

Preliminary communication

METAL CARBONYL COMPLEXES OF BIS(DIISOPROPYLAMINO)- PHOSPHINE AND DIISOPROPYLAMINOCHLOROPHOSPHINE*

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Summary

Reactions of $(i\text{-Pr}_2\text{N})_2\text{PH}$ with the tetrahydrofuran (THF) metal carbonyl complexes $(\text{THF})\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$), $(\text{THF})\text{Fe}(\text{CO})_4$, and $(\text{THF})\text{Mn}(\text{CO})_2\text{-C}_5\text{H}_5$ give $(i\text{-Pr}_2\text{N})_2\text{PHM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$), $(i\text{-Pr}_2\text{N})_2\text{PHFe}(\text{CO})_4$, and $(i\text{-Pr}_2\text{N})_2\text{PHMn}(\text{CO})_2\text{C}_5\text{H}_5$, respectively. One of the diisopropylamino groups in these complexes can be selectively cleaved with hydrogen chloride to give the complexes $i\text{-Pr}_2\text{NP}(\text{H})\text{ClM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) and $i\text{-Pr}_2\text{NP}(\text{H})\text{ClFe}(\text{CO})_4$ containing the unknown phosphorus compound $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$ as a ligand.

Recently [1,2] we have found that reaction of $(i\text{-Pr}_2\text{N})_2\text{PCl}$ with LiAlH_4 provides a facile preparation of the bis(dialkylamino)phosphine $(i\text{-Pr}_2\text{N})_2\text{PH}$. We now wish to report the first metal carbonyl complexes of this phosphine. These complexes are of particular interest since they undergo facile selective cleavage of one of the diisopropylamino groups to give the corresponding metal carbonyl complexes of the novel chlorophosphine, $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$, which is unknown in the free state. These latter metal complexes are of potential interest because of the reactivity of their chlorine atom towards nucleophilic reagents to give novel organophosphorus derivatives and/or their metal carbonyl complexes.

Table 1 summarizes some important properties of new metal carbonyl derivatives of these ligands that we have prepared up to the present time. The $(i\text{-Pr}_2\text{N})_2\text{-PH}$ complexes listed in the Table are prepared in moderate to good yields by reactions of the ligand at ambient temperature with tetrahydrofuran solutions of the complexes $(\text{THF})\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) [3], $(\text{THF})\text{Fe}(\text{CO})_4$ [4], and $(\text{THF})\text{Mn}(\text{CO})_2\text{C}_5\text{H}_5$ [5] generated by the cited standard methods. The iron complex $(i\text{-Pr}_2\text{N})_2\text{PHFe}(\text{CO})_4$ has also been obtained in modest ($\sim 20\%$) yield by re-

*This paper is dedicated to Prof. Sei Otsuka in recognition of his major contributions to the field of organometallic chemistry.

TABLE I
METAL CARBONYL COMPLEXES OF BIS(DIISOPROPYLAMINO)PHOSPHINE AND DIISOPROPYLAMINOCHLOROPHOSPHINE^a

Compound	Color	M.p. (°C)	Subl. temp. (°C/Torr)	IR $\nu(\text{CO})$ (cm^{-1})	³¹ P NMR		¹ H NMR		
					$\delta(\text{P})$ (ppm)	¹ J(PH) (Hz)	$\delta(\text{P-H})$ (ppm)		
<i>(i-Pr₂N)₂PH complexes</i>									
(<i>i-Pr</i> ₂ <i>N</i>) ₂ PHCr(CO) ₅	yellow	77-78	75/0.01	2060w,1940s,1910vw	91.8	363	7.32		
(<i>i-Pr</i> ₂ <i>N</i>) ₂ PHMo(CO) ₅	yellow	60-62(dec)	80/0.04	2070w,1945s,1918vw	67.0	356	7.43		
(<i>i-Pr</i> ₂ <i>N</i>) ₂ PHW(CO) ₅	yellow	102-103	90/0.04	2066w,1940s,1910vw	41.7	359	7.84		
(<i>i-Pr</i> ₂ <i>N</i>) ₂ PHFe(CO) ₄	yellow	62-63	50/0.15	2043m,1974m,1942s,1932s	93.9	410	7.44		
(<i>i-Pr</i> ₂ <i>N</i>) ₂ PHMn(CO) ₅ Cp	yellow	108-110	80/0.005	1945s,1872s	123.1	381	7.66		
<i>i-Pr₂NP(H)Cl complexes</i>									
<i>i-Pr</i> ₂ <i>NP(H)ClCr(CO)₅</i>	yellow	52-53	55/0.01	2074w,1998w,1957s,1925vw	112.0	376	8.27		
<i>i-Pr</i> ₂ <i>NP(H)ClMo(CO)₅</i>	yellow	66-68	55/0.001	2080w,2000w,1962s,1925vw	83.1	374	8.26		
<i>i-Pr</i> ₂ <i>NP(H)ClW(CO)₅</i>	yellow	75-76	50/0.001	2085w,1995w,1954s,1927vw	50.1	393	8.61		
<i>i-Pr</i> ₂ <i>NP(H)ClFe(CO)₄</i>	red-orange	liquid	104/0.02	2063m,1995m,1965s,1955s	113.3	444	8.35		

