NOVEL DIALKYLAMINO DERIVATIVES OF PHOSPHORUS AND SILICON(U) GEORGIA UNIV ATHENS DEPT OF CHEMISTRY R B KING 19 OCT 87 AFOSR-TR-87-1691 AFOSR-84-0050
NOVEL DIALKYLAMINO DERIVATIVES OF PHOSPHORUS AND SILICON

Major achievements from this research project include the preparation and characterization of new types of dialkylaminophosphorus derivatives and their metal carbonyl complexes. Reductions with LiAlH₄ of dialkylaminodichlorophosphines, R₂NPCl₂, having sufficiently large dialkylamino groups were found to lead to the corresponding dialkylaminophosphines, R₂NPH₂ (R₂N = dicyclohexylamino and 2,2,6,6-tetramethylpiperidino) as very air-sensitive liquids. Dehalogenation of R₂NPCl₂ (R= isopropyl or cyclohexyl) with magnesium in tetrahydrofuran was found to give the corresponding cyclotetraphosphines (R₂N)₄P₄; the corresponding biphosphines

(Continued on back page)
(iPr2N)2P2X2 (X = Cl and Br) can be isolated from reactions of iPr2NPX2 with more limited quantities of magnesium. Reactions of R2NPCl2 (R = isopropyl, cyclohexyl) with Na2Fe(CO)4 were found to give the phosphorus-bridging carbonyl derivatives (R2NP)2COFe2(CO)6 as the major products in diethyl ether solution and the triphosphine complexes (R2NP)3Fe2(CO)6 as the major products in tetrahydrofuran solution (R = isopropyl or cyclohexyl). Treatment of (iPr2NP)2COFe2(CO)6 with NaBH4 in methanol was found to result in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol (iPr2NP)2CHOFe2(CO)6. Similar treatment of (iPr2NP)2COFe2(CO)6 with LiAlH4 in diethyl ether was found to result in more extensive reduction to give a product shown by X-ray diffraction to be (iPr2NPHCHPNiPr2)Fe2(CO)8 in which an iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of (iPr2NP)2COFe2(CO)6 with the alkylolithiums RLi (R = Me, nBu) was found to result in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols (iPr2NP)2COFe2(CO)6. Reactions of (iPr2NP)2COFe2(CO)6 with the alcohols ROH (R = Me, Et) under relatively vigorous conditions result in expulsion of the phosphorus-bridging carbonyl groups to give yellow (iPr2NPOR)(iPr2NPH)Fe2(CO)8. Reactions of the triphosphine complex (iPr2NP)3Fe2(CO)6 with hydrogen halides or with alcohols in the presence of catalytic acetic acid at elevated temperatures were found to result in selective cleavage of the diisopropylamino group attached to the center phosphorus atom of the triphosphine chain to give (iPr2NP)2P(X)Fe2(CO)6 (X = Cl, Br, OMe, OEt). Reactions of (iPr2NP)2P(Cl)Fe2(CO)6 with NaMn(CO)5 and with (THF)Cr(CO)5 give the heterobimetallic derivatives (iPr2NP)2P[Mn(CO)5]Fe2(CO)6 and (iPr2NP)2P(Cl)[Cr(CO)5]Fe2(CO)6, respectively. The readily available ligand (iPr2N)2PH reacts with (THF)M(CO)n and with (THF)Mn(CO)2C5H5 to give the complexes (iPr2N)2PHM(CO)n (n = 4, M = Fe; n = 5, M = Cr, Mo, W) and (iPr2N)2PHMn(CO)2C5H5, respectively. In general these (iPr2N)2PH complexes react rapidly with the hydrogen halides HX (X = Cl, Br) to cleave selectively in good yield one of the two diisopropylamino groups to give the corresponding iPr2NP(H)X complexes. Attempts to prepare novel dialkylaminosilicon and dialkylaminoboron derivatives by dehalogenations of (CH2)3(NCMe3)2SiCl2 and R2NBBr2 using alkali metals, magnesium, or (Me3Si)2Hg did not lead to tractable products in significant quantities.
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NOVEL DIALKYLAMINO DERIVATIVES OF PHOSPHORUS AND SILICON

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Dr. R. B. King

Regents' Professor of Chemistry

University of Georgia

Athens

Georgia 30602

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PERSONNEL ASSOCIATED WITH THIS RESEARCH PROGRAM

(1) Dr. R. B. King, Regents' Professor of Chemistry and Principal Investigator
   January 1, 1984, to September 30, 1987

(2) Dr. N. D. Sadanani, Postdoctoral Associate
   January 1, 1984, to March 31, 1985

(3) Dr. Mario Grenz, Postdoctoral Associate
   September 1, 1984, to August 31, 1985

