Journal of Organometallic Chemistry, 383 (1990) 295–305
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20392

Formation and chemical reactivity of metal carbonyl complexes containing phosphorus-bridging carbonyl groups

R.B. King, F.-J. Wu,

Department of Chemistry, University of Georgia, Athens, Georgia 30602 (U.S.A.)

E.M. Holt

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078 (U.S.A.)

(Received March 23rd, 1989)

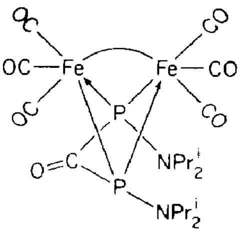
Abstract

Reactions of $Na_2Fe(CO)_4$ with sterically hindered R_2NPCl_2 derivatives (R_2N = diisopropylamino, dicyclohexylamino, 2,2,6,6-tetramethylpiperidino) in diethyl ether solution result in migration of a carbonyl group from iron to phosphorus to give the air-stable P_2Fe_2 phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ in yields up to 35%. In addition, the corresponding P_3Fe_2 phosphorus-bridging carbonyl derivatives $(R_2NP)_3COFe_2(CO)_6$ are minor products of the reactions of $Na_2Fe(CO)_4$ with the same R_2NPCl_2 derivatives in tetrahydrofuran solution, the major products being the triphosphine complexes $(R_2NP)_3Fe_2(CO)_6$. The ketone-like reactivity of the phosphorus-bridging carbonyl group in $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ is indicated by its reactions with $NaBH_4$ and with RLi (R = Me, n-Bu) to given the corresponding alcohols $(i\text{-}Pr_2NP)_2C(R)(OH)Fe_2(CO)_6$ (R = H, Me, n-Bu). Reduction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ gives a product of stoichiometry "$(i\text{-}Pr_2NP)_2CH_2Fe_2(CO)_6$" shown by X-ray diffraction to be $(i\text{-}Pr_2NPCHPHN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$, in which an Fe–P bond has broken and a new Fe–C bond has formed. Reduction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion $[i\text{-}Pr_2NPCOPFe_2(CO)_6]^-$, which can be isolated as its bis(triphenylphosphine)iminium salt or converted to $(i\text{-}Pr_2N)(Me_3Sn)P_2COFe_2(CO)_6$ or $[(i\text{-}Pr_2NP)(i\text{-}Pr_2N)ClPP]Fe_2(CO)_6$ by reaction with Me_3SnCl or $i\text{-}Pr_2NPCl_2$, respectively. Reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with the alcohols ROH (R = Me, Et) under relatively vigorous conditions or with HBr under relatively mild conditions result in expulsion of the phosphorus-bridging carbonyl group to give $(i\text{-}Pr_2NPOR)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ or $(i\text{-}Pr_2NPBr)(HPBr)Fe_2(CO)_6$, respectively.

1. Introduction

The report of a volatile binary metal carbonyl, namely $Ni(CO)_4$, by Mond, Langer, and Quincke in 1890 [1] demonstrated for the first time that carbon monoxide can form volatile binary compounds with transition metals. This seminal discovery a century ago spawned the extensive development of metal carbonyl chemistry, which in recent years has accelerated greatly because of major improvements in spectroscopic and X-ray diffraction methods for structure determination. Carbon monoxide is now known to bond to transition metals in a number of diverse ways and carbonyl derivatives are known for essentially all transition metals.

This paper for the special issue of the *Journal of Organometallic Chemistry* commemorating the centennial of the original report of $Ni(CO)_4$ reviews work in recent years at the University of Georgia on a new type of metal carbonyl derivative discovered serendipitously in our laboratory,namely metal carbonyl derivatives containing phosphorus-bridging carbonyl groups as exemplified by compounds of the type $(R_2NP)_2COFe_2(CO)_6$ (I: R = large alkyl group such as isopropyl or cyclohexyl). The distinctive feature of such molecules is the carbonyl group bridging the two phosphorus atoms but not bonded to either iron atom. This phosphorus-bridging carbonyl group arises from an unprecedented migration of a carbonyl group from iron to phosphorus. Furthermore, the overall stability as well as the ready availability of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) has allowed the demonstration of ketone-like reactivity of its phosphorus-bridging carbonyl group. Such reactions probably represent the first demonstrations of ketone-like reactivity for a carbonyl group not bonded to carbon.

