basic set modified by the species (14,12), (15,12), (16,12), (32,18), etc.; i.e., these values can be compared with the pK_a values of the mononuclear monobasic non-metal oxoacids in terms of the average number of terminal oxygen atoms available for each negative charge (cf. Figure 5, ref 1). The average positive deviation of ~ 1.4 pK_a units with respect to the non-metal oxoacids is attributed to the stronger p_π–d_π bonding between the transition-metal and oxygen atoms, as has been postulated previously to explain the weaker acidity of the mononuclear transition-metal oxoacids in comparison with the non-metal oxoacids.[23,24]

Existence Area Diagram. The existence area diagram (Figure 1) for the various species of scheme G* (data of Cruywagen) has been constructed to illustrate the effect of the ionic medium, 1 M NaCl in comparison with 3 M $NaClO_4$,[1] and also to give a vivid representation of the concentration ranges of the lower aggregated species.

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(Dialkylamino)phosphines and Their Metal Carbonyl Complexes[1]

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Reductions with $LiAlH_4$ of (dialkylamino)dichlorophosphines, R_2NPCl_2, having sufficiently large dialkylamino groups lead to the corresponding (dialkylamino)phosphines, R_2NPH_2 (R_2N = dicyclohexylamino and 2,2,6,6-tetramethylpiperidino), as very air-sensitive liquids characterized by proton and phosphorus-31 NMR spectroscopy. These (dialkylamino)phosphines react with $(THF)M(CO)_n$ (M = Cr and W, $n = 5$; M = Fe, $n = 4$) to give the corresponding metal carbonyl complexes $R_2NPH_2M(CO)_n$. The complexes of the type $R_2NPH_2M(CO)_5$ (M = Cr and W) are yellow, sublimable solids, which are considerably more stable than the free R_2NPH_2 ligands. Reduction of (diisopropylamino)dichlorophosphine, $i\text{-}Pr_2NPCl_2$, with $LiAlH_4$ gives a solution shown by phosphorus-31 NMR to contain $i\text{-}Pr_2NPH_2$, but this product decomposes upon attempted isolation. However, the metal carbonyl complexes $i\text{-}Pr_2NPH_2M(CO)_5$ (M = Cr and W) can be isolated as relatively stable yellow sublimable solids by the $LiAlH_4$ reduction of the corresponding $i\text{-}Pr_2NPCl_2M(CO)_5$ complexes.

Introduction

During the past several years we have been interested in the synthesis and chemical reactivity of $(R_2N)_nPH_{3-n}$ derivatives. Previous papers from our laboratory[2-4] discuss bis(dialkylamino)phosphines, $(R_2N)_2PH$, a class of compounds that apparently was first prepared in the uncomplexed form by Soviet workers.[5,6] An important idea arising from our observations is the stabilization of uncomplexed $(R_2N)_2PH$ derivatives by the use of sufficiently bulky R_2N groups. Thus $(i\text{-}Pr_2N)_2PH$ is relatively stable and readily obtained by the $LiAlH_4$ reduction of $(i\text{-}Pr_2N)_2PCl$.[2-4] Analogous methods give $(Et_2N)_2PH$ in considerably lower yield but fail to give any detectable quantities of $(Me_2N)_2PH$.[4] O'Neal and Neilson[7] have also reported the P–H derivatives $(Me_3Si)_2NP(R)H$ (R = *i*-Pr, *t*-Bu, CH_2SiMe_3, $N(SiMe_3)_2$, and Ph) stabilized by the bulky bis(trimethylsilyl)amino group. These are prepared by reactions of the corresponding P–Cl derivatives $(Me_3Si)_2NP(R)Cl$ with $LiAlH_4$ or, less effectively, *i*-PrMgCl.

This paper describes attempts to apply similar ideas to the synthesis of stable R_2NPH_2 derivatives. Such derivatives are of interest since they can be regarded either as analogues of primary phosphines, RPH_2, or as dialkylamides of the unknown phosphinous acid, H_2POH, the phosphorus analogue of hydroxylamine. The only reported[8,9] examples of uncomplexed R_2NPH_2 derivatives appear to be the bis(trialkylsilyl)amino derivatives $(Me_3Si)_2NPH_2$ and $(t\text{-}BuMe_2Si)_2NPH_2$. In addition, a recent communication[10] describes the preparation of the tungsten pentacarbonyl complex $Et_2NPH_2W(CO)_5$.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, GA. Proton NMR spectra (Table I) were taken on a Varian T-60 spectrometer. Carbon-13 and phosphorus-31 (Table I) NMR spectra were taken on a JEOL FX-90Q spectrometer operating in the Fourier-transform mode using proton noise decoupling in all of the carbon-13 spectra and in the phosphorus-31 spectra except when phosphorus–hydrogen coupling constants were being determined. Chemical shifts (δ) are reported in parts per million *downfield* from internal tetramethylsilane (for proton and carbon-13 spectra) and external 85% phosphoric acid (for phosphorus-31 spectra).