(4) Dr. Gayatri Chorghade, Postdoctoral Associate
   October 1, 1985, to September 30, 1987

(5) Mr. (now Dr.) Wen-Ker (Martin) Fu, Graduate Student
   January 1, 1984, to August 31, 1985

(6) Mr. (now Dr.) Feng-Jung Wu, Graduate Student
   November 1, 1984, to December 31, 1986

(7) Mr. S. Mukhopadhyay, Graduate Student
   June 1, 1984, to November 30, 1984
INTRODUCTION

The original scientific objective of this basic research program was the understanding of the synthesis and chemical reactivity of dialkylamino derivatives of phosphorus and silicon. Such compounds are of potential importance as intermediates in the manufacture of materials of possible value to the Air Force in diverse applications including antioxidants, lubricity agents, elastomers, flame retardants, fuel cell catalysts, thermally stable polymers, and refractory materials.

This project originated from the principal investigator's previous work in synthetic organophosphorus chemistry. His active research in this area was initiated in late 1968 under support from the Air Force Office of Scientific Research. Initial achievements of this project included the development of new methods for preparing chelating polyphosphine ligands which have been used by coordination chemists throughout the world. A more recent project on organophosphorus chemistry, also funded by the Air Force Office of Scientific Research and initiated in early 1981, focused on polyphosphorus compounds containing phosphorus-nitrogen bonds. This project resulted in the discovery of efficient routes for the preparation of certain \((R_2N)_2PH\), \(R_2NPH_2\), and \((R_2NP)_4\) derivatives. The studies on the preparation and properties of the latter two types of phosphorus-nitrogen compounds were completed in the initial phases of the current project. The use of LiAlH\(_4\) to form the P-H bonds in the syntheses of \((R_2N)_2PH\) and \(R_2NPH_2\) derivatives also led to the formation of a novel volatile dialkylaminophosphorus-aluminum hydride derivative, probably \((Et_2N)_2PAiH_4\), which is the focus of a joint proposal by Prof. Michael Norton and the principal investigator on the chemical vapor deposition of aluminum phosphide and other Group III-V materials. This proposal was recently submitted to materials science divisions of the Army Research Office and the Department of Energy.

A productive aspect of this research project arose from merging the principal
investigator's interests in dialkylaminophosphorus chemistry and metal carbonyl chemistry. Numerous unusual types of dialkylaminophosphorus metal carbonyls were prepared and characterized during the course of this research project. The most exciting such compounds were derivatives of the types \((R_2NP)_2\text{COFe}_2(\text{CO})_6\) (I: \(R = \) isopropyl or cyclohexyl or \(R_2N = 2,2,6,6\)-tetramethylpiperidino) containing a novel phosphorus-bridging carbonyl group. Such compounds may be considered to be phosphorus analogues of organic ketones. These compounds are major products from reactions of \(\text{Na}_2\text{Fe(CO)}_4\) with \(R_2\text{NPCl}_2\) derivatives provided that the \(R_2N\) group is sufficiently large and the reaction is carried out in diethyl ether. Furthermore, the reactions of \(\text{Na}_2\text{Fe(CO)}_4\) with \(R_2\text{NPCl}_2\) derivatives under a variety of conditions yielded a variety of interesting products and in addition raised a number of questions of mechanistic interest. The availability of \((i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) (I: \(R = \) isopropyl) in 30 gram quantities from a single reaction of \(\text{Na}_2\text{Fe(CO)}_4\) with \(i\text{Pr}_2\text{NPCl}_2\) has made this compound available in sufficient quantities for a study of the chemical reactivity of the phosphorus-bridging carbonyl group. Thus ketone-like behavior was noted in the reactions of \((i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) with \(\text{NaBH}_4\) and with alkyllithiums to give alcohols of the type \((i\text{Pr}_2\text{NP})_2\text{C}(\text{R})(\text{OH})\text{Fe}_2(\text{CO})_6\) (\(R = \) H, Me, nBu, etc.).

\[
\begin{align*}
\text{O} & \quad \text{Fe} & \quad \text{OC} \\
\text{OC} & \quad \text{Fe} & \quad \text{CO} \\
\text{OC} & \quad \text{Fe} & \quad \text{CO} \\
\text{OC} & \quad \text{Fe} & \quad \text{CO} \\
\text{OC} & \quad \text{Fe} & \quad \text{CO} \\
\text{NR}_2 & \quad \text{P} & \quad \text{NR}_2
\end{align*}
\]

I

In terms of scientific publications this research project was very productive leading to 20 publications in major scientific journals and seven presentations at key scientific meetings. Funds for the continuation of aspects of this project involving dialkylaminophosphorus metal carbonyl derivatives are currently being sought from the National Science Foundation.
NEW RESULTS FROM THIS RESEARCH PROGRAM