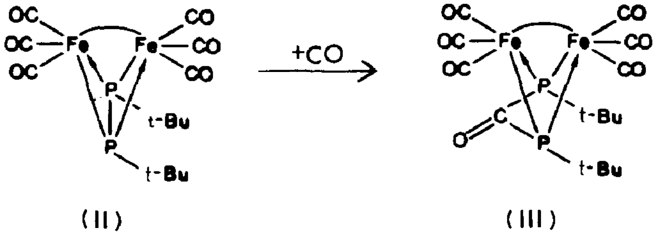

(I)

2. Formation of phosphorus-bridging carbonyl derivatives

During the early 1980's one of the objectives of our work on organophosphorus chemistry was the reduction of the readily available halides R_2NPCl_2 [2] to the then unknown derivatives R_2NPH_2, cyclo-$(R_2NP)_n$, and $R_2NP{=}PNR_2$. In this connection reductions of R_2NPCl_2 derivatives containing sterically hindered R_2N groups (e.g., R = isopropyl or cyclohexyl) with $LiAlH_4$ and with magnesium metal in tetrahydrofuran were found to give previously unknown derivatives of the types R_2NPH_2 [3] and cyclo-$(R_2NP)_4$ [4]. However, preparation of isolable diphosphenes $R_2NP{=}PNR_2$ proved to be much more difficult even when the largest readily available hydrocarbon R_2N groups such as 2,2,6,6-tetramethylpiperidine were used although Niecke and Rüger [5] subsequently isolated the diaminodiphosphene $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ containing the even more bulky $(Me_3Si)_2N$ substituents. We therefore investigated reactions of R_2NPCl_2 derivatives with metal carbonyl anions, particularly $Fe(CO)_4^{2-}$, as possible sources of diphosphenes $R_2NP{=}PNR_2$ stabilized by coordination to metal carbonyl fragments. In this connection work by Cowley [6], Power [7–10], and their coworkers on reactions of $Na_2Fe(CO)_4$ with alkyldichlorophosphines and aryldichlorophosphines, $RPCl_2$, served as useful models since such reactions were found to give a number of types of iron carbonyl complexes of the diphosphenes RP=PR.

With these considerations in mind we investigated the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 using diethyl ether as a solvent. Orange air-stable crystals of apparent stoichometry $(R_2NP)_2Fe_2(CO)_7$ were readily isolated from this reaction mixture. The observation of a fairly conspicuous apparent ν(CO) frequency around 1720 cm^{-1} in addition to the expected terminal ν(CO) frequencies around 2000 cm^{-1} initially suggested the presence of a bridging carbonyl group in addition to the expected terminal carbonyl groups. However, the solid state structure as determined by X-ray crystallography soon indicated that this bridging carbonyl group was not the familiar type of carbonyl group bridging two transition metal atoms but instead the then unprecedented type of carbonyl group bridging two phosphorus atoms in structure I [11].

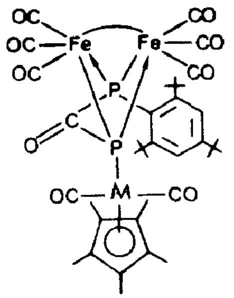
Shortly after the appearance in late 1985 of our initial communication on $(R_2NP)_2COFe_2(CO)_6$ derivatives I [11] compounds of closely related types were reported by workers in other laboratories. In all of these reported syntheses of phosphorus-bridging carbonyl derivatives, the phosphorus-bridging carbonyl group originates from carbon monoxide and coordination of carbon monoxide to a transition metal atom followed by migration of the resulting carbonyl group from the transition metal to a phosphorus atom appears to play a role in the reaction-pathway. Thus De, Wolters, and Vahrenkamp [12] reported the insertion of carbon monoxide at 80 °C/50 atm into the phosphorus–phosphorus bond of the diphosphadimetallatetrahedrane $(Me_3CP)_2Fe_2(CO)_6$ (II) to give the phosphorus-bridging carbonyl derivative $(Me_3CP)_2COFe_2(CO)_6$ (III) according to the reaction:



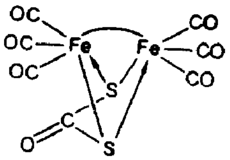
(II) (III)

Weber, Reizig, Bungardt, and Boese [13,14] reported the reactions of the diphosphenes $Me_5C_5M(CO)_2P{=}PC_6H_2(CMe_3)_3$-2,4,6 (M = Fe, Ru, Os) with $Fe_2(CO)_9$ to give the phosphorus-bridging carbonyl derivatives $[Me_5C_5M(CO)_2PCOPC_6H_2(CMe_3)_3$-2,4,6$]Fe_2(CO)_6$ (IV: M = Fe, Ru, Os).

