Table VI. Final Molecular Parameters for $(CH_3)_2NB_2H_5$

Parameter	$(CH_3)_2NB_2H_5$		$H_2NB_2H_5$	B_2H_6
	This work	Ref 1	Ref 2	Ref 7
B-B, Å	1.916 ± 0.004	1.92 ± 0.11	1.93 ± 0.10	1.775 ± 0.003
$B-H_t$, Å	$1.191^{+0.010}_{-0.003}$		1.15 ± 0.09	$1.196^{+0.008}_{-0.006}$
$B-H_{br}$, Å	1.365 ± 0.006			$1.339_3{}^{+0.002}_{-0.006}$
B-N, Å	1.544 ± 0.010[a]	1.554 ± 0.026	1.564 ± 0.026	
C-N, Å	1.488 ± 0.010[a]	1.483 ± 0.029		
H_tBH_t, deg	119.6 ± 0.5			120.2 ± 1.8
$BH_{br}B$, deg	89.1 ± 0.9			83.0 ± 0.3
BNB, deg	76.8 ± 1[a]	76.4 ± 5.5	76.2 ± 2.8	
CNC, deg	110.0 ± 1[a]	111.5 ± 2.5		
ϵ,[b] deg	16.7 ± 1		15 ± 20	

[a] A tetrahedral methyl group with a C-H bond length of 1.091 Å has been assumed. The uncertainty in these parameters includes a ±0.01-Å uncertainty in the C-H length as well as those listed in the table. [b] ϵ is the angle made by the BH_2 plane and the plane perpendicular to the C_{2v} symmetry axis.

is 0.14 Å greater than that in diborane the $B-H_{br}$ distance is increased by only 0.03 Å.

The B-H-B angle, however, is increased by 6.1°. The primary effect of the increase in B-B distance is thus an increase of the B-H-B angle rathen than an increase in the B-H bond length. In order for the B_2H_5 group to accommodate the large nitrogen atom the B-H-B angle must increase. The overall effect is similar to opening a rigid molecule in the BNB plane using the bridge hydrogen as a hinge. As a result the BH_2 groups are tilted from the plane perpendicular to the symmetry axis by 16.7 ± 1°. This tilt is called ϵ in Table IV and is illustrated in Figure 1.

While the C-N-C angle is very close to tetrahedral, the B-N-B angle on the other hand is only 76.8°. Hence the B-N bonding orbitals probably lie in the BNBH plane, but subtend a larger angle than the B-N-B angle of 76.8°. This is similar to the "banana bonds" hypothesized in cyclopropane.

Registry No. $(CH_3)_2NB_2H_5$, 23273-02-1; $(CH_3)_2N^{10}B^{11}BH_5$, 39526-76-6; $(CH_3)_2N^{11}B^{11}BH_5$, 39526-77-7; $(CH_3)_2N^{11}B^{11}BD_5$, 39561-27-8; $(CH_3)_2N^{10}B^{11}BD_5$, 39561-28-9; $(CH_3)_2N^{11}B^{11}BD_4H_t$, 39526-78-8; $(CH_3)_2{}^{15}N^{10}B^{11}BH_5$, 39526-79-9; $(CH_3)_2{}^{15}N^{11}B^{11}BH_5$, 39526-80-2.

Acknowledgment. We wish to thank Professors A. B. Burg and D. J. Basi for the sample of $(CH_3)_2NB_2H_5$ and Professor Burg for the synthesis of $(CH_3)_2{}^{15}NB_2N_5$. This work was supported primarily by the United States Air Force Office of Scientific Research under Grant 849-67 to the University of Southern California and in some part by NASA Contract NAS-7-100 with the Jet Propulsion Laboratory.

Contribution No. 1980 from the Central Research Department,
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Reaction of Phosphine with Some Transition Metal Complexes[1]

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Received December 4, 1972

The syntheses and properties of the new phosphine complexes $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$ (x = 1-4), $Ni(PH_3)[P(C_6H_5)_3]_3$, $Ni(PH_3)_2[P(C_6H_5)_3]_2$, and $MnBr(CO)_3(PH_3)_2$ are described. The reaction of phosphine with $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ (X = Cl, $B(C_6H_5)_4$) gives $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]\}X$ at −70°, but a reversible, oxidative addition occurs at room temperature to give the hydridophosphide complexes $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$. The syntheses of the related complexes $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]\}X$ are also described. Infrared and nuclear magnetic resonance spectra of the new complexes are presented.

Introduction

The discovery[2,3] that phosphine (PH_3) forms stable complexes with transition metals has led to the isolation and characterization of many novel species. Examples of transition metal-phosphine complexes include $V(\pi\text{-}C_5H_5)(CO)_3(PH_3)$,[2,4] $Cr(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5] 3,[6] 4[7]), $Mo(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5,8] 3[8]), $W(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5] 3[9]), $Mn(CO)_9PH_3$,[10] $cis\text{-}Mn(\pi\text{-}C_5H_5)(CO)_2$-

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(1) This work was presented in part at The Chemical Society of London symposium "Structure and Reactivity of Complexes of Transition Metals in Low Valence States," University of Sheffield, Aug 1969.