(1) Dialkylaminophosphines, \( R_2\text{NPH}_2 \)

Reductions with LiAlH\(_4\) of dialkylaminodichlorophosphines,\(^4\) \( R_2\text{NPCl}_2 \), having sufficiently large dialkylamino groups were found to lead to the corresponding dialkylaminophosphines, \( R_2\text{NPH}_2 \) (\( R_2\text{N} = \text{dicyclohexylamino} \) and 2,2,6,6-tetramethylpiperidino), as very air-sensitive liquids characterized by proton and phosphorus-31 NMR spectroscopy.\(^2,6\) These dialkylaminophosphines react with \( (\text{THF})\text{M(CO)}_n \) (\( \text{M} = \text{Cr and W, } n = 5; \text{M} = \text{Fe, } n = 4 \)) to give the corresponding metal carbonyl complexes \( R_2\text{NPH}_2\text{M(CO)}_n \). The complexes of the type \( R_2\text{NPH}_2\text{M(CO)}_5 \) (\( \text{M} = \text{Cr and W} \)) are yellow, sublimable solids, which are considerably more stable than the free \( R_2\text{NPH}_2 \) ligands. Reduction of diisopropylaminodichlorophosphine, \( \text{iPr}_2\text{NPCl}_2 \), with LiAlH\(_4\) gives a solution shown by phosphorus-31 NMR to contain \( \text{iPr}_2\text{NPH}_2 \), but this product decomposes upon attempted isolation. However, the metal carbonyl complexes \( \text{iPr}_2\text{NPH}_2\text{M(CO)}_5 \) (\( \text{M} = \text{Cr and W} \)) can be isolated as relatively stable yellow sublimable solids by the LiAlH\(_4\) reduction of the corresponding \( \text{iPr}_2\text{NPCl}_2\text{M(CO)}_5 \) complexes.\(^2,6\)

(2) Tetraids(dialkylamino)cycotetraphosphines, \( (R_2\text{N})_4\text{P}_4 \), and Bis(dialkylamino)dihalobiphosphines, \( (R_2\text{N})_2\text{P}_2\text{X}_2 \)

Dehalogenation of \( R_2\text{NPCl}_2 \) (\( \text{R} = \text{isopropyl or cyclohexyl} \))\(^4\) with magnesium in tetrahydrofuran was found to give the corresponding cycotetraphosphines \( (R_2\text{N})_4\text{P}_4 \); the corresponding biphosphines \( (\text{iPr}_2\text{N})_2\text{P}_2\text{X}_2 \) (\( \text{X} = \text{Cl and Br} \)) can be isolated from reactions of \( \text{iPr}_2\text{NPX}_2 \) with more limited quantities of magnesium.\(^5\) Dehalogenations with magnesium of \( R_2\text{NPCl}_2 \) derivatives having \( R_2\text{N} \) groups smaller than diisopropylamino lead to redistribution of the dialkylamino groups giving \( (R_2\text{N})_2\text{P-P(NR}_2)_2 \) (\( R_2\text{N} = \text{piperidino} \)) or \( (R_2\text{N})_3\text{P} \) (\( R_2\text{N} = \text{diethylamino} \) or dimethylamino). Such redistribution reactions can be suppressed but not eliminated by using the
homogeneous dehalogenating agent \((\text{Me}_3\text{Si})_2\text{Hg}\) in hydrocarbon solvents. The steric bulk of the diisopropylamino groups in \((\text{iPr}_2\text{N})_4\text{P}_4\) reduces its chemical reactivity relative to other cyclotetraphosphines; thus \((\text{iPr}_2\text{N})_4\text{P}_4\) is unreactive towards oxygen, carbon disulfide, potassium metal, and various metal carbonyls \(\text{e.g., } \text{Cr(CO)}_6, \text{Mo(CO)}_6, \text{and } \text{Fe}_2(\text{CO})_9\) under conditions where other cyclotetraphosphines react with these reagents. However, the \(\text{P}_4\) ring in \((\text{iPr}_2\text{N})_4\text{P}_4\) is cleaved under mild conditions by hydrogen chloride as well as by bromine and iodine.

