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**Supplementary Material Available:** Tables of positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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## (Carbonylbis((dialkylamino)phosphido))hexacarbonyldiiron Complexes: Migration of a Carbonyl Group from Iron to Phosphorus

*Sir:*

The chemistry of $Fe_2(CO)_6$ complexes includes derivatives in which a carbonyl group bridges two nitrogen atoms (e.g. $(RNCONR)Fe_2(CO)_6$, R = $C_6H_5$[1,2] and $CH_3$[3]) or two sulfur atoms (e.g. $S_2COFe_2(CO)_6$).[4] This communication describes the first $Fe_2(CO)_6$ complex in which a carbonyl group bridges two phosphorus atoms. Of particular interest is the apparent origin of this phosphorus-bridging carbonyl from a terminal carbonyl group bonded to iron. Such carbonyl migration from iron to phosphorus suggests that phosphido bridges might play an active role in metal carbonyl systems for the catalytic reduction of carbon monoxide.

A suspension of $Na_2Fe(CO)_4 \cdot 1.5$(dioxane)[5] in diethyl ether was treated at −78 °C with a stoichiometric amount of (diisopropylamino)dichlorophosphine.[6] After the mixture was stirred for 3 days at room temperature, solvent was removed under reduced pressure. The residue was extracted with *n*-hexane in several portions until the extracts were no longer colored. Concentrating and cooling the filtered *n*-hexane extracts gave orange air-stable crystalline $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (Table I) in 35% yield. Analogous reactions of $Na_2Fe(CO)_4 \cdot 1.5$(dioxane) with (dicyclohexylamino)dichlorophosphine[6] and (2,2,6,6-tetramethylpiperidino)dichlorophosphine[6] gave analogous $(R_2NP)_2COFe_2(CO)_6$ derivatives (Table I). However, analogous reactions of $Na_2Fe(CO)_4 \cdot 1.5$(dioxane) with significantly less sterically hindered (dialkylamino)dichlorophosphines did *not* give analogous $(R_2NP)_2COFe_2(CO)_6$ compounds; the products from such reactions are still under investigation.

Bridging carbonyl groups in these $(R_2NP)_2COFe_2(CO)_6$ derivatives are indicated by single $\nu$(CO) frequencies in the range 1715–1721 $cm^{-1}$. In order to determine the configuration of the carbonyl groups in these complexes as well as other important features of their structures, the structure of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ was determined by X-ray diffraction;[7] see Figure 1. The most significant feature of this structure is the carbonyl group (C1–O1 in Figure 1) bridging the two phosphorus atoms (P1–C1 = 1.884 (9) Å, P2–C1 = 1.895 (10) Å, P1–C1–P2 = 84.4 (4)°). The bonding Fe–Fe distance of 2.603 (2) Å is significantly longer than the Fe–Fe distance of 2.488 (1) Å reported[4] for the closely related $S_2COFe_2(CO)_6$ but is close to the 2.62–2.67 Å range found for bis($\mu$-phosphido)diiron hexacarbonyl complexes[8] (e.g. 2.623 (2) Å reported[9] for $(Ph_2P)_2Fe_2(CO)_6$).

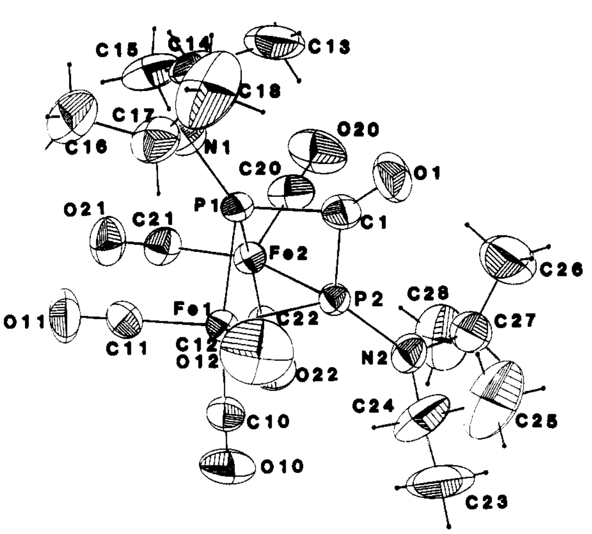
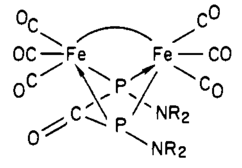
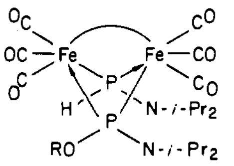


**Figure 1.** ORTEP diagram of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I, R = isopropyl).

The carbon-13 NMR spectrum of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ exhibits a triplet resonance at $\delta$ 209.1 ($|^1J(P\text{–}C)|$ = 83 Hz) assigned to the phosphorus-bridging carbonyl in addition to a singlet terminal carbonyl resonance at $\delta$ 212.2.



