1)  $\text{\AA}$ ,  $c = 11.094$  (2)  $\text{\AA}$ ,  $\alpha = 87.26$  ( $1^\circ$ ),  $\beta = 82.33$  ( $2^\circ$ ),  $\gamma = 112.13$  ( $1^\circ$ ),  $Z = 2$ ,  $d_{\text{calcd}} = 2.129\text{ g cm}^{-3}$ , space group  $P\bar{1}$ ,  $R_w = 0.067$ .