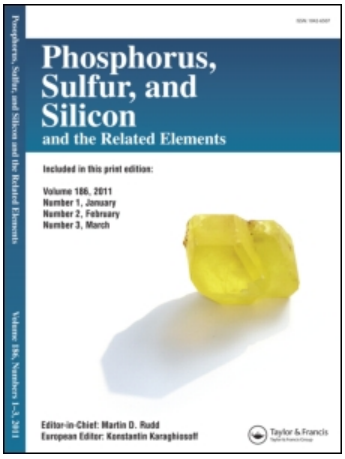

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Reactions of Dialkylaminodichlorophosphines with Tetracarbonylferrate (II): Routes to Novel Phosphorus Bridging Carbonyl Derivatives and Triphosphine Complexes

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REACTIONS OF DIALKYLAMINODICHLOROPHOSPHINES WITH TETRACARBONYLFERRATE(-II): ROUTES TO NOVEL PHOSPHORUS-BRIDGING CARBONYL DERIVATIVES AND TRIPHOSPHINE COMPLEXES

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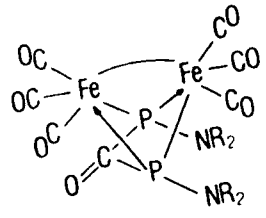
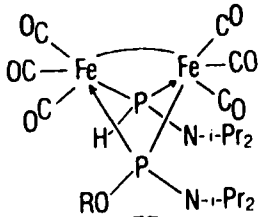
Abstract Reaction of iPr_2NPCl_2 with $Na_2Fe(CO)_4$ gives the phosphorus-bridging carbonyl derivative $(iPr_2NP)_2COFe_2(CO)_6$ or the triphosphine derivative $(iPr_2NP)_3Fe_2(CO)_6$ as the major product depending upon whether the reaction is run in diethyl ether or tetrahydrofuran, respectively. Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ gives totally different types of products resulting from migration of diethylamino groups. The chemistry of these and related compounds is discussed.

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] We have now found that reactions of sterically hindered R_2NPCl_2 derivatives with $Na_2Fe(CO)_4 \cdot 1.5$ dioxane[5] in diethyl ether give the corresponding orange air-stable phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ (I:R = isopropyl or cyclohexyl or R_2N = 2,2,6,6-tetramethylpiperidino) in up to 35% yield. X-ray diffraction on $(iPr_2NP)_2COFe_2(CO)_6$ confirms structure I in which the two phosphorus atoms are bridged by one of the carbonyl groups thereby indicating a novel migration of a carbonyl group from iron to phosphorus.[6] In $(iPr_2NP)_2COFe_2(CO)_6$ the phosphorus-bridging carbonyl group exhibits a strong $\nu(CO)$ frequency at 1720 $cm.^{-1}$ and a carbon-13 resonance at δ209.1 ($|^1J(P\text{-}C)|$ = 83 Hz.).



I



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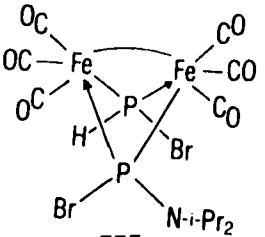
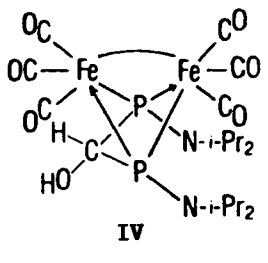


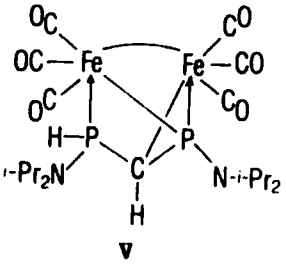
III

Several reactions of $(iPr_2NP)_2COFe_2(CO)_6$ have been investigated. Thus treatment with methanol or ethanol in boiling toluene for 16 hr. results in loss of the phosphorus-bridging carbonyl to give $(iPr_2NPOR)(iPr_2NPH)Fe_2(CO)_6$ (II:R = Me or Et). The proton-decoupled phosphorus-31 NMR spectra of these complexes reveal a pair of doublets indicating coupled non-equivalent phosphorus atoms (e.g., for R = Me: δ 270.5 and 145.7, J(P-P) = 128 Hz.). Turning off the proton decoupling splits further the higher field doublet corresponding to the ^{1}J(P-H) coupling indicating that one of the phosphorus atoms is directly bonded to hydrogen in accord with structure II. Reaction of $(iPr_2NP)_2COFe_2(CO)_6$ with hydrogen bromide in hexane follows a similar course except the more strongly acidic reagent also cleaves one of the of the diisopropylamino groups to give $(iPr_2NPBr)(HPBr)Fe_2(CO)_6$(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.