The relationship between species in the P_2Fe_2 manifold and other species of possible significance suggested by these reactions is indicated in scheme 1 (M = Fe, $n = 4$). Our study on the reaction of $Na_2Fe(CO)_4$ with sterically hindered R_2NPCl_2 derivatives in diethyl ether suggested the Scheme 2 [15]. The major isolated product from the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 is the phosphorus-bridging carbonyl derivative (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) as noted above. The hydrolysis product [i-$Pr_2NP(H)Fe(CO)_4]_2O$ (V: R = isopropyl) was isolated in minute quantities (< 1% yield) and its structure was confirmed by X-ray diffraction



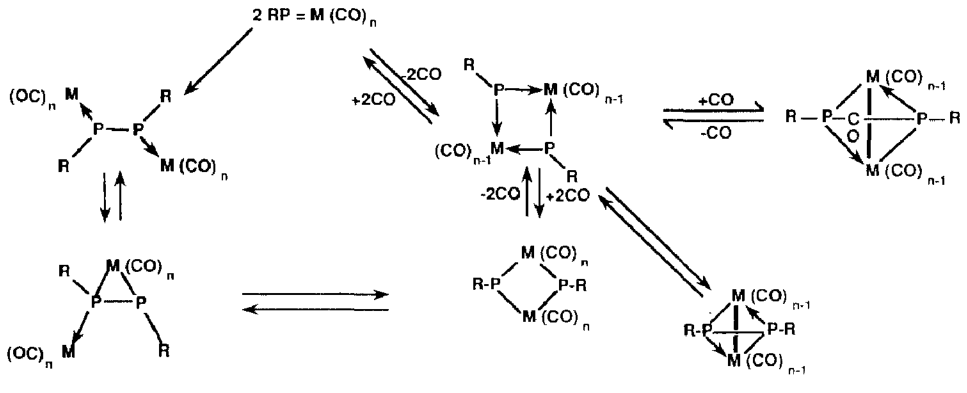
(IV)



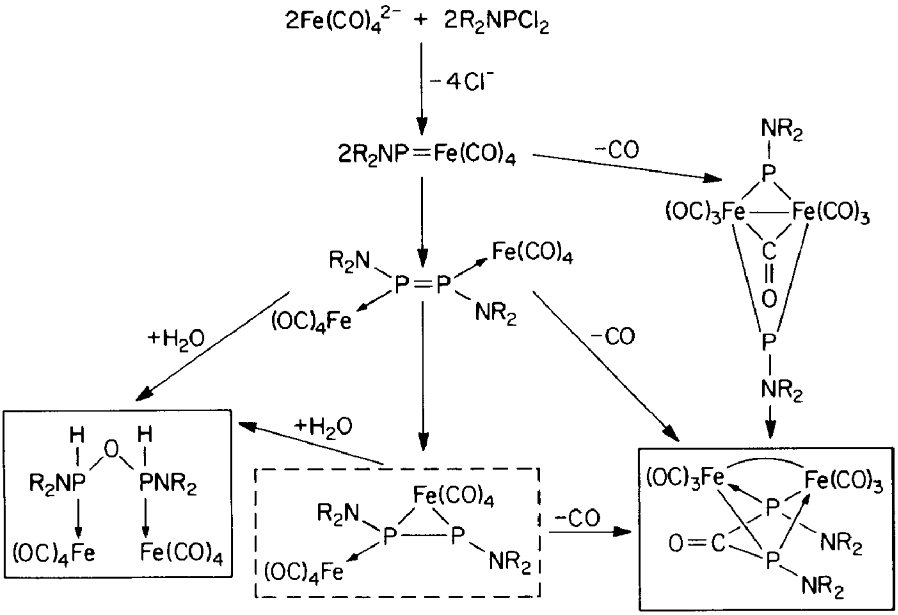
(VII)

[15]. The unsymmetrical diphosphenebis(iron tetracarbonyl) derivative (i-$Pr_2N)_2$-$P_2[Fe(CO)_4]_2$ (VI: R = isopropyl) was postulated on the basis of the reproducible observation of an AX pattern in the ^{31}P NMR spectrum of the reaction mixture with resonances at δ 97.3 and 61.7 ppm with $|^1J(P-P)|$ 477 Hz. similar to the ^{31}P NMR spectra of the known $R_2P_2[Fe(CO)_4]_2$ derivatives ($R = C_6H_5$ and 2,4,6-$(Me_3C)_3C_6H_2O$) [9,16]. Another related compound is the structurally-characterized sulfur-bridging carbonyl derivative $S_2COFe_2(CO)_6$ (VII) obtained in minute (< 1%) as a byproduct from the reaction of S_8 with $Fe_3(CO)_{12}$ [17].

