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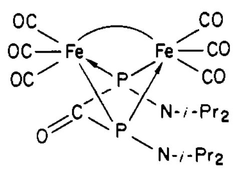
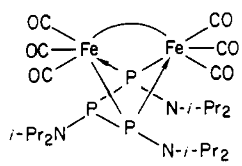
Novel ((Diisopropylamino)triphosphine)hexacarbonyldiiron Complexes

Sir:

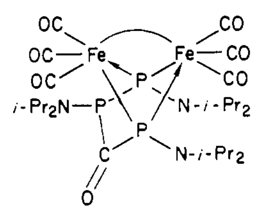
Recently we reported the reaction of $Na_2Fe(CO)_4$ with *i*-Pr_2NPCl_2 in diethyl ether to give the novel phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I).[1] We now report that the course of this interesting reaction is highly solvent-dependent. Thus, conducting the reaction in tetrahydrofuran rather than diethyl ether leads to the novel triphosphine derivative $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II) as the major product. In addition, a new type of phosphorus-bridging carbonyl derivative, namely $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (III), has also been isolated from this reaction.



I



II



III

An orange suspension of 440 mmol of $Na_2Fe(CO)_4\cdot 1.5C_4H_8O_2$[2] in 4000 mL of tetrahydrofuran was treated with 410 mmol of *i*-Pr_2NPCl_2 at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 36 h at room temperature. Solvent was removed under vacuum, and the residue was dried at 25 °C/0.1 mm for 24 h. After the residue was exposed to air for 2 to 3 days, the mixture was extracted with 2000 mL of hexane in three portions. Concentration of the filtered hexane extracts to 800 mL and cooling to −10 °C gave 27 g (30% yield) of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$. Further concentration of the filtrate gave a mixture of four iron carbonyl complexes, which were separated by chromatography on silica gel in hexane solution. Elution of the chromatogram with hexane gave successively $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ (IV), $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II), $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I), and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (III) (Table I), but the complete separation of III and I required fractional crystallization from hexane and mechanical separation of the crystals. The yields of IV, II, I, and III based on the

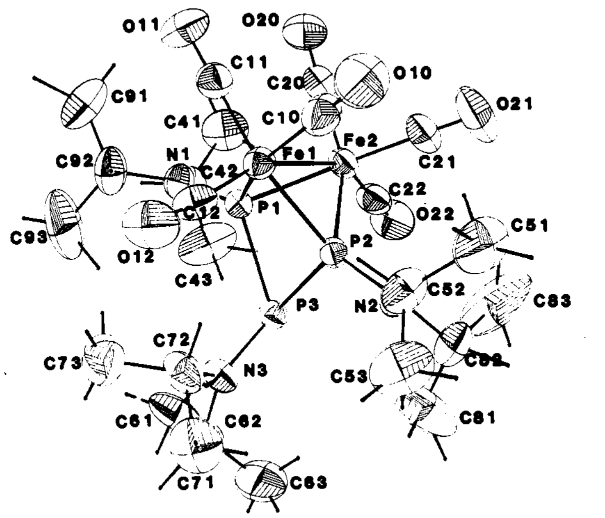
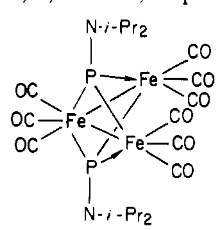
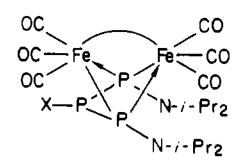


Figure 1. Projection view of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$: Fe1–Fe2, 2.602 (2) Å, P1–P3, 2.278 (2) Å; P2–P3, 2.243 (2) Å; Fe–P(av), 2.248 (2) Å; P1–P3–P2, 68.19 (7)°.

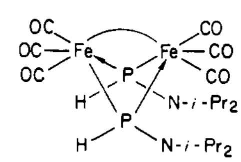
phosphorus-31 NMR spectrum of the original reaction mixture were 5, 35, 5, and 5%, respectively.