I



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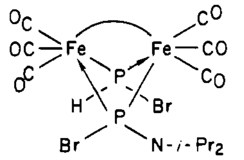

III

Several reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ have been investigated. Treatment with methanol or ethanol in boiling toluene for 16 h results in loss of the phosphorus-bridging carbonyl to give $(i\text{-}Pr_2NPOR)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ (II, R = Me or Et). The proton-decoupled phosphorus-31 NMR spectra of these complexes (Table I) reveals a pair of doublets indicating coupled nonequivalent phosphorus atoms. Turning off the proton decoupling splits further the higher field doublet corresponding to the $^1J$(P–H) coupling, indicating that one of the phosphorus atoms is directly bonded to hydrogen. Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with

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(7) Crystal data for $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I): $Fe_2C_{19}H_{28}N_2O_7P_2$, $M_r$ 570.08, monoclinic crystals, space group $P2_1/n$, $a$ = 10.197 (3) Å, $b$ = 31.403 (13) Å, $c$ = 9.170 (3) Å, $\beta$ = 112.18 (2)°, $V$ = 2719.1 (17) Å$^3$, $D_{calcd}$ = 1.392 g/cm$^3$, $Z$ = 4, anisotropic least-squares refinement (Mo K$\alpha$ radiation, $\mu$(Mo K$\alpha$) = 12.18 $cm^{-1}$, $F(000)$ = 1176, 3109 observed reflections, $R$ = 0.075 $R_w$ = 0.094).

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**Table I.** New ((Dialkylamino)phosphido)hexacarbonyldiiron Derivatives

| compd[a,b] | color | mp, °C | NMR $\delta(^{31}P)$[c] | IR, $\nu$(CO),[d] cm$^{-1}$ |
|---|---|---|---|---|
| $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ | orange | 114–115 | 225.6 s | 2060 m, 2016 s, 1996 s, 1975 s, 1964 m, 1720 m[e] |
| $(Cx_2NP)_2COFe_2(CO)_6$ | orange | 164 dec | 229.7 s | 2060 m, 2016 s, 1996 s, 1973 s, 1962 m, 1721 m[e] |
| $[(CH_2)_3(CMe_2)_2NP]_2COFe_2(CO)_6$ | orange | 160 | 204.6 s | 2058 m, 2016 s, 1992 s, 1977 s, 1962 m, 1715 m[e] |
| $(i\text{-}Pr_2NPOMe)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ | yellow | 121 | 270.5 d (128), 145.7 dd (398, 128) | 2050 m, 2012 s, 1987 s, 1977 m, 1962 s, 1952 m |
| $(i\text{-}Pr_2NPOEt)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ | yellow | 114 | 264.4 d (127), 146.1 dd (398, 127) | 2055 m, 2015 s, 1987 s, 1977 m, 1961 s, 1954 m |
| $(i\text{-}Pr_2NPBr)(HPBr)Fe_2(CO)_6$[f] | orange | 119 | 242.1 d (136), 151.1 dd (418, 136) | 2080 s, 2045 s, 2026 s, 2002 s, 1993 s |
| $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ | orange | 97 | 173.7 d (100), 7.7 dd (420, 100) | 2050 m, 2007 s, 1980 s, 1968 m, 1955 m |
| $(i\text{-}Pr_2NP)_2CHOHFe_2(CO)_6$[g] | yellow | 125 dec | 169.4 s | 2050 m, 2007 s, 1995 s, 1959 m, 1945 m |

[a] Key: *i*-Pr = isopropyl, Cx = cyclohexyl, Me = methyl, Et = ethyl. [b] All compounds listed here gave excellent C, H, N, and, where applicable, Br analyses. [c] $CDCl_3$ solutions without proton decoupling to measure $|^1J(P-H)|$; s = singlet, d = doublet, dd = double doublet. Coupling constants in Hz are given in parentheses. [d] Hexane solutions. [e] P–C(O)–P $\nu$(CO) frequency. [f] Before the final crystallization a second stereoisomer of $(i\text{-}Pr_2NPBr)(HPBr)Fe_2(CO)_6$ was detected by $^{31}P$ NMR: $\delta$ 273.0 d (91), 167.3 dd (440, 91). [g] $\nu(OH)$ = 3450 cm$^{-1}$ in Nujol.