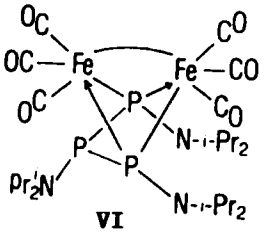
Reaction of $(iPr_2NP)_2COFe_2(CO)_6$ with hydridic reducing agents results in reduction of the phosphorus-bridging carbonyl group, an unprecedented type of reaction. Thus treatment of $(iPr_2NP)_2COFe_2(CO)_6$ (I:R = isopropyl) with $NaBH_4$ in methanol gives the corresponding secondary alcohol $(iPr_2NP)_2CHOHFe_2(CO)_6$ (IV). Reduction of $(iPr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ in diethyl ether forms not only this alcohol but also the rearranged product $(iPr_2NPHCHPNiPr_2)Fe_2(CO)_6$, shown by X-ray diffraction to have structure V. In converting I to V 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[7,8] and $C_6H_4(CH_2PPh)_2Fe_2(CO)_6$ with n-butyllithium.[9]



IV



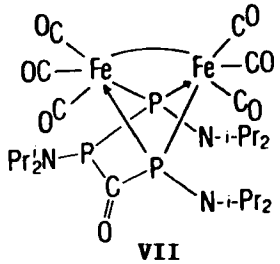
V



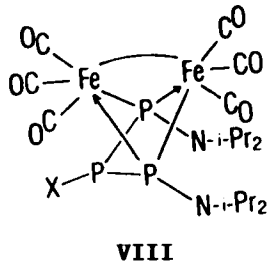
VI

The reaction of iPr_2NPCl_2 with $Na_2Fe(CO)_4 \cdot 1.5$ dioxane[5] is highly solvent dependent. Thus if this reaction is carried out in tetrahydrofuran rather than diethyl ether the major product is the orange air-stable triphosphine complex $(iPr_2NP)_3Fe_2(CO)_6$, isolated in 30% yield and shown by X-ray diffraction to have structure VI.[10] A minor product from this reaction is the phosphorus-bridging carbonyl derivative $(iPr_2NP)_3COFe_2(CO)_6$, shown by X-ray diffraction to have structure VII. The

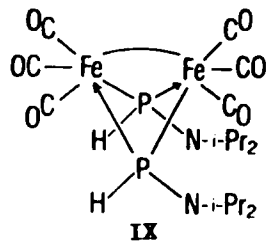
phosphorus-bridging carbonyl group in VII exhibits a $\nu(CO)$ frequency at 1645 $cm.^{-1}$



VII



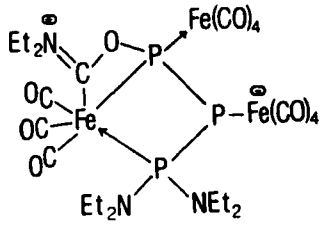
VIII



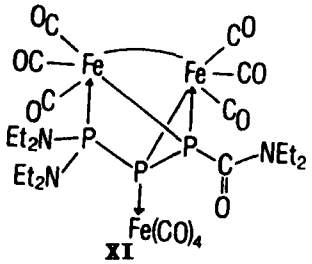
IX

An important chemical property of the triphosphine complex $(iPr_2NP)_3Fe_2(CO)_6$ (VI) 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 as indicated by the AX_2 patterns in the phosphorus-31 NMR spectra of the products. Thus treatment of $(iPr_2NP)_3Fe_2(CO)_6$ (VI) with boiling methanol or ethanol in the presence of a catalytic amount of acetic acid for several days gives the corresponding alkoxytriphosphine derivatives $(iPr_2NP)_2P(OR)Fe_2(CO)_6$ (VIII: X = OMe, OEt). Similarly treatment of $(iPr_2NP)_3Fe_2(CO)_6$ (VI) in hexane with the hydrogen halides HX (X = Cl, Br) gives the corresponding halotriphosphine derivatives $(iPr_2NP)_2P(X)Fe_2(CO)_6$ (VIII:X = Cl, Br) in essentially quantitative yields. Treatment of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ (VIII:X = Cl) with $NaBH_4$ in tetrahydrofuran at room temperature for 2 days gives $(iPr_2NP)_2P(H)Fe_2(CO)_6$ (VIII:X = H). However, treatment of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ with $LiAlH_4$ in tetrahydrofuran results in phosphorus-phosphorus bond cleavage to give a 42% yield of $(iPr_2NPH)_2Fe_2(CO)_6$ (IX) analogous to several reported $(\mu_2\text{-}RPH)_2Fe_2(CO)_6$ derivatives.[11,12]

The reactions of R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ require relatively large R_2N groups such as dicyclohexylamino, diisopropylamino, or 2,2,6,6-tetramethylpiperidino in order to obtain products such as I and VI. Reaction of the much less sterically hindered Et_2NPCl_2 with $Na_2Fe(CO)_4 \cdot 1.5$ dioxane in diethyl ether results in diethylamino migration to give rather complicated products, the structures of which have been determined by X-ray diffraction. The initial product from this reaction has stoichiometry $(Et_2N)_3P_3Fe_3(CO)_{12}$ and structure X. This product undergoes facile decarbonylation in solution at room temperature to give a product of stoichiometry $(Et_2N)_3P_3Fe_3(CO)_{11}$ and structure XI. Conversion of X to XI involves formation of an iron-iron bond and converstion of a P-Fe bridging Et_2NCO group to a phosphorus-bonded terminal Et_2NCO group.



X



XI

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