(3) Dialkylaminophosphorus Metal Carbonyl Derivatives

Reactions of \(\text{R}_2\text{NPCl}_2\) \((\text{R} = \text{isopropyl, cyclohexyl})\) with \(\text{Na}_2\text{Fe(CO)}_4\) were found to give the orange phosphorus-bridging carbonyl derivatives \((\text{R}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) \((\text{I})\) as the major products in diethyl ether solution and the orange triphosphine complexes \((\text{R}_2\text{NP})_3\text{Fe}_2(\text{CO})_6\) \((\text{II})\) as the major products in tetrahydrofuran solution.\(^8,12,14,15,18,19\) The structures of both products \((\text{R} = \text{isopropyl})\) have been confirmed by X-ray diffraction.\(^8,12,14,15\) Minor products from the reaction of \(\text{iPr}_2\text{NPCl}_2\) with \(\text{Na}_2\text{Fe(CO)}_4\) in tetrahydrofuran include \((\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) \((\text{I}: \text{R} = \text{isopropyl})\) and the trinuclear derivative \((\text{iPr}_2\text{NP})_2\text{Fe}_3(\text{CO})_9\) \((\text{III}: \text{R} = \text{isopropyl})\) as well as orange \((\text{iPr}_2\text{NP})_3\text{COFe}_2(\text{CO})_6\) shown by X-ray diffraction to have structure \(\text{IV} (\text{R} = \text{isopropyl})\) similar to that of \((\text{iPr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6\) \((\text{II}: \text{R} = \text{isopropyl})\) but with a carbonyl group inserted into the triphosphine chain.\(^12,14,15\) Reaction of \(\text{Et}_2\text{NPCl}_2\) with \(\text{Na}_2\text{Fe(CO)}_4\) in diethyl ether gives deep orange \((\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{12}\) below \(0^\circ\text{C}\) and orange \((\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{11}\) at room temperature shown by X-ray crystallography\(^13,14,15\) to have structures \(\text{V} \text{and VI}, \text{respectively}, \text{arising from migrations of diethylamino groups. Reactions of the binuclear iron carbonyl anion } \text{Na}_2\text{Fe}_2(\text{CO})_8 \text{with } \text{R}_2\text{NPCl}_2 \text{derivatives} \ (\text{R} = \text{methyl, ethyl, isopropyl, cyclohexyl or } \text{R}_2\text{N} = \text{piperidino, 2,6-dimethylpiperidino, 2,2,6,6-tetramethylpiperidino}) \text{give the trinuclear derivatives } \text{(R}_2\text{NP})_2\text{Fe}_3(\text{CO})_9 \text{(III)} \text{and } \text{R}_2\text{NPFe}_3(\text{CO})_{10} \text{(VII). No evidence was obtained for the formation of any } \text{(R}_2\text{NP})_2\text{COFe}_2(\text{CO})_6 \text{(I)} \text{or } \text{(R}_2\text{NP})_3\text{Fe}_2(\text{CO})_6 \text{(II) derivatives in}
significant quantities from any of the reactions of \( \text{Na}_2\text{Fe}_2(\text{CO})_8 \) with \( \text{R}_2\text{NPCl}_2 \) derivatives.

The facile preparation of air-stable \((\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) \((\text{I}; \text{R} = \text{isopropyl})\) in 30 gram quantities from the reaction of \( \text{Na}_2\text{Fe}(\text{CO})_4 \) with \( \text{iPr}_2\text{NPCl}_2 \) in diethyl ether\(^{8,12,14,15,18}\) has prompted a detailed study of the chemical reactivity of this compound which is of particular interest because of the presence of the unusual phosphorus-bridging carbonyl group\(^{8,16}\). Thus treatment of \((\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) \((\text{I}; \text{R} = \text{isopropyl})\) with \( \text{NaBH}_4 \) in methanol was found to result in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol \((\text{iPr}_2\text{NP})_2\text{CHOFe}_2(\text{CO})_6\) \((\text{VIII}; \text{R} = \text{H})\). Similar treatment of \((\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6\) with \( \text{LiAlH}_4 \) in diethyl ether was found to result in more extensive reduction to give a dark orange product of stoichiometry "\((\text{iPr}_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6\)" shown, however, by X-ray diffraction to be \((\text{iPr}_2\text{NP})\text{CHPNiPr}_2(\text{Fe}_2(\text{CO})_6\) \((\text{IX})\) in which an
iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of (iPr$_2$NP)$_2$COFe$_2$(CO)$_6$ with the alkyllithiums RLi (R = Me, nBu) was found to result in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols (iPr$_2$NP)$_2$C(R)(OH)Fe$_2$(CO)$_6$ (VIII: R = Me or nBu). Reduction of (iPr$_2$NP)$_2$COFe$_2$(CO)$_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion [iPr$_2$NPCOPFe$_2$(CO)$_6$]$^-$ which can be isolated as its orange bis(triphenylphosphine)iminium salt or as the light orange trimethyltin derivative (iPr$_2$N)(Me$_3$Sn)P$_2$COFe$_2$(CO)$_6$ (X) still containing a phosphorus-bridging carbonyl group. Reaction of [iPr$_2$NPCOPFe$_2$(CO)$_6$]$^-$ with iPr$_2$NPCl$_2$ results in rearrangement with expulsion of the phosphorus-bridging carbonyl group to give orange [iPr$_2$NP(iPr$_2$N)(Cl)PP]Fe$_2$(CO)$_6$