Formation of the phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ (I) from reactions of R_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether appears to require the R_2N group to be at least as sterically hindered as diisopropylamino. Reaction of the less sterically hindered Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether does not lead to an analogous derivative $(Et_2NP)_2COFe_2(CO)_6$ (I: R = ethyl). Instead the initial major product is a trinuclear iron carbonyl derivative of stoichiometry $(Et_2NP)_3Fe_3(CO)_{12}$ which undergoes a slow decarbonylation in solution at room temperature to give a second trinuclear iron carbonyl derivative of stoichiometry $(Et_2NP)_3Fe_3(CO)_{11}$ [15,18]. Determination of the structure of $(Et_2NP)_3Fe_3(CO)_{12}$ by X-ray diffraction indicates structure VIII containing a bent triphosphine unit with two diethylamino groups bonded to one of the terminal phosphorus atoms and $Fe(CO)_4$ units coordinated both to the center and other terminal phosphorus atoms. In addition, an $Fe(CO)_3$ unit bridges the terminal phosphorus atoms to form a four-membered FeP_3 ring and a diethylcarbamoyl group (Et_2NCO) bridges an



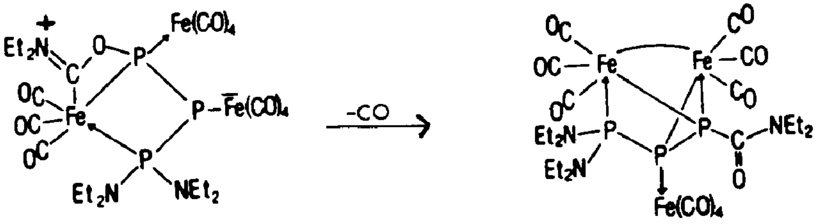
Scheme 1. Relationship between organophosphorus metal carbonyl derivatives in the P_2M_2 manifold. This paper discusses the system where M = Fe and $n = 4$.



V VI I

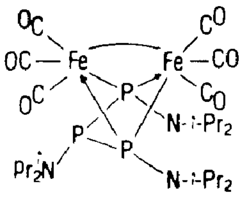
Scheme 2. Reaction of $Na_2Fe(CO)_4$ with sterically hindered R_2NPCl_2 derivatives suggested in R.B. King, F.-J. Wu, and E.M. Holt, J. Am. Chem. Soc., 109 (1987) 7764.

iron–phosphorus bond to form a four-membered FePOC ring. Determination of the structure of $(Et_2NP)_3Fe_3(CO)_{11}$ by X-ray diffraction indicates structure IX in which the loss of one carbonyl group from $(Et_2NP)_3Fe_3(CO)_{12}$ (VIII) to form $(Et_2NP)_3Fe_3(CO)_{11}$ (IX) is accompanied by the conversion of the bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group, formation of an iron–iron bond, and formation of a new iron–phosphorus bond. An essential step in the formation of VIII and then IX from Et_2NPCl_2 and $Na_2Fe(CO)_4$ is migration of a diethylamino group from one phosphorus atom to another leading to a phosphorus atom in both VIII and IX bearing two diethylamino groups. Use of the larger diisopropylamino group inhibits this type of dialkylamino migration to give a structure having two dialkylamino groups bonded to the same phosphorus atom. This allows the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ to follow a different pathway leading ultimately to the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl). There appears to be no reason why the less hindered and still unknown $(Et_2NP)_2COFe_2(CO)_6$ (I: R = ethyl) should be inherently unstable. However, the successful synthesis of $(Et_2NP)_2COFe_2(CO)_6$ will require an appropriate reaction under conditions where an unwanted diethylamino migration cannot occur.

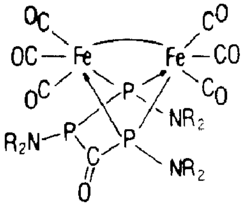


(VIII) (IX)

The reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 appears to be solvent dependent. Thus if this reaction is run in tetrahydrofuran rather than diethyl ether, the major iron carbonyl product (~ 30% isolated yield) is not the phosphorus-bridging carbonyl derivative (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) but instead the triphosphine complex (i-$Pr_2NP)_3Fe_2(CO)_6$ (X), the structure of which has been confirmed by X-ray diffraction [15,19]. A minor product (~ 3% isolated yield) from the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 is a phosphorus-bridging carbonyl derivative of a different type, namely the P_3Fe_2 bridging carbonyl derivative (i-$Pr_2NP)_3COFe_2(CO)_6$ (XI: R = isopropyl), the structure of which has been confirmed by X-ray diffraction [15,19]. The P–C–P angle of 117.8° at the phosphorus-bridging carbonyl group in (i-$Pr_2NP)_3COFe_2(CO)_6$ (XI: R = isopropyl) contrasts with the P–C–P angle of 84.4° at the phosphorus-bridging carbonyl group in (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) thereby accounting for the significantly different phosphorus-bridging ν(CO) frequencies in (i-$Pr_2NP)_3COFe_2(CO)_6$ (1645 cm^{-1}) and (i-$Pr_2NP)_2COFe_2(CO)_6$ (1720 cm^{-1}). A similar effect of bond angle at the carbonyl carbon on the ν(CO) frequency has long been known for cycloalkanones [20].