All reactions were carried out in an efficient hood with aqueous calcium hypochlorite traps to decompose noxious materials in the effluent vapors before passing them into the hood exhaust. All air-sensitive organophosphorus and organometallic compounds were handled under nitrogen in Schlenk ware[11] or a polyethylene glovebag where necessary. All solvents were distilled under nitrogen over appropriate drying agents before use.

A recent paper from our laboratory[12] describes the preparations of the (dialkylamino)dichlorophosphine starting materials. Commercial Fe-

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Table I. NMR Data on the PH_2 Groups in (Dialkylamino)phosphines and Their Metal Carbonyl Complexes

	δ(PH_2)		Hz		
compd	^1H	^{31}P	$\lvert {}^1J(P\text{-}H) \rvert$	$\lvert {}^1J(P\text{-}W) \rvert$	solvent
$i\text{-}Pr_2NPH_2$	*a*	−82.9	196		THF
Cx_2NPH_2	4.75	−72.3	200		C_6D_6
$(CH_2)_3(CMe_2)_2NPH_2$	4.51	−86.6	202		C_6D_6
$Et_2NPH_2W(CO)_5$	5.81	−17.9	342	244	C_6D_6[b]
$i\text{-}Pr_2NPH_2W(CO)_5$	6.00	−54.4	343	244	C_6D_6
$Cx_2NPH_2W(CO)_5$	6.13	−47.6	341	244	C_6D_6
$(CH_2)_3(CMe_2)_2NPH_2W(CO)_5$	6.00	−59.8	321	264	C_6D_6
$i\text{-}Pr_2NPH_2Cr(CO)_5$	5.86	−2.7	333		C_6D_6
$Cx_2NPH_2Cr(CO)_5$	6.40	+6.2	330		$CDCl_3$
$(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_5$	5.85	−5.4	319		C_6D_6
$Cx_2NPH_2Fe(CO)_4$	6.73	+14.6	372		$CDCl_3$

[a] Since $i\text{-}Pr_2NPH_2$ was only obtained in tetrahydrofuran solutions, its PH_2 proton resonance was not observed because of interference from the much stronger solvent resonances. [b] Data of: Mercier, F.; Mathey, F. *Chem. Commun.* **1984**, 782.

$(CO)_5$ was converted to $Fe_2(CO)_9$ by ultraviolet irradiation.[13] The metal hexacarbonyls were purchased from Pressure Chemical Co., Pittsburgh, PA.

Preparation of (Dicyclohexylamino)phosphine, Cx_2NPH_2. A slurry of 1.64 g (43.2 mmol) of $LiAlH_4$ in 50 mL of tetrahydrofuran was treated at −78 °C dropwise with a solution of 12.0 g (42.6 mmol) of (dicyclohexylamino)dichlorophosphine, Cx_2NPCl_2, in 30 mL of tetrahydrofuran. The reaction mixture was stirred at −78 °C for 4 h and then at room temperature for 16 h. It was then filtered to remove the white precipitate. Solvent was removed from the filtrate at ~25 °C (25 mm). The very light yellow viscous liquid residue was extracted with 60 mL of dry pentane. The pentane solution was filtered under nitrogen through a fine-porosity glass frit. Removal of solvent from the filtrate at ~25 °C (25 mm) gave 6.3 g (69% yield) of (dicyclohexylamino)phosphine as a colorless air-sensitive liquid. *Caution*! Filter paper impregnated with (dicyclohexylamino)phosphine ignited upon exposure to air.

Attempted vacuum distillation of this liquid at 0.25 mm resulted in decomposition to give dicyclohexylamine. Therefore, the crude product was used for reactions with metal carbonyls and for the spectroscopic observations: IR ν(P–H) 2230 (sh) and 2200 (s) cm^{-1}; proton-decoupled carbon-13 NMR (C_6D_6) δ 62.6 (doublet, J(P–C) = 9 Hz), 33.2 (doublet, J(P–C) = 5 Hz), 26.7 (singlet), 25.9 (doublet, J(P–C) = 7 Hz).