shown by X-ray diffraction to have the unusual structure XI. Reactions of (iPr$_2$NP)$_2$COFe$_2$(CO)$_6$ (I: R = isopropyl) with the alcohols ROH (R = Me, Et) under relatively vigorous conditions results in expulsion of the phosphorus-bridging carbonyl
groups to give yellow \((\text{iPr}_2\text{N} \text{P} \text{O} \text{R}) (\text{iPr}_2\text{N} \text{PH}) \text{Fe}_2(\text{CO})_6\). Reaction of \((\text{iPr}_2\text{N} \text{P})_2\text{COFe}_2(\text{CO})_6\) with hydrogen bromide results in expulsion of the phosphorus-bridging carbonyl group and selective cleavage of one of the diisopropylamino groups to give orange \((\text{iPr}_2\text{NPBr}) (\text{HPBr}) \text{Fe}_2(\text{CO})_6\); both of the possible stereoisomers of this compound have been detected by phosphorus-31 NMR spectroscopy and one has been isolated in the pure state. Reaction of \((\text{iPr}_2\text{N} \text{POEt}) (\text{iPr}_2\text{N} \text{PH}) \text{Fe}_2(\text{CO})_6\) with hydrogen bromide results in selective cleavage of one of the two diisopropylamino groups to give orange \((\text{iPr}_2\text{N} \text{POEt}) (\text{HPBr}) \text{Fe}_2(\text{CO})_6\) shown by X-ray crystallography to have structure XII, which is the first example of a bis(phosphido)hexacarbonyldiiron derivative with four different terminal groups (iPr, EtO, H, and Br).

The triphosphine complex \((\text{iPr}_2\text{N} \text{P})_3\text{Fe}_2(\text{CO})_6\) (II: \(R = \text{isopropyl}\)) is also available in quantity from the reaction of \(\text{Na}_2\text{Fe}(\text{CO})_4\) with \(\text{iPr}_2\text{N} \text{PCl}_2\) if the reaction is carried out in tetrahydrofuran rather than diethyl ether.\textsuperscript{12,14,15,19} Some studies on the chemical reactivity of this interesting substance were therefore carried out.\textsuperscript{12,17} Reactions of \((\text{iPr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6\) (II: \(R = \text{isopropyl}\)) with hydrogen halides were found to result in selective cleavage of the diisopropylamino group attached to the center phosphorus atom of the triphosphine chain to give orange \((\text{iPr}_2\text{NP})_2\text{P}(X) \text{Fe}_2(\text{CO})_6\) (XIII: \(X = \text{Cl}, \text{Br}\)). The complex \((\text{iPr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6\) (II: \(R = \text{isopropyl}\)) was found to react analogously with the boiling alcohols \(\text{ROH} (R = \text{Me}, \text{Et})\) in the presence of catalytic acetic acid to give orange \((\text{iPr}_2\text{NP})_2\text{P}(\text{OR}) \text{Fe}_2(\text{CO})_6\) (XIII: \(X = \text{OMe}, \text{OEt}\)). The derivative \((\text{iPr}_2\text{NP})_2\text{P} (\text{Cl}) \text{Fe}_2(\text{CO})_6\) (XIII: \(X = \text{Cl}\)) is a useful precursor to other
triphosphine diiron hexacarbonyl derivatives through nucleophilic substitution of the chlorine attached to the central phosphorus atom. Thus treatment of (iPr₂NP)₂P(Cl)Fe₂(CO)₆ with NaBH₄ in tetrahydrofuran solution gives (iPr₂NP)₂P(H)Fe₂(CO)₆ (XIII: X = H). However, reduction of (iPr₂NP)₂P(Cl)Fe₂(CO)₆ with LiAlH₄ results in phosphorus-phosphorus bond cleavage to give (iPr₂NP)₂Fe₂(CO)₆. Nucleophilic substitution of the chlorine atom in (iPr₂NP)₂P(Cl)Fe₂(CO)₆ (XIII: X = Cl) with NaMn(CO)₅ provides a route to the heterobimetallic derivative (iPr₂NP)₂P[Mn(CO)₅]Fe₂(CO)₆ (XIII: X = Mn(CO)₅). The heterobimetallic derivatives (iPr₂NP)₂P(Cl)Cr(CO)₅Fe₂(CO)₆, (iPr₂NP)₂P(H)[Cr(CO)₅]Fe₂(CO)₆, and (iPr₂NP)₂P(H)[Fe(CO)₄]Fe₂(CO)₆ can be obtained by complexation of the central phosphorus atoms in (iPr₂NP)₂P[H]Fe₂(CO)₆ (XIII: X = H, Cl) with (THF)Cr(CO)₅ and Fe₂(CO)₉/THF.¹⁷