IV



V



VI

The product $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ (IV) appears to be analogous to known $(\mu_3\text{-}RP)_2Fe_3(CO)_9$ compounds[3-7] having a structure with

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Table I. Diisopropylamino–Phosphorus–Iron Carbonyl Complexes

compd[a]	color	mp, °C	^{31}P NMR,[b] δ	IR ν(CO),[c] cm^{-1}
$(i\text{-}Pr_2NP)_2Fe_3(CO)_9$	black	128–129	398.6 s	2062 w, 2030 s, 2010 s, 1998 s, 1990 m, 1982 m, 1976 s
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	orange	181–185 dec	292.2 t (264), 170.3 d (264)	2048 s, 2008 s, 1986 s, 1961 s, 1950 m
$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$	orange	114–115	225.6 s	2060 m, 2016 s, 1996 s, 1975 s, 1964 m, 1720 m[d]
$(i\text{-}Pr_2NP)_3COFe_2(CO)_6$	deep orange	178–179	223.8 dd (405, 83), 189.4 dd (83, 24), 1.2 dd (405, 24)	2057 m, 2020 s, 1995 s, 1985 m, 1975 s, 1964 m, 1645 w[d]
$(i\text{-}Pr_2NP)_2PClFe_2(CO)_6$	yellow-orange	91–92	318.7 t (254), 147.8 d (254)	2062 s, 2023 s, 1996 s, 1982 s, 1967 s
$(i\text{-}Pr_2NP)_2PBrFe_2(CO)_6$	orange	99–100	302.9 t (257), 142.2 d (257)	2059 m, 2020 s, 1993 s, 1984 m, 1967 m
$(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$	orange	91–92	382.8 t (242), 155.1 d (242)	2058 m, 2019 s, 1993 s, 1975 m, 1961 m
$(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$	orange	137–138	378.8 t (238), 157.0 d (238)	2056 m, 2016 s, 1991 s, 1973 m, 1960 m
$(i\text{-}Pr_2NP)_2PHFe_2(CO)_6$	orange	120–121	277.3 t (154, 132[e]) 102.3 d (154)	2050 m, 2008 s, 1991 s, 1967 s, 1957 m
$(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$	yellow	126–127	156.0 s[f]	2040 m, 2008 s, 1985 m, 1975 s, 1964 s

[a] All compounds listed here gave excellent C, H, N, and, where applicable, halogen analyses. [b] $CDCl_3$ solutions were used without proton decoupling to measure $|^1J(\text{P–H})|$; multiplicites are given for the spectra obtained with proton noise decoupling: s = singlet, d = doublet, t = triplet, dd = double doublet. Coupling constants in Hz are given in parentheses; chemical shifts are measured in ppm *downfield* from external 85% phosphoric acid. [c] Hexane or cyclohexane solutions. [d] P–C(O)–P ν(CO) frequency. [e] $|^1J(\text{P–H})|$. [f] Turning off the proton decoupling gave a complicated second-order ^{31}P NMR spectrum with two triplets, two double triplets, and two singlets not inconsistent with an $A_2M_2X_4$ system (A = P, M = P*H*, X = C*H*).

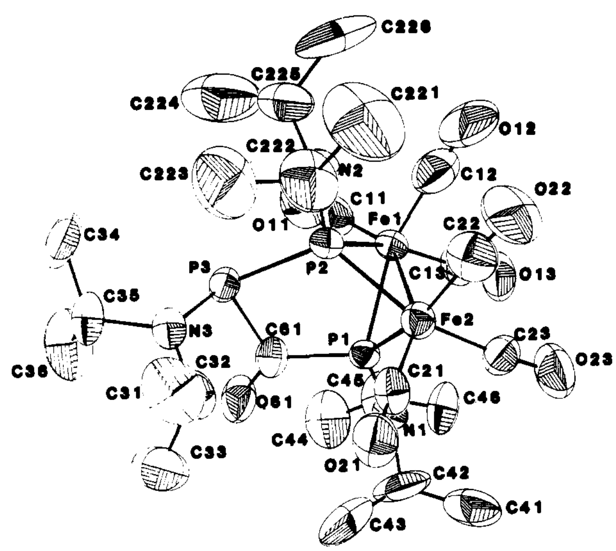

Figure 2. Projection view of $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$: Fe1–Fe2, 2.587 (2) Å; P3–P2, 2.233 (5) Å; C61–P3, 1.868 (12) Å; P1–C61, 1.835 (11) Å; C61–O61, 1.23 (2) Å; Fe–P(av), 2.243 (4) Å.