Preparation of $Cx_2NPH_2Cr(CO)_5$. A yellow-orange solution of $(THF)Cr(CO)_5$ was prepared by overnight ultraviolet irradiation of 5.2 g (23.6 mmol) of $Cr(CO)_6$ in 400 mL of tetrahydrofuran. This solution was stirred at room temperature for 48 h with 5.0 g (23.4 mmol) of Cx_2NPH_2. Solvent was removed from the reaction mixture at ~25 °C (25 mm). The residue was extracted with ~300 mL of hexane in several portions. Removal of hexane from the extract at ~25 °C (25 mm) gave a yellow solid. Unreacted $Cr(CO)_6$ (1.12 g, 21.5% recovery) was recovered from this solid by sublimation at 40–50 °C (0.01 mm) Further sublimation of the residue at 120–125 °C (0.01 mm) gave 3.35 g (35% conversion, 45% yield) of light yellow $Cx_2NPH_2Cr(CO)_5$: mp 109–110 °C; IR ν(P–H) (hexane) 2320 (w) and 2220 (w) cm^{-1}, ν(CO) (pentane) 2060 (m), 1935 (vs), and 1915 (m) cm^{-1}; proton-decoupled carbon-13 NMR (C_6D_6) δ 221.2 (CO trans to Cx_2NPH_2, J(P–C) = 7 Hz), 216.9 (4 CO cis to Cx_2NPH_2, J(P–C) = 13 Hz), 57.9 (doublet, J(P–C) = 3 Hz), 32.1 (doublet, J(P–C) = 3 Hz), 26.3 (singlet), 25.6 (singlet); mass spectrum $Cx_2NPH_2Cr(CO)_n^+$ (n = 5, 4, 2, 1, 0). Anal. Calcd for $C_{17}H_{24}CrNO_5P$: C, 50.4; H, 6.0; N, 3.5 Found: C, 50.5; H, 6.0; N, 3.5.

Preparation of $Cx_2NPH_2W(CO)_5$. A reddish yellow solution of $(THF)W(CO)_5$ was prepared by overnight ultraviolet irradiation of 8.26 g (23.4 mmol) of $W(CO)_6$ in 400 mL of tetrahydrofuran. This solution was stirred at room temperature for 48 h with 4.97 g (23.3 mmol) of Cx_2NPH_2. Solvent was removed at 25 °C (25 mm). The residue was extracted with 250 mL of hexane in several portions. Evaporation of hexane from the extract at ~25 °C (25 mm) gave a dirty yellow sticky product from which unreacted $W(CO)_6$ (2.05 g, ~25% recovery) and dicyclohexylamine (a few drops) were removed by sublimation at 55–60 °C (0.2 mm) and 65–70 °C (0.2 mm), respectively. Sublimation of the residue at 130 °C (0.005 mm) gave 3.2 g (26% conversion, 34% yield) of light yellow $Cx_2NPH_2W(CO)_5$: mp 117 °C; IR (hexane) ν(P–H) 2320 (vw) cm^{-1}, ν(CO) 2070 (m), 1985 (vw), 1940 (vs), and 1915 (w) cm-1; carbon-13 NMR (C_6D_6) δ 196.5 (4 CO cis to Cx_2NPH_2, J(P–C) = 7 Hz), 58.3 (doublet, J(P–C) = 7 Hz), 32.1 (singlet), 26.3 (singlet), 25.6 (singlet), CO trans to Cx_2NPH_2 not observed. Anal. Calcd for $C_{17}H_{24}NO_5PW$: C, 38.0; H, 4.5; N, 2.6. Found: C, 38.0; H, 4.5; N, 2.7.

An attempt to prepare $Cx_2NPH_2Mo(CO)_5$ from $Mo(CO)_6$ and Cx_2NPH_2 via $(THF)Mo(CO)_5$ using an analogous procedure failed.

Preparation of $Cx_2NPH_2Fe(CO)_4$. A mixture of 4.4 g (14.28 mmol) of $Fe_2(CO)_9$, 250 mL of tetrahydrofuran, and 2.83 g (13.3 mmol) of Cx_2NPH_2 was stirred for 16 h at room temperature. During this time all of the $Fe_2(CO)_9$ dissolved, and a dark brown solution formed. Solvent was removed from the reaction mixture at 25 °C (25 mm). The residue was extracted with 50 mL of pentane in several portions. Removal of pentane from the extract at ~25 °C (25 mm) gave dark brown liquid $Cx_2NPH_2Fe(CO)_4$ in yields up to 32%. Cooling a concentrated pentane solution of this product in a −78 °C bath precipitated a brown solid from which the supernatant liquid was separated at −78 °C with a syringe. The pure liquid melted below room temperature. Proton and phosphorus-31 NMR spectra of this brown liquid (Table I) indicated it to be $Cx_2NPH_2Fe(CO)_4$. The infrared spectrum of this liquid in pentane exhibited ν(P–H) bands at 2330 (vw) and 2250 (vw) cm^{-1} and ν(CO) frequencies at 2050 (m), 2020 (w), 2000 (m), 1985 (s), and 1945 (vs) cm^{-1}.