The readily available bis(dialkylamino)phosphine, (iPr₂N)₂PH, is an interesting ligand for metal carbonyl chemistry since after complexation the phosphorus-nitrogen bonds can be selectively cleaved by acidic reagents to give metal carbonyl complexes of organophosphorus ligands not available in the uncomplexed state.¹⁷ The complexes (iPr₂N)₂PHM(CO)ₙ (n = 4, M = Fe; n = 5, M = Cr, Mo, W) and (iPr₂N)₂PHMn(CO)₂C₅H₅ are obtained as air-stable sublimable hydrocarbon-soluble solids by reactions of (iPr₂N)₂PH with the corresponding tetrahydrofuran complexes (THF)M(CO)ₙ and (THF)Mn(CO)₂C₅H₅.¹³ In general these (iPr₂N)₂PH complexes react rapidly with the hydrogen halides HX (X = Cl, Br) to cleave selectively in good
yield one of the two diisopropylamino groups to give the corresponding iPr_2NP(H)X complexes; the exception to this reactivity pattern is the reaction of (iPr_2N)_2PHMn(CO)_2C_5H_5 with HBr, which proceeds all the way to Br_2P(H)Mn(CO)_2C_5H_5. Dehydrochlorination of iPr_2NP(H)ClFe(CO)_4 with excess triethylamine gives a low yield of the phosphorus-bridging carbonyl derivative (iPr_2NP)_2COFe(CO)_5 (I: R = isopropyl) discussed in detail above. The reactions of (iPr_2N)_2PH with the metal-metal bonded metal carbonyls Mn_2(CO)$_{10}$ and Co$_2$(CO)$_8$ have been shown to follow a different course than those outlined above. Thus, photolysis of (iPr_2N)_2PH with Mn_2(CO)$_{10}$ in tetrahydrofuran solution results in cleavage of the phosphorus-hydrogen bond to give yellow air-stable sublimable [μ-(iPr_2N)_2P] (μ-H)Mn_2(CO)$_8$ shown by X-ray diffraction to have structure XIV in which a manganese-manganese bond in bridged symmetrically by both a hydrogen atom and a bis(diisopropylamino)phosphido group. One of the two diisopropylamino groups in XIV is selectively cleaved with the hydrogen halides HX (X = Cl, Br) to give the corresponding complex (μ-iPr_2NPX)(μ-H)Mn_2(CO)$_8$ shown by its infrared ν(CO) and NMR spectra to have a structure analogous to XIV. Reaction of (iPr_2N)$_2$PH with Co$_2$(CO)$_8$ in hexane at ambient temperature gives a complex mixture of relatively unstable products from which paramagnetic (2.0 μ_B) black air-sensitive crystalline (μ$_3$-iPr$_2$NP)Co$_3$(CO)$_9$ can be isolated after chromatography on silica gel. X-ray crystallography on this complex indicates the expected structure XV with a PCo$_3$ tetrahedron.

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\text{XIV} \quad \text{XV}
\]
The reactivity of the phosphorus-halogen bonds in the \( \text{iPr}_2 \text{NP(H)XM(CO)}_n \) derivatives towards nucleophiles provides a novel approach for the synthesis of interesting heterobimetallic derivatives.\(^7\,11\) Thus reactions of \( \text{iPr}_2 \text{NP(H)XM(CO)}_5 \) (\( X = \text{Br}, \text{M} = \text{Cr}; X = \text{Cl}, \text{M} = \text{Mo, W} \)) and \( \text{iPr}_2 \text{NP(H)ClMn(CO)}_2 \text{C}_5 \text{H}_5 \) with \( \text{NaFe(CO)}_2 \text{C}_5 \text{H}_5 \) result in nucleophilic substitution of the phosphorus-bonded halogen with the iron nucleophile to give relatively good yields of deep orange \( \text{C}_5 \text{H}_5 \text{Fe(CO)}_2 \text{PH(NiPr}_2 \text{M(CO)}_5 \) and deep red \( \text{C}_5 \text{H}_5 \text{Fe(CO)}_2 \text{PH(NiPr}_2 \text{Mn(CO)}_2 \text{C}_5 \text{H}_5 \), respectively, which do not contain metal-metal bonds. Photolyses of \( \text{C}_5 \text{H}_5 \text{Fe(CO)}_2 \text{PH(NiPr}_2 \text{M(CO)}_5 \) (\( \text{M} = \text{Cr, W} \)) and \( \text{C}_5 \text{H}_5 \text{Fe(CO)}_2 \text{PH(NiPr}_2 \text{Mn(CO)}_2 \text{C}_5 \text{H}_5 \) in pentane or cyclohexane solution result in rapid decarbonylation to give black \( \text{C}_5 \text{H}_5 \text{FeM(CO)}_6 \text{PH(NiPr}_2 \) (\( \text{M} = \text{Cr, W} \)) and \( \text{C}_5 \text{H}_5 \text{2FeMn(CO)}_3 \text{PH(NiPr}_2 \), respectively. X-ray diffraction of \( \text{C}_5 \text{H}_5 \text{FeM(CO)}_6 \text{PH(NiPr}_2 \) (\( \text{M} = \text{Cr, W} \)) indicates structures of the type XVI (\( \text{M} = \text{Cr, W} \)) in which a heteronuclear Fe-M bond is bridged by both a carbonyl group and a \( \text{iPr}_2 \text{NPH} \) phosphido group. A related structure XVII is postulated for \( \text{(C}_5 \text{H}_5 \text{2FeMn(CO)}_3 \text{PH(NiPr}_2 \) on the basis of the observation of two terminal and one bridging \( \nu \text{(CO)} \) frequencies.