two Fe–Fe bonds.[5] The products $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II) and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (III) are of types that have not previously been characterized structurally; their structures were therefore determined by X-ray diffraction.[8,9] Both products had the expected iron–iron bonds (2.602 (2) Å in II and 2.587 (2) Å in III). The expected triphosphine chain is found in II (Figure 1): P1–P3 = 2.278 (2) Å; P3–P2 = 2.243 (2) Å; P1–P3–P2 = 68.19 (7)°. The dihedral angles between the plane P1, P2, P3 and the planes P1, Fe1, P2 and P1, Fe2, P2 are 60.8° and 34.4°, respectively, indicating an unsymmetrical triphosphine bridge in which the P1, P2, P3 plane does not bisect the Fe1–Fe2 bond. In III (Figure 2) carbonyl insertion into the triphosphine chain is verified: P2–P3 = 2.233 (5) Å; P3–C61 = 1.868 (12) Å; C61–P1 = 1.835 (11) Å; P2–P3–C61 = 89.9 (4)°; P3–C61–P1 = 117.8 (7)°. The angle of 117.8° at the phosphorus-bridging carbonyl group in the five-membered FeP_3C rings of III contrasts with the angle of 84.4° at the phosphorus-bridging carbonyl group in the four-membered FeP_2C rings of I, thereby accounting for the significantly different phosphorus-bridging carbonyl frequencies in III (1645 cm^{-1}) and I (1720 cm^{-1}). This dependence of phosphorus-bridging ν(CO) frequency on the bond angle at the carbonyl carbon is completely analogous to that known for many years for the ν(CO) frequencies in cycloalkanones.[10]

An important chemical property of the triphosphine complex $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ is the ability to replace the diisopropylamino group on the central phosphorus atom with other groups without disturbing the diisopropylamino groups on the terminal phosphorus atoms. The replacement of the diisopropylamino group on the central rather than on a terminal phosphorus atom in such reactions is indicated by the AX_2 patterns in the phosphorus-31 NMR spectra of such products (Table I). Apparently, the bonding of the terminal phosphorus atoms to both iron atoms reduces the reactivity of their phosphorus–nitrogen bonds toward electrophilic cleavage. Thus, treatment of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II) in hexane solution with the hydrogen halides, HX (X = Cl, Br), gives the corresponding halotriphosphine derivatives $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ (V; X = Cl, Br) in essentially quantitative yields (Table I).

Treatment of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ with boiling methanol or ethanol in the presence of a catalytic amount of acetic acid for several days gives the corresponding alkoxytriphosphine derivatives $(i\text{-}Pr_2NP)_2P(OR)Fe_2(CO)_6$ (V; X = OMe, OEt). Treatment of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (V; X = Cl) with $NaBH_4$ in tetrahydrofuran at room temperature for 2 days gives $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (V; X = H). However, treatment of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $LiAlH_4$ in tetrahydrofuran at room temperature results in phosphorus–phosphorus bond cleavage to give a 42% yield of $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VI). Several related $(\mu\text{-}RPH)_2Fe_2(CO)_6$ derivatives have been reported.[3,6]

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Supplementary Material Available: Positional parameters, anisotropic thermal parameters, and bond angles (deg) and distances (Å) for $Fe_2(PN\text{-}i\text{-}Pr_2)_3(CO)_6$ (Tables 1–3), positional parameters, anisotropic thermal parameters, and bond angles (deg) and distances (Å) for $Fe_2(PN\text{-}i\text{-}Pr_2)_3(CO)_7$ (Tables 4–6), and elemental analyses (Table 7) (12 pages). Ordering information is given on any current masthead page.

(8) Crystal data for $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II): $Fe_2C_{24}H_{42}N_3O_6P_3$, mol wt 673.22, monoclinic crystals, space group $P2_1/n$; a = 11.554 (2) Å, b = 14.294 (6) Å, c = 20.405 (4) Å, β = 90.96 (2)°, V = 3369.4 (18) Å^3, D_{calcd} = 1.327 g/cm^3, Z = 4; anisotropic least-squares refinement (Mo Kα radiation, μ(Mo Kα) = 10.37 cm^{-1}, $F(000)$ = 1408, 4164 observed reflections, R = 0.059, R_w = 0.074).

(9) Crystal data for $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (III): $Fe_2C_{25}H_{42}N_3O_7P_3$, mol wt 701.24, monoclinic crystals, space group $P2_1/a$; a = 14.910 (5) Å, b = 12.064 (6) Å, c = 19.733 (10) Å, β = 105.31 (4)°, V = 3423.6 (28) Å, D_{calcd} = 1.360 g/cm^3, Z = 4; anisotropic least-squares refinement (Mo Kα radiation, μ(Mo Kα) = 10.25 cm^{-1}, $F(000)$ = 1464, 3021 observed reflections, R = 0.074, R_w = 0.096).

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