Preparation of $(CH_2)_3(CMe_2)_2NPH_2$. A slurry of 1.58 g (41.6 mmol) of $LiAlH_4$ in 120 mL of tetrahydrofuran was treated at −78 °C with 10.0 g (41.3 mmol) of $(CH_2)_3(CMe_2)_2NPCl_2$. After the mixture was stirred for several days at room temperature, solvent was removed at ~25 °C (25 mm). The residue was extracted with pentane. Removal of solvent from the filtered pentane extracts gave 6.0 g (84% yield) of colorless liquid air-sensitive $(CH_2)_3(CMe_2)_2NPH_2$: IR ν(P–H) 2280 (w) and 2210 (w) cm^{-1}. Attempted vacuum distillation of this liquid led to decomposition, giving free 2,2,6,6-tetramethylpiperidine.

Preparation of $(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_5$. A yellow-orange solution of $(THF)Cr(CO)_5$ was prepared by overnight ultraviolet irradiation of 8.85 g (40.2 mmol) of $Cr(CO)_6$ in 450 mL of tetrahydrofuran. This solution was stirred at room temperature for 3 days with 6.7 g (38.7 mmol) of $(CH_2)_3(CMe_2)_2NPH_2$. Solvent was removed at ~25 °C (25 mm). The residue was extracted with 600 mL of hexane in several portions, and solvent was removed from the extract at ~25 °C (25 mm). Water accidentally entered the flask owing to backup from the aspirator generating the vacuum. Therefore, the hexane solution of the product was separated from the water layer and dried over sodium sulfate. Complete evaporation of the hexane gave a light yellow solid. After removal of excess $Cr(CO)_6$ by sublimation, the product was isolated by sublimation at 110 °C (0.005 mm) to give 5.56 g (39% yield) of $(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_5$: mp 101–103 °C; IR (hexane) ν(CO) 2063 (m), 1983 (w), 1950 (vs), and 1915 (w) cm^{-1}; proton-decoupled carbon-13 NMR (C_6D_6) δ 221 (CO trans to R_2NPH_2, barely observable), 216.8 (4 CO cis to R_2NPH_2, J(P–C) = 14 Hz), 55.1 (doublet, J(P–C) = 3 Hz), 40.6 (doublet, J(P–C) = 6 Hz), 27.4 (doublet, J(P–C) = 4 Hz), 17.2 (singlet); mass spectrum $(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_n^+$ (n = 5, 4, 3, 2, 1, 0), $(CH_2)_3(CMe_2)(CMe)NPH_2^+$. Anal. Calcd for $C_{14}H_{20}CrNO_5P$: C, 46.0; H, 5.5; N, 3.8. Found: C, 45.9; H, 5.5; N, 3.8.

Preparation of $(CH_2)_3(CMe_2)_2NPH_2W(CO)_5$. A yellow solution of $(THF)W(CO)_5$ was prepared by overnight ultraviolet irradiation of 8.3 g (23.5 mmol) of $W(CO)_6$ in 400 mL of tetrahydrofuran. This solution was treated dropwise with 4.0 g (23.1 mmol) of $(CH_2)_3(CMe_2)_2NPH_2$. After the mixture was stirred for 3 days at room temperature, solvent was removed from the reaction mixture at ~25 °C (25 mm). Owing to limited solubility of the product in hexane, the product was extracted with a mixture of hexane, benzene, and dichloromethane. After evaporation of the solvents from the combined extracts and removal of unreacted $W(CO)_6$ by vacuum sublimation, the product was sublimed at 120–130 °C (0.02 mm) to give a total of 1.17 g (10% yield) of $(CH_2)_3(CMe_2)_2NPH_2W(CO)_5$: mp 105–106 °C; IR (hexane) ν(CO) 2073 (w),

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1986 (s), 1948 (vs), and 1915 (vw) cm^{-1}; proton-decoupled carbon-13 NMR (C_6D_6) δ 197.3 (4 CO cis to R_2NPH_2, J(P–C) = 8 Hz), 55.3 (doublet, J(P–C) = 5 Hz), 40.6 (doublet, J(P–C) = 6 Hz), 27.4 (doublet, J(P–C) = 5 Hz), 17.1 (singlet), CO trans to R_2NPH_2 not observed. Anal. Calcd for $C_{14}H_{20}NO_5PW$: C, 33.8; H, 4.1; N, 2.8. Found: C, 32.7; H, 3.8; N, 2.3.