(4) Dialkylaminosilicon Derivatives

The general objective of this portion of the project was the preparation of cyclic derivatives of the stoichiometry \([\text{R}_2 \text{N}_2 \text{Si}]_n\). In this connection attempts to dehalogenate \( \text{(CH}_2 \text{)}_3 \text{(NMe}_3 \text{)}_2 \text{SiCl}_2 \) (\( \text{XVIII} \)) and \( \text{R} \text{(iPr}_2 \text{N)} \text{SiCl}_2 \) led to the following observations:
(a) (CH$_2$)$_3$(NCMe)$_3$SiCl$_2$: This dichlorosilane did not appear to react with magnesium metal (boiling tetrahydrofuran), lithium metal (boiling tetrahydrofuran), sodium metal (boiling toluene), (Me$_3$Si)$_2$Hg (pentane at room temperature), LiAlH$_4$ (diethyl ether at room temperature), and Na$_2$Fe(CO)$_4$ (tetrahydrofuran at room temperature). Reactions of (CH$_2$)$_3$(NCMe)$_3$SiCl$_2$ (XVIII) with potassium metal in boiling tetrahydrofuran gave a mixture of unidentified products apparently resulting from cleavage of one or both silicon-nitrogen bonds. Reaction of (CH$_2$)$_3$(NCMe)$_3$SiCl$_2$ with sodium naphthalenide in boiling tetrahydrofuran gave a mixture of unreacted starting material and unidentified products incorporating the naphthalene.

(b) Me(iPr$_2$N)SiCl$_2$: This dichlorosilane did not appear to react with lithium metal in tetrahydrofuran or with (Me$_3$Si)$_2$Hg in a mixture of pentane and hexane. Reactions of Me(iPr$_2$N)SiCl$_2$ with sodium or potassium metal under various conditions appeared to give complex mixtures from which tractable products of interest could not be isolated.

From these experiments the following general conclusions can be drawn:

(a) The introduction of dialkylamino substituents into chlorosilanes makes them very difficult to dehalogenate.

(b) The silicon-nitrogen bond is too readily cleaved to allow forcing conditions for reactions of dialkylaminochlorosilanes with very strong reducing agents.

(c) In some reactions ether solvents such as tetrahydrofuran or diethyl ether are cleaved in significant amounts.

These negative results suggested that reactions of HSiCl$_3$ and H$_2$SiCl$_2$ with...
secondary amines might provide better entries for the preparation of cyclic [(R₂N)₂Si]ₙ derivatives. In this connection the reaction of HSiCl₃ with excess diisopropylamine in boiling hexane was found to give (iPr₂N)₂SiHCl as an air-sensitive colorless liquid, b.p. 112°/1mm. An attempt to prepare (iPr₂N)₂SiFe(CO)₄ by reaction of (iPr₂N)₂SiHCl with Fe₂(CO)₉ did not appear promising and unreacted (iPr₂N)₂SiHCl was identified as the only hexane-soluble silicon compound in the reaction mixture.

We also investigated replacement of the chlorine atoms in (CH₂)₃(NCMe₃)₂SiCl₂, PhMeSiCl₂, and Me(iPr₂N)SiCl₂ with trimethylsilyl groups through reaction with the LiSiMe₃ obtained by treatment of (Me₃Si)₂Hg with lithium metal in a hydrocarbon solvent in order to provide intermediates for the preparation of [(R₂N)₂Si]ₙ derivatives by subsequent photolytic elimination of hexamethyldisilane or trimethylsilane. Mass spectrometric evidence was obtained for the formation of (CH₂)₃(NCMe₃)₂Si(H)SiMe₃ and Me(iPr₂N)Si(SiMe₃)₂ from reactions of this type, but these compounds were not obtained in useful quantities for further chemistry.