(X)



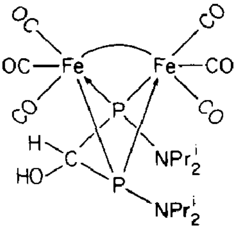
(XI)

3. Chemical reactivity of the phosphorus-bridging carbonyl group

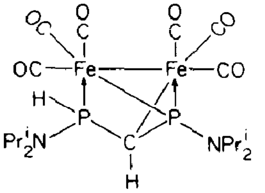
The air-stable phosphorus-bridging carbonyl derivative (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) is readily available in ~ 40-gram quantities from the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 in diethyl ether. It has therefore been possible to examine the reactions of the phosphorus-bridging carbonyl group in (i-$Pr_2NP)_2COFe_2(CO)_6$ in some detail. However, the other type of phosphorus-bridging carbonyl derivative, namely (i-$Pr_2NP)_3COFe_2(CO)_6$ (XI: R = isopropyl) is available in only minute quantities as a minor byproduct from the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 in tetrahydrofuran. Therefore, very little work has been done on the chemical reactivity of its phosphorus-bridging carbonyl group. The known chemical reactions involving the phosphorus-bridging carbonyl group in (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) are of the two types: (1) Reduction of the phosphorus-bridging carbonyl group using reagents such as $NaBH_4$, $LiAlH_4$, alkyllithiums, and sodium amalgam; (2) Expulsion of the phosphorus-bridging carbonyl group upon treatment with protic reagents to give novel bis(phosphido)hexacarbonyldiiron derivatives containing phosphorus-hydrogen bonds [21].

The phosphorus-bridging carbonyl group in (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) resembles the carbonyl group in a sterically hindered organic ketone. An important property of the ketone carbonyl group is its facile reduction by hydridic reducing agents to give the corresponding secondary alcohol. Analogous behavior was noted for the phosphorus-bridging carbonyl group in (i-$Pr_2NP)_2COFe_2(CO)_6$, which underwent reduction by $NaBH_4$ in methanol at ambient temperature or

$LiAlH_4$ in diethyl ether at −78 °C to give the corresponding yellow secondary alcohol $(i\text{-}Pr_2NP)_2CH(OH)Fe_2(CO)_6$ (XII) [11,21]. However, if the reaction mixture of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and $LiAlH_4$ in diethyl ether is allowed to warm slowly from −78 °C to room temperature without quenching, a color change from yellow to an eventual deep orange starting from −45 °C can be observed. After quenching this reaction at room temperature with saturated aqueous ammonium chloride, a product of apparent stoichiometry $(i\text{-}Pr_2NP)_2CH_2Fe_2(CO)_6$ was isolated. The idea that "$(i\text{-}Pr_2NP)_2CH_2Fe_2(CO)_6$" might contain a phosphorus-bridging methylene group was disproved by single crystal X-ray structure determination which showed that this complex is actually the isomeric $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ (XIII) [11,21]. In the conversion of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) to $(i\text{-}Pr_2NPHCHPN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ (XIII) by treatment with $LiAlH_4$, an iron–phosphorus bond in I is broken and a new iron–carbon bond is formed in XIII. Closely related rearrangements have been observed in reactions of $CH_2S_2Fe_2(CO)_6$ with $i\text{-}Pr_2NLi$ [22,23,24] and of $C_6H_4(CH_2PPh)_2Fe_2(CO)_6$ with n-BuLi [25].

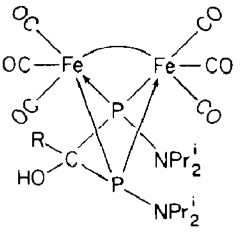


(XII)



(XIII)

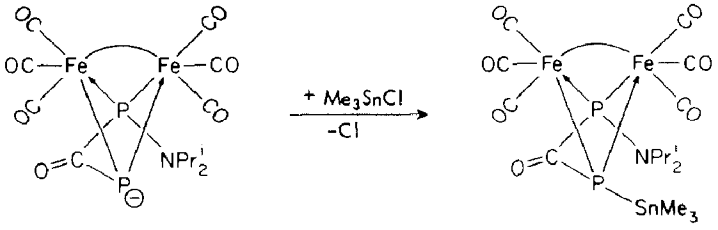
Another important reaction of the ketone carbonyl group is the facile addition of organolithium compounds to give the corresponding tertiary alcohols. Analogous behavior was noted for the phosphorus-bridging carbonyl group in $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, which underwent reactions with methyllithium and with n-butyllithium to give the corresponding tertiary alcohols $(i\text{-}Pr_2NP)_2CR(OH)Fe_2(CO)_6$ (XIV: R = Me, n-Bu) after quenching with an acid. However, the analogous reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with the more reactive t-butyllithium was found to give a complicated reaction mixture from which the corresponding alcohol could not be isolated.