Preparation of *i*-Pr_2NPH_2. A suspension of 0.76 g (20.0 mmol) of $LiAlH_4$ in 70 mL of tetrahydrofuran was treated dropwise at −78 °C with a solution of 8.0 g (39.6 mmol) of *i*-Pr_2NPCl_2 in 25 mL of tetrahydrofuran. The reaction mixture was stirred overnight at −78 °C. A phosphorus-31 NMR spectrum of the reaction mixture at this point run with and without proton decoupling indicated a triplet PH_2 resonance assigned to *i*-Pr_2NPH_2 (Table I). In an attempt to isolate *i*-Pr_2NPH_2, the volatile materials from this reaction were pumped through a −40 °C and a −78 °C trap. Phosphorus-31 NMR spectra of the material collected in the traps indicated the absence of any *i*-Pr_2NPH_2. The pale yellow liquid in the −40 °C trap gave a brown precipitate when allowed to warm to room temperature. This brown precipitate failed to give any sublimate upon heating up to 150–160 °C at 0.01 mm.

Preparation of *i*-$Pr_2NPCl_2Cr(CO)_5$. A yellow solution of (THF)$Cr(CO)_5$ was prepared by ultraviolet irradiation for 10 h of 13.0 g (59.1 mmol) of $Cr(CO)_6$ in 450 mL of tetrahydrofuran. This solution was stirred at room temperature for 24 h with 10.0 g (49.5 mmol) of *i*-Pr_2NPCl_2. Removal of solvent from the reaction mixture at ~25 °C (25 mm) followed by vacuum sublimation first to remove unreacted $Cr(CO)_6$ and then to separate the product gave 7.3 g (37.5% yield) of light yellow *i*-$Pr_2NPCl_2Cr(CO)_5$: sublimed 70–75 °C (0.1 mm); mp 75–80 °C dec; IR (hexane) ν(CO) 2080 (w), 1980 (m), 1973 (s), 1966 (s), and 1961 (vs) cm^{-1}; phosphorus-31 NMR (CH_2Cl_2) δ 183.7. Anal. Calcd for $C_{11}H_{14}Cl_2CrNO_5P$: C, 33.5; H, 3.6; Cl, 18.0; N, 3.5. Found: C, 33.2; H, 3.9; Cl, 17.9; N, 3.6.

Preparation of *i*-$Pr_2NPH_2Cr(CO)_5$. A yellow solution of 7.3 g (18.5 mmol) of *i*-$Pr_2NPCl_2Cr(CO)_5$ in 200 mL of tetrahydrofuran was treated at −78 °C with 0.5 g (13.1 mmol) of $LiAlH_4$. The resulting reaction mixture was allowed to warm overnight to room temperature while magnetic stirring was maintained. Solvent was removed from the filtered reaction mixture at ~25 °C (25 mm). The residue was extracted with 200 mL of hexane. Removal of solvent at 25 °C (25 mm) followed by vacuum sublimation of the residue gave 3.6 g (60% yield) of yellow *i*-$Pr_2NPH_2Cr(CO)_5$: mp 39–40 °C; IR (hexane) ν(PH) 2225 (vvw) cm^{-1}, ν(CO) 2069 (m), 1980 (s), 1950 (vs), and 1920 (vw) cm^{-1}. Anal. Calcd for $C_{11}H_{16}CrNO_5P$: C, 40.6; H, 5.0; N, 4.3. Found: C, 39.6; H, 5.0; N, 4.2.

Preparation of *i*-$Pr_2NPCl_2W(CO)_5$. A yellow solution of (THF)$W(CO)_5$ was prepared by ultraviolet irradiation for 12 h of a solution of 18.5 g (52.5 mmol) of $W(CO)_6$ in 400 mL of tetrahydrofuran. This solution was stirred for 24 h with 10.0 g (49.5 mmol) of *i*-Pr_2NPCl_2. After removal of solvent and unreacted $W(CO)_6$ under vacuum, the product was sublimed at 70–75 °C (0.05 mm) to give 10.3 g (40% yield) of light yellow *i*-$Pr_2NPCl_2W(CO)_5$: mp 120–125 °C dec; IR (hexane) ν(CO) 2084 (m), 1985 (w), 1970 (vs), and 1960 (vs) cm^{-1}; phosphorus-31 NMR (CH_2Cl_2) δ 116.8 ($|^1J$(P–W)$|$ = 371 Hz).