^a All of these complexes gave correct analyses for C, H, N, and Cl where applicable.

duction of the reported [6] $(i\text{-Pr}_2\text{N})_2\text{P}(\text{Cl})\text{Fe}(\text{CO})_4$ with LiAlH_4 in diethyl ether. Pure products are isolated from these reactions by crystallization from pentane and/or vacuum sublimation under the conditions listed in Table 1. The complexes $(i\text{-Pr}_2\text{N})_2\text{PHM}(\text{CO})_5$ ($\text{M} = \text{Cr}$ and W) appear to be air stable and all of the complexes listed in Table 1 are much less air-sensitive than the very air-sensitive [1] free ligand $(i\text{-Pr}_2\text{N})_2\text{PH}$.

The most interesting reaction of these $(i\text{-Pr}_2\text{N})_2\text{PH}$ metal carbonyl complexes is the facile selective cleavage of one diisopropylamino group with hydrogen chloride in hexane solution to give the corresponding $i\text{-Pr}_2\text{NP}(\text{H})\text{ClM}(\text{CO})_n$ complexes ($n = 5$, $\text{M} = \text{Cr}$, Mo , and W ; $n = 4$, $\text{M} = \text{Fe}$) in nearly quantitative yields. Thus HCl is able to cleave easily one of the $\text{P}-\text{N}$ bonds in $(i\text{-Pr}_2\text{N})_2\text{PHM}(\text{CO})_n$ derivatives without cleaving the $\text{P}-\text{H}$ bond. The chromium complex $i\text{-Pr}_2\text{NP}(\text{H})\text{ClCr}(\text{CO})_5$ has also been obtained from $(i\text{-Pr}_2\text{N})_2\text{PHCr}(\text{CO})_5$ and acetyl chloride but similar reactions of $(i\text{-Pr}_2\text{N})_2\text{PHCr}(\text{CO})_5$ with $(\text{CH}_3)_3\text{SiCl}$ and with phosgene failed to result in significant amounts of diisopropylamino cleavage. Attempts to cleave both diisopropylamino groups from $(i\text{-Pr}_2\text{N})_2\text{PHCr}(\text{CO})_5$ under forcing conditions using excess hydrogen chloride or boiling acetyl chloride instead gave only $i\text{-Pr}_2\text{NP}(\text{H})\text{ClCr}(\text{CO})_5$ with no evidence for the formation of any $\text{Cl}_2\text{P}(\text{H})\text{Cr}(\text{CO})_5$.

The spectroscopic properties of the new $(i\text{-Pr}_2\text{N})_2\text{PH}$ and $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$ metal carbonyl complexes agree with the proposed formulations (Table 1). The lower symmetry around the phosphorus atoms in $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$ metal carbonyl complexes relative to corresponding $(i\text{-Pr}_2\text{N})_2\text{PH}$ complexes is reflected in the following spectroscopic observations:

- (1) The B_1 mode which is infrared inactive in ideal C_{4v} symmetry [7] appears as a weak band around 2000 cm^{-1} in the $\nu(\text{CO})$ infrared spectra of the $i\text{-Pr}_2\text{NP}(\text{H})\text{ClM}(\text{CO})_5$ complexes but not the corresponding $(i\text{-Pr}_2\text{N})_2\text{PHM}(\text{CO})_5$ complexes. ($\text{M} = \text{Cr}$, Mo , and W).
- (2) The methyl resonances of the isopropyl groups in the $(i\text{-Pr}_2\text{N})_2\text{PH}$ metal carbonyl complexes exhibit a single doublet around δ 1.3 ppm ($J \approx 7$ Hz) whereas the methyl resonances of the isopropyl groups in the $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$ metal carbonyl complexes exhibit in this region two such doublets of equal relative intensities.

Preliminary experiments based on ^{31}P NMR analysis of crude reaction mixtures suggest that the chlorine atom in $i\text{-Pr}_2\text{NP}(\text{H})\text{Cl}$ metal carbonyl complexes is reactive towards nucleophiles such as alkoxides and amines. Efforts are currently in progress to isolate and characterize pure products from some of these reaction mixtures.

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