(XIV)

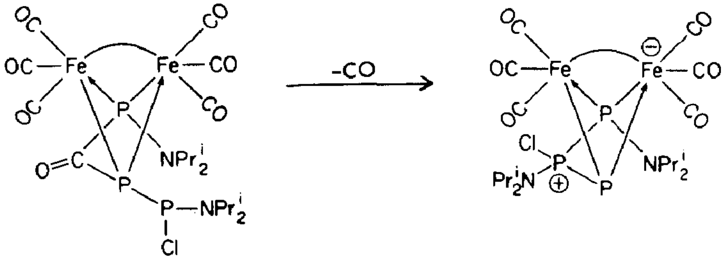
A property of ketones lacking hydrogens bonded to α-carbon atoms is their reduction by active metals to radical anions (i.e., ketyls) which can then couple to form dimers (e.g., pinacols). The phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) is similarly reactive towards reduction with sodium amalgam in tetrahydrofuran at ambient temperature. Relatively little color change occurs during this reaction but the ^{31}P NMR spectrum after 10 min indicates replacement of the singlet δ 225.6 ppm resonance of (i-$Pr_2NP)_2COFe_2(CO)_6$ with a mixture of approximately equal quantities of two products, a symmetrical anion exhibiting a singlet resonance at δ 212 ppm and an unsymmetrical anion exhibiting two coupled doublet ^{31}P resonances at δ 207 and 167 ppm with $|^1J(P-P)|$ 61 Hz [21].

After destroying the symmetrical anion with a minimum amount of CF_3CO_2H, addition of $[(Ph_3P)_2N]Cl$ gives a solid salt of the unsymmetrical anion, shown to have the stoichiometry $[(Ph_3P)_2N]$[i-$Pr_2NPCOPFe_2(CO)_6]$ by elemental analyses and integration of the methyl resonance relative to the phenyl resonance in the proton NMR spectrum [21]. This suggests that the major result of the reaction of (i-$Pr_2NP)_2COFe_2(CO)_6$ with sodium amalgam is the reductive cleavage of one of the diisopropylamino groups to give the unsymmetrical anion [i-$Pr_2NPCOPFe_2(CO)_6]^-$ having structure XV. This structure for the unsymmetrical anion retaining the phosphorus-bridging carbonyl group is also supported by its reaction with trimethyltin chloride to give the unsymmetrical phosphorus-bridging carbonyl derivative (i-$Pr_2NP)(Me_3SnP)COFe_2(CO)_6$ (XVI). The presence of the phosphorus-bridging carbonyl group in XVI is supported by a strong infrared ν(CO) frequency at 1715 cm^{-1} and a double doublet carbonyl resonance in the ^{13}C NMR spectrum centered at δ 212.5 ppm. Thus in (i-$Pr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl), where the carbonyl group bridges equivalent phosphorus atoms, its ^{13}C resonance is a triplet whereas in (i-$Pr_2NP)(Me_3SnP)COFe_2(CO)_6$ (XVI), where the carbonyl group bridges strongly non-equivalent phosphorus atoms, its ^{13}C resonance is a double doublet. Unfortunately, the available crystals of XVI were of unsuitable quality for a structure determination by X-ray diffraction.



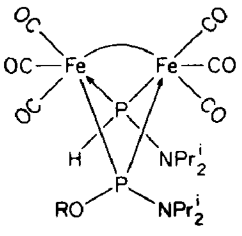
(XV) (XVI)