Preparation of *i*-$Pr_2NPH_2W(CO)_5$. A yellow solution of 10.0 g (19.0 mmol) of *i*-$Pr_2NPCl_2W(CO)_5$ in 150 mL of tetrahydrofuran was treated at −78 °C with 0.5 g (13.1 mmol) of $LiAlH_4$. This mixture was stirred at −78 °C for 5 h and then overnight at room temperature. Solvent was removed from the filtered reaction mixture at 25 °C (25 mm), and the residue was extracted with 150 mL of hexane. Removal of hexane from the filtered extract at ~25 °C (25 mm) followed by vacuum sublimation at 70–75 °C (0.5 mm) gave 6.2 g (71% yield) of yellow *i*-$Pr_2NPH_2W(CO)_5$: mp 47–50 °C, IR (hexane) ν(PH) 2230 (vw) cm^{-1}, ν(CO) 2079 (m), 1984 (w), 1948 (vs), and 1918 (w) cm^{-1}. Anal. Calcd for $C_{11}H_{16}NO_5PW$: C, 28.9; H, 3.5; N, 3.1. Found: C, 28.8; H, 3.5; N, 2.9.

Results and Discussion

The reduction of (dialkylamino)dichlorophosphines,[12] R_2NPCl_2, with $LiAlH_4$ to give isolable (dialkylamino)phosphines, R_2NPH_2, depends upon the size of the dialkylamino group analogous to the previously reported[4] $LiAlH_4$ reductions of bis(dialkylamino)chlorophosphines, $(R_2N)_2PCl$, to the corresponding bis(dialkylamino)phosphines, $(R_2N)_2PH$. However, since the (dialkylamino)phosphines, R_2NPH_2, contain only one dialkylamino group, larger dialkylamino groups are needed to give stable (dialkylamino)phosphines relative to bis(dialkylamino)phosphines. Thus, $LiAlH_4$ reductions of (dicyclohexylamino)dichlorophosphine, Cx_2NPCl_2, and (2,2,6,6-tetramethylpiperidino)dichlorophosphine, $(CH_2)_3(CMe_2)_2NPCl_2$, give the corresponding (dialkylamino)phosphines Cx_2NPH_2 and $(CH_2)_3(CMe_2)_2NPH_2$, respectively, which can be isolated as very air-sensitive liquids by pentane extractions of the crude reaction products after removal of the tetrahydrofuran reaction solvent. Phosphorus-31 NMR spectra of the mixture obtained from reaction of *i*-Pr_2NPCl_2 with $LiAlH_4$ in tetrahydrofuran indicate the presence of *i*-Pr_2NPH_2, but this product decomposes upon attempted isolation to give an intractable nonsublimable brown solid. Thus, *i*-Pr_2NPH_2 is unstable in contrast to (*i*-$Pr_2N)_2PH$, which is an air-sensitive liquid readily isolated in quantity by vacuum distillation.[4] Phosphorus-31 NMR spectra of the mixture obtained from reaction of (2,6-dimethylpiperidino)dichlorophosphine, $(CH_2)_3(CHMe)_2NPCl_2$, with $LiAlH_4$ in tetrahydrofuran provided no evidence for the presence of significant quantities of $(CH_2)_3(CHMe)_2NPH_2$, suggesting that the 2,6-dimethylpiperidino group is not large enough to stabilize the corresponding R_2NPH_2 derivative.

The (dialkylamino)phosphines, R_2NPH_2, are most definitely identified by running twice their phosphorus-31 NMR spectra, once with and once without proton decoupling. The relatively high-field phosphorus-31 resonance is observed as a singlet with proton decoupling but as a 1:2:1 triplet when the proton decoupling is turned off. The $|^1J$(P–H)$|$ coupling constants from the latter spectra were found to be close to 200 Hz (Table I). The infrared spectra of the two isolable R_2NPH_2 derivatives exhibit the expected two ν(P–H) frequencies in the 2300–2200-cm^{-1} range.