(5) Dialkyaminoboron Derivatives

The general objective of this portion of the research project was the preparation of cyclic dialkyaminoboranes of the general formula (R₂NB)ₙ by the dehalogenation of corresponding dialkyaminodihaloboranes. Cyclic dialkyaminoboranes are of potential interest as precursors both to novel boride refractory materials as well as for more efficient syntheses of polyhedral boranes and carboranes for ingredients in high energy materials and high temperature polymers.

Our studies on the dehalogenation of R₂NBX₂ compounds with strong reducing agents can be summarized as follows:

(a) Reaction of Et₂NBBr₂ with excess sodium in boiling toluene gave a liquid product suggested by mass spectrometry to contain cyclic derivatives of the stoichiometries (Et₂NB)ₙ (n = 4, 5, 6, 7). This mixture did not form a chromium carbonyl complex upon reaction with norbornadienetetracarbonylchromium. A similar reaction of
Et₂NBBr₂ with sodium in boiling hexane led to redistribution of diethylamino groups to give (Et₂N)₃B and (Et₂N)₃B·NHEt₂.

(b) Treatment of R₂NBBr₂ (R = isopropyl or R₂N = 2,2,6,6-tetramethylpiperidino) with sodium amalgam at room temperature resulted only in recovery of the starting material.

(c) Reaction of Et₂NBBr₂ with (Me₃Si)₂Hg in toluene solution at low temperatures resulted in a low yield of a complex mixture of products which could not be separated or conclusively identified.
PUBLICATIONS SUPPORTED IN PART BY AIR FORCE GRANT AFOSR-84-0050


(3) King, R. B.; Fu, W.-K.; Holt, E. M. "Bis(diisopropylamino)phosphido and Diisopropylaminophosphinidene Metal Carbonyl Complexes from Reactions of Manganese and Cobalt Carbonyls with Bis(diisopropylamino)phosphine: X-ray Crystal Structures of (iPr₂N)₂PMn₂(CO)₉H and iPr₂NPCo₃(CO)₉," Chem. Comm. 1984, 1439-1440.


2. Bis(diisopropylamino)phosphido and Diisopropylaminophosphinidene Metal  
Carbonyl Complexes from Reactions of Manganese and Cobalt Carbonyls with  

3. Heterobimetallic $\mu_2$-Phosphido Derivatives from Reactions of  
Diisopropylaminohalophosphine Metal Carbonyl Complexes with Sodium  

(12) King, R. B.; Wu, F.-J.; Holt, E. M. "Novel Diisopropylamino Triphosphine  

(13) King, R. B.; Wu, F.-J.; Holt, E. M. "Novel Diethylamino Migrations in the Reaction  
of Diethylaminodichlorophosphine with Sodium Tetracarbonylferrate (-II)," J.  

(14) King, R. B.; Wu, F.-J.; Holt, E. M. "Reactions of Dialkylaminodichlorophosphines  
with Tetracarbonylferrate(-II): Routes to Novel Phosphorus-Bridging Carbonyl  
Derivatives and Triphosphine Complexes," Phosphorus and Sulfur 1987, 30,  
169-172.

(15) King, R. B.; Wu, F.-J.; Holt, E. M. "Dialkylaminophosphorus Metal Carbonyls.  
4. Novel Phosphorus-Bridging Carbonyl Derivatives and Triphosphine Derivatives  
from Reactions of Tetracarbonylferrate(-II) with Dialkylaminodichlorophosphines,"  

5. Chemical Reactivity of the Phosphorus-Bridging Carbonyl Group in  
Carbonylbis(diisopropylaminophosphido)hexacarbonyldiiron," J. Am. Chem. Soc.,  
in press.

6. Chemistry of Diisopropylamino Triphosphine Diiron Hexacarbonyl Derivatives


(20) King, R. B.; Chorghade, G. S. "Dialkylaminophosphorus Metal Carbonyls. 7. Trinuclear Iron Carbonyl Derivatives from Reactions of Disodium Octacarbonyldiferrate with Dialkylaminodichlorophosphines," submitted for publication (J. Organometal. Chem.).
MEETING PRESENTATIONS


American Chemical Society, Denver, Colorado, April, 1987: paper INOR 131 in abstracts.

(7) King, R. B.; Wu, F.-J.; Holt, E. M. "Novel Phosphorus-bridging Carbonyl Derivatives and Triphosphine Derivatives from Reactions of Tetracarbonylferrate (−II) with Dialkylaminodichlorophosphines," presented by R. B. King at the Symposium on Binuclear Complexes with Phosphorus-Donor Bridging Ligands at the 19th Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June, 1986: paper 184 in abstracts.
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