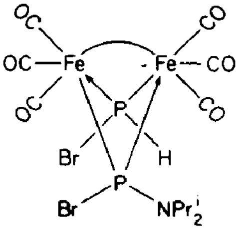
Nucleophilic reactions of the anion [i-$Pr_2NPCOPFe_2(CO)_6]^-$ (XV) with various electrophiles provide a potential source of unusual dialkylaminophosphorus iron carbonyl derivatives. In this connection reaction of XV with i-Pr_2NPCl_2 was found to give a novel triphosphorus derivative of stoichiometry [(i-$Pr_2NP)$(i-$Pr_2N)(Cl)PP]$-$Fe_2(CO)_6$ shown by X-ray diffraction to have the unusual structure XVII containing a tricoordinate phosphorus atom bonded to both iron atoms and a tetracoordinate phosphorus atom bonded to no iron atoms. The presence of the strongly pyramidal tricoordinate phosphorus atom suggests that XVII could serve as a ligand by bonding to transition metal fragments such as $Fe(CO)_4$ or $Cr(CO)_5$ although this possibility has not yet been investigated. The formation of XVII from [i-$Pr_2NPCOPFe_2(CO)_6]^-$ (XV) and i-Pr_2NPCl_2 is expected to involve a phosphorus-bridging carbonyl intermediate (i-$Pr_2NP)$(i-$Pr_2NP(Cl)P)COFe_2(CO)_6$ (XVIII) analogous to (i-$Pr_2NP)(Me_3SnP)COFe_2(CO)_6$ (XVI) obtained from [i-$Pr_2NPCOPFe_2(CO)_6]^-$ and Me_3SnCl as discussed above. Attack of the uncomplexed trivalent phosphorus atom in XVIII on the phosphorus atom to which it is not directly bonded with concurrent displacement of the phosphorus-bridging carbonyl group could then lead to the observed [(i-Pr_2NP)(i-Pr_2N)(Cl)PP]$Fe_2(CO)_6$ (XVII) as indicated below.

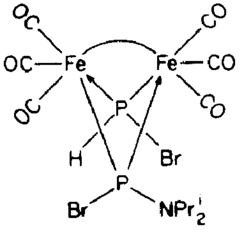


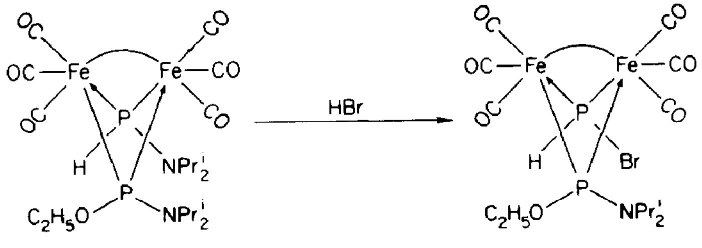
(XVIII) (XVII)

The reactions of (i-Pr_2NP)$_2$CO$Fe_2(CO)_6$ (I: R = isopropyl) involving expulsion of the phosphorus-bridging carbonyl group upon treatment with protic reagents do not have a direct counterpart in the chemistry of typical organic ketones. Such carbonyl expulsion reactions occur upon treatment of (i-Pr_2NP)$_2$CO$Fe_2(CO)_6$ with methanol or ethanol under vigorous reaction conditions (boiling toluene for 2 to 4 days) to give high yields of yellow air-stable (i-Pr_2NPOR)(i-Pr_2NPH)$Fe_2(CO)_6$ (XIX: R = Me, Et) with no evidence for alcoholysis of the diisopropylamino groups [11,21]. Treatment of (i-Pr_2NP)$_2$CO$Fe_2(CO)_6$ with hydrogen bromide in hexane at room temperature follows a similar course to the alcoholysis reactions except that the much more strongly acidic hydrogen bromide reacts under much milder conditions and also cleaves one of the diisopropylamino groups to give (i-Pr_2N-PBr)(BrPH)$Fe_2(CO)_6$. Both of the possible stereoisomers XXs and XXa have been detected by ^{31}P NMR. A similar reaction of (i-Pr_2NPOEt)(i-Pr_2NPH)$Fe_2(CO)_6$ (XIX: R = Et) with hydrogen bromide similarly results in cleavage of one of the diisopropylamino groups to give (i-Pr_2NPOEt)(BrPH)$Fe_2(CO)_6$ (XXI) as indicated below.


(XIX)


(XXs)


(XXa)



(XIX : R = Et) (XXI)

The stereochemistry of XXI has been confirmed by structure determination using X-ray diffraction [21]. This compound is of interest in representing the first example of a bis(phosphido)hexacarbonyldiiron derivative in which the four phosphorus terminal positions are occupied not only by different groups, but by groups bonded to phosphorus through different atoms, namely Br, H, O, and N.