The two isolable R_2NPH_2 derivatives are air-sensitive liquids that decompose upon attempted vacuum distillation. They were therefore converted to stable metal carbonyl derivatives by reactions with the tetrahydrofuran complexes (THF)$M(CO)_n$ (n = 5, M = Cr and W; n = 4, M = Fe) according to the well-established type of reaction

$$\mathrm{(THF)M(CO)}_n + \mathrm{R_2NPH_2} \rightarrow \mathrm{R_2NPH_2M(CO)}_n + \mathrm{THF} \quad (1)$$

The complexes $R_2NPH_2M(CO)_5$ (R_2N = 2,2,6,6-tetramethylpiperidino, dicyclohexylamino; M = Cr, W) are yellow, relatively air-stable solids that can be sublimed under vacuum without decomposition. These complexes also appear to be relatively stable toward water, as indicated by the isolation of $(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_5$ in 39% yield from its preparation by eq 1 after accidental introduction of gross amounts of water during the solvent removal step. The infrared spectra of the $R_2NPH_2M(CO)_5$ exhibit the expected patterns of ν(CO) frequencies for $LM(CO)_5$ derivatives.[14–16] The phosphorus-31 NMR spectra of the $R_2NPH_2M(CO)_5$ derivatives (Table I) exhibit singlets with proton decoupling and triplets without proton decoupling in accord with expectation. As usual,[17] the coordination chemical shifts are much larger for the chromium derivatives than their tungsten analogues. The $|^1J$(P–H)$|$ values of ~200 Hz for the free R_2NPH_2 ligands increase to more than 300 Hz upon complexation with metal carbonyls with the $|^1J$(P–H)$|$ coupling constants increasing in the sequence $R_2NPH_2Cr(CO)_5$ < $R_2NPH_2W(CO)_5$ < $R_2NPH_2Fe(CO)_4$ (Table I). The $|^1J(^{31}P-^{183}W)|$ coupling constants for the $R_2NPH_2W(CO)_5$ derivatives as determined by the satellites in the phosphorus-31 NMR spectra fall in the range 244–264 Hz, consistent with observed values in other phosphine $LW(CO)_5$ derivatives.[10,17–19] The iron compound $Cx_2NPH_2Fe(CO)_4$, a brown liquid, appears to be significantly less stable than its chromium and tungsten analogues in accord with expectation. However, it has been characterized by its proton and phosphorus-31 NMR spectra (Table I). Its ν(CO) frequencies at 2050, 1985, and 1945 cm^{-1} correspond to the A_1, A_1, and E bands, respectively, expected for an axially substituted $LFe(CO)_4$ derivative,[20] but the remaining two weaker bands at 2020 and 2000

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cm^{-1} suggest an impurity, possibly some $Fe(CO)_5$ produced as a byproduct in its preparation from $Fe_2(CO)_9$ and Cx_2NPH_2.

The diisopropylamino derivative $i\text{-}Pr_2NPH_2$ appeared to be too unstable to use directly for the preparation of metal carbonyl complexes. However, its metal carbonyl complexes $i\text{-}Pr_2NPH_2M(CO)_5$ (M = Cr, W) can be obtained from $i\text{-}Pr_2NPCl_2$ by the reaction sequence

$$i\text{-}Pr_2NPCl_2 + (THF)M(CO)_5 \rightarrow i\text{-}Pr_2NPCl_2M(CO)_5 + THF \quad (2a)$$

$$i\text{-}Pr_2NPCl_2M(CO)_5 \xrightarrow[THF]{LiAlH_4} i\text{-}Pr_2NPH_2M(CO)_5 \quad (2b)$$

A similar method has been used by Mercier and Mathey[10] to prepare $Et_2NPH_2W(CO)_5$. The complexes $i\text{-}Pr_2NPH_2M(CO)_5$ (M = Cr, W) are yellow, relatively air-stable solids that can be sublimed under vacuum without significant decomposition. Their spectroscopic properties are similar to those of the other $R_2NPH_2M(CO)_5$ derivatives. The $|^1J(^{31}P-^{183}W)|$ coupling constant of 371 Hz in $i\text{-}Pr_2NPCl_2W(CO)_5$ falls to 244 Hz upon reduction to $i\text{-}Pr_2NPH_2W(CO)_5$ in accord with the expected greater π-acceptor strength of $i\text{-}Pr_2NPCl_2$ relative to $i\text{-}Pr_2NPH_2$; the relationship of $|^1J(^{31}P-^{183}W)|$ to ligand π-acceptor strength has been known for some time.[17-19]