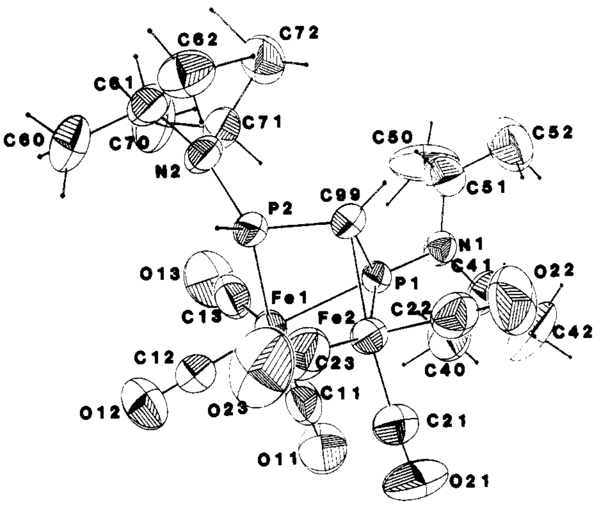
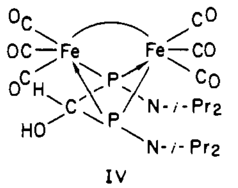
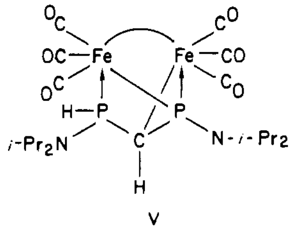


**Figure 2.** ORTEP diagram of $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ (V).

hydrogen bromide in hexane follows a similar course except the more strongly acidic reagent also cleaves one of the diisopropylamino groups to give $(i\text{-}Pr_2NPBr)(HPBr)Fe_2(CO)_6$ (III). In this case the phosphorus-31 NMR spectrum indicates two stereoisomers in the crude product, one of which could be isolated pure by careful crystallization.

The reduction of the phosphorus-bridged carbonyl group in $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with hydridic reducing agents is of particular interest. The initial product, formed, for example, by using $NaBH_4$ in methanol, appears to be the expected alcohol $(i\text{-}Pr_2NP)_2CHOHFe_2(CO)_6$ (IV). Reduction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ in diethyl ether forms not only this product but also $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ (Table I), the structure of which has been determined by X-ray diffraction;[10] see Figure 2.


IV


V

In the conversion I (R = isopropyl) to V the iron–iron bond lengthens slightly (Fe–Fe = 2.726 (2) Å), an iron-phosphorus bond is broken, and an iron–carbon bond is formed. Related rearrangements have been observed in reactions of $CH_2S_2Fe_2(CO)_6$ with lithium diisopropylamide[11,12] and $C_6H_4(CH_2PPh)_2Fe_2(CO)_6$ with *n*-butyllithium.[13]

**Acknowledgment.** We are indebted to the Air Force Office of Scientific Research for partial support of this work at the University of Georgia under Grant AFOSR-84-0050.

**Supplementary Material Available:** Tables of positional parameters, anisotropic thermal parameters, and bond angles and distances for $Fe_2(CO)_6(i\text{-}Pr_2NP)_2(CO)$ and $Fe_2(i\text{-}Pr_2NPH)(i\text{-}Pr_2NP)(CO)_6(CH)$ (11 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ (V). $Fe_2C_{19}H_{30}N_2O_6P_2$, $M_r$ 556.10, triclinic crystals, space group $P\bar{1}$; $a$ = 14.412 (6) Å, $b$ = 10.409 (5) Å, $c$ = 10.014 (4) Å, $\alpha$ = 111.80 (3)°, $\beta$ = 82.19 (3)°, $\gamma$ = 106.86 (4)°, $V$ = 1334.1 (9) Å$^3$, $D_{calcd}$ = 1.384 g/cm$^3$, $Z$ = 2, anisotropic least-squares refinement (Mo K$\alpha$ radiation, $\mu$(Mo K$\alpha$) = 12.37 cm$^{-1}$, $F(000)$ = 576, 3585 observed reflections, $R$ = 0.057, $R_w$ = 0.059).

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## Influence of the Lone-Pair Electrons on the Stability of the Oxygenated Complex of Heme

*Sir:*

The remarkable stability of oxymyoglobin and oxyhemoglobin has been attributed to hydrogen bonding, a low dielectric constant, and acidity about the heme.[1-5] However, the influence of lone-pair electrons of imidazole on the stability of the oxygenated complex of heme has not been studied, though the imidazole contained in the distal histidine residue has the lone-pair electrons. In order to probe the effect of lone-pair electrons, two models of porphyrins were synthesized and the stabilities of their oxygenated complexes were examined. In consequence, it is clarified that the stability of the oxygenated complex is affected by lone-pair electrons on nitrogen atom.

The first model, bipyridine–porphyrin, includes the chain bridged between opposite meso phenyl groups, and the bipyridine moiety is inserted within this chain. The length (four atoms) of chain bridged between bipyridine and meso phenyl groups is very short. Thus, it is expected that a strong interaction between

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