4. Summary

The air-stable phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ (I) are now readily available from reactions of $Na_2Fe(CO)_4$ with sterically hindered R_2NPCl_2 derivatives in diethyl ether solution. Such reactions necessarily involve migration of a carbonyl group from iron to phosphorus. The ketone-like reactivity of the phosphorus-bridging carbonyl group in $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ is indicated by its reactions with $NaBH_4$ and with RLi (R = Me, n-Bu) to give the corresponding alcohols $(i\text{-}Pr_2NP)_2C(R)(OH)Fe_2(CO)_6$ (R = H, Me, n-Bu). Reduction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ gives a product of stoichiometry "$(i\text{-}Pr_2NP)_2CH_2Fe_2(CO)_6$" shown by X-ray structure determination to be $(i\text{-}Pr_2NPCHPHN\text{-}i\text{-}Pr_2)Fe_2(CO)_6$ in which an Fe–P bond has broken and a new Fe–C bond has formed. Reduction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion $[i\text{-}Pr_2NPCOPFe_2(CO)_6]^-$, which forms novel products upon reactions with certain electrophiles such as Me_3SnCl and $i\text{-}Pr_2NPCl_2$. Reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with alcohols ROH (R = Me, Et) and with HBr results in expulsion of the phosphorus-bridging carbonyl group to give $(i\text{-}Pr_2NPOR)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ and $(i\text{-}Pr_2NPBr)(HPBr)Fe_2(CO)_6$, respectively.

Acknowledgment

We are indebted to the Air Force Office of Scientific Research for partial support of this research at the University of Georgia during the period 1985-1987.

References

1 L. Mond, C. Langer, and F. Quincke, J. Chem. Soc., 57 (1890) 749.
2 R.B. King and N.D. Sadanani, Syn. React. Inorg. Metal-Org. Chem. 15 (1985) 149.
3 R.B. King and N.D. Sadanani, Inorg. Chem., 24 (1985) 3136.
4 R.B. King and N.D. Sadanani, J. Org. Chem., 50 (1985) 1719.
5 E. Niecke and R. Rüger, Angew. Chem. Int. Ed. Engl., 22 (1983) 155.
6 A.H. Cowley, J.E. Kilduff, J.G. Lasch, N.C. Norman, M. Pakulski, F. Ando, and T.C. Wright, Organometallics, 3 (1984) 1044.
7 K.M. Flynn, M.M. Olmstead, and P.P. Power, J. Am. Chem. Soc., 105 (1983) 2085.
8 K.M. Flynn, B.D. Murray, M.M. Olmstead, and P.P. Power, J. Am. Chem. Soc., 105 (1983) 7460.
9 K.M. Flynn, H. Hope, B.D. Murray, M.M. Olmstead, and P.P. Power, J. Am. Chem. Soc., 105 (1983) 7751.
10 K.M. Flynn, R.A. Bartlett, M.M. Olmstead, and P.P. Power, Organometallics, 5 (1986) 813.
11 R.B. King, F.-J. Wu, N.D. Sadanani, and E.M. Holt, Inorg. Chem., 24 (1985) 4449.
12 R.L. De, D. Wolters, and H. Vahrenkamp, Z. Naturforsch B, 41 (1986) 283.
13 L. Weber, K. Reizig, and R. Boese, Angew. Chem. Int. Ed. Engl., 25 (1986) 755.
14 L. Weber, K. Reizig, D. Bungardt, and R. Boese, Chem. Ber., 120 (1987) 1421.
15 R.B. King, F.-J. Wu, and E.M. Holt, J. Am. Chem. Soc., 109 (1987) 7764.
16 R. Mathieu, A.-M. Caminade, J.-P. Majoral, S. Attali, and M. Sanchez, Organometallics, 5 (1986) 1914.
17 N.S. Nametkin, B.I. Kolobkov, V.D. Tyurin, A.N. Muratov, A.I. Nekhaev, M. Mavlonov, A.Ya. Sideridu, G.G. Aleksandrov, A.V. Lebedev, M.T. Tashev, and H.B. Dustov, J. Organomet. Chem., 276 (1984) 393.

18 R.B. King, F.-J. Wu, and E.M. Holt, J. Organomet. Chem., 314 (1986) C27.

19 R.B. King, F.-J. Wu, and E.M. Holt, Inorg. Chem., 25 (1986) 1733.

20 J.O. Halford, J. Chem. Phys., 24 (1956) 830.

21 R.B. King, F.-J. Wu, and E.M. Holt, J. Am. Chem. Soc., 110 (1988) 2775.

22 D. Seyferth, G.B. Womack, L.-C. Song, M. Cowie, and B.W. Hames, Organometallics, 2 (1983) 928.

23 D. Seyferth, G.B. Womack, M. Cowie, and B.W. Hames, Organometallics, 2 (1983) 1696.

24 D. Seyferth, G.B. Womack, M.K. Gallagher, M. Cowie, B.W. Hames, J.P. Fackler, Jr., and A.M. Mazany, Organometallics, 6 (1987) 283.

25 D. Seyferth, T.G. Wood, J.P. Fackler, Jr., and A.M. Mazany, Organometallics, 3 (1984) 1121.