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Registry No. Cx_2NPH_2, 93583-23-4; $(CH_2)_3(CMe)_2NPH_2$, 93583-24-5; $i\text{-}Pr_2NPH_2$, 93583-25-6; $Cx_2NPH_2Cr(CO)_5$, 93492-97-8; $Cx_2NPH_2W(CO)_5$, 93492-98-9; $Cx_2NPH_2Fe(CO)_4$, 94152-55-3; $(CH_2)_3(CMe_2)_2NPH_2Cr(CO)_5$, 97704-71-7; $(CH_2)_3(CMe_2)_2NPH_2W(CO)_5$, 97704-72-8; $i\text{-}Pr_2NPH_2Cr(CO)_5$, 97704-73-9; $i\text{-}Pr_2NPH_2W(CO)_5$, 97704-74-0; $i\text{-}Pr_2NPCl_2Cr(CO)_5$, 97704-75-1; $i\text{-}Pr_2NPCl_2W(CO)_5$, 97704-76-2; Cx_2NPCl_2, 93583-22-3; $(CH_2)_3(CMe_2)_2NPCl_2$, 64945-24-0; $i\text{-}Pr_2NPCl_2$, 921-26-6; $(THF)Cr(CO)_5$, 15038-41-2; $(THF)W(CO)_5$, 36477-75-5.

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Relationship between Structure and Reactivity for Metal Clusters Formed in Ion–Molecule Reactions in Decacarbonyldimanganese and Pentacarbonyl(pentacarbonylmanganio)rhenium

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Relative rate constants for ion–molecule reactions in $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$ are reported. Electron-impact-produced fragment ions react with the parent to form cluster ions containing three and four metal atoms. Subsequent sequential reactions lead to cluster ions containing as many as eight metal atoms. Most of the clusters formed in $ReMn(CO)_{10}$ contain equal numbers of Re and Mn atoms. A rough correlation is found between the average electron deficiency per metal atom and the rate constant. Electron deficiencies are assigned with use of the effective atomic number rule and on the assumption of closed-polyhedral structures for most of the ions. The rate constants tend to increase with electron deficiency until the deficiency reaches two per metal atom. Exceptions to this behavior are rationalized in terms of ligand crowding and electronic effects such as multiple bonding and ligand-induced restructuring analogous to that observed in coordinatively unsaturated metal surfaces. Several cases are identified where substituting Mn for Re in a metal cluster changes its behavior substantially.

Introduction

We have recently reported relative rate constants for gas-phase cationic clustering reactions in $Re_2(CO)_{10}$[2] and for gas-phase anionic clustering reactions in $Fe(CO)_5$.[3] A direct correlation was found to exist between the relative rate constants of the reactant species and their electron deficiencies. Species that are nearly coordinatively saturated and have low electron deficiencies react slowly, if at all. On the other hand, species with large electron deficiencies react rapidly.

Electron deficiencies were calculated for the anionic species[3] by utilizing the 18-electron rule. The difference between 18 and the average number of valence electrons available to each metal atom is the electron deficiency. For the cationic species[2] electron deficiencies were calculated by using a modified 18-electron rule that allows for the effects of delocalized bonding based on Teo's topological electron-counting theory.[4] Relative rate constants for the clustering reactions observed in both $Re_2(CO)_{10}$ and $Fe(CO)_5$ showed a similar relationship to electron deficiency. $Re_n(CO)_m^+$ and $Fe_n(CO)_m^-$ ions with large electron deficiencies react rapidly with the neutral parents, $Re_2(CO)_{10}$ and $Fe(CO)_5$, respectively, to form larger clusters. In fact, for species with electron deficiencies greater than 2 the rates of reaction are relatively constant and approximately equal to the collision rate. For species with electron deficiencies less than 2 the rate constants drop smoothly and dramatically with decreasing electron deficiency until the clusters become nearly coordinatively saturated. This is consistent with the general behavior of coordination compounds, since a cluster with an electron deficiency of 2 has on the average a vacancy for a two-electron donor such as CO at each metal center and therefore should be quite reactive. As the vacancies fill and the electron deficiency drops, the species should become less and less reactive.

In order to assign electron deficiencies to the anions in $Fe(CO)_5$ and the cations in $Re_2(CO)_{10}$, it was necessary to estimate the number of metal–metal bonds in the clusters. This was done by analogy with known condensed-phase structures or by assumption of closed-polyhedral structures. The correlation of rate constant with electron deficiencies suggested that these structural assignments were correct. In a few cases the correlation was actually used to assign structures if other considerations led to an ambiguous assignment.[2,3]

Our present study reports some relative rate constants for gas-phase positive ion clustering reactions in $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$. These compounds were chosen because they are periodic congeners of $Re_2(CO)_{10}$. They provide an opportunity

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