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(PH_3),[2,4,11] *cis*-$MnBr(CO)_4(PH_3)$,[3] *cis*-$MnI(CO)_4(PH_3)$,[12] *cis*-$MnI(CO)_3(PH_3)_2$,[12] $Fe(CO)_4PH_3$,[2,4,12] *cis*-$FeI_2(CO)_3(PH_3)$,[12] $FeI_2(CO)_2(PH_3)_2$,[12] $CoH(PH_3)(PF_3)_3$,[13] $Co(NO)(CO)_2(PH_3)$,[14] $Ni(CO)_3(PH_3)$,[12,15] $Ni(PH_3)(PF_3)_3$,[16] and $Ni(PH_3)_2(PF_3)_2$.[16] The synthesis of $Ni(PH_3)_4$ was reported[17] while this work was in progress.

In this paper, the synthesis and properties of new phosphine complexes of nickel and iridium containing tertiary phosphine and phosphite ligands and the oxidative addition of phosphine to iridium(I) complexes are described.

Experimental Section

Note! Phosphine is a highly toxic, spontaneously flammable gas and extreme care must be taken in its use. Commercially available phosphine (Matheson Co.) may contain small amounts of P_2H_4 and H_2. The P_2H_4 may be removed by passing the gas through a trap cooled to −78°. *P_2H_4 is also highly toxic and spontaneously flammable* and decomposes at about 25° to an amorphous yellow powder. In vacuum-line reactions, hydrogen was removed after the phosphine was condensed in a trap cooled in liquid nitrogen. Excess phosphine was burned in a gas flame.

All experimental procedures including isolation and purification were performed either under vacuum or in an inert atmosphere using conventional bench-top techniques or a nitrogen-filled glove box.[18] All solvents were dried over Linde 4A molecular sieves and deoxygenated before use.

Infrared spectra were recorded on a Perkin-Elmer 237 Grating Infracord spectrometer. Proton nmr spectra were recorded on a Varian HR-220, HA-100, or A-60 spectrometer. Fourier-mode, proton-noise-decoupled ^{31}P nmr spectra were recorded on a Brucker HFX-90 spectrometer equipped with a Digilab FTS/nmr Fourier transform accessory.

Preparation of $MnBr(CO)_3(PH_3)_2$. Phosphine was bubbled slowly through an orange refluxing solution of 6.7 g (0.024 mol) of $MnBr(CO)_5$[19] in 100 ml of tetrahydrofuran for 1.5 hr. The resulting clear, dark orange solution was flushed with nitrogen and the solvent was removed under vacuum. The orange, solid residue was extracted with 200 ml of benzene and the extract was chromatographed on Woelm grade 1 neutral alumina. Elution with benzene followed by benzene–dichloromethane, dichloromethane, and tetrahydrofuran gave *ca.* 700 ml of a pale yellow eluate. Solvent removal gave *ca.* 0.1 g of yellow-orange solid which was identified as $MnBr(CO)_4(PH_3)$ from the infrared spectrum.

The benzene-insoluble solid was then extracted with 75 ml of dichloromethane and 150 ml of *n*-heptane was added to the orange filtrate. Concentrating the solution on a rotary evaporator formed orange crystals which were collected and washed with *n*-heptane. The crude product (2.8 g) was extracted with 75 ml of dichloromethane and 100 ml of *n*-hexane was added to the filtered extract. On standing at 25° for 2 hr the clear, orange solution deposited orange crystals which were collected and dried at 25° (0.1 μ) for 16 hr to give 2.0 g (29%) of $MnBr(CO)_3(PH_3)_2$, dec pt 209°. An additional 0.6 g was obtained by concentration of the filtrate. *Anal.* Calcd for $C_3H_6BrMnO_3P_2$: C, 12.5; H, 2.1; Mn, 19.1; P, 21.2. Found: C, 13.1; H, 1.9; Mn, 18.5; P, 21.2.

The analysis and the infrared spectrum (Table I) suggest the presence of *ca.* 5% of $MnBr(CO)_4(PH_3)$.

The complex is soluble in chloroform, dichloromethane, and tetrahydrofuran, slightly soluble in benzene, and insoluble in hexane. The solid complex decomposes only slowly in air and solutions are also moderately stable.

Preparation of $Ni(PH_3)[P(OC_6H_5)_3]_3$. Phosphine was bubbled slowly through a refluxing solution of 5.0 g (0.00384 mol) of $Ni[P(OC_6H_5)_3]_4$[20] in 150 ml of tetrahydrofuran for 1 hr. The colorless solution slowly became pale yellow. The mixture was cooled to 25° and flushed with nitrogen, and 100 ml of *n*-heptane was added. Concentration of the mixture under vacuum and addition of 100 ml of *n*-heptane produced a white solid which was collected and washed with *n*-heptane. This crude product (3.7 g) was crystallized from 250 ml of boiling *n*-heptane and the white crystals were dried at 25° (0.1 μ) for 16 hr to give 2.5 g (64%) of $Ni(PH_3)[P(OC_6H_5)_3]_3$, dec pt 120–160°. *Anal.* Calcd for $C_{54}H_{48}NiO_9P_4$: C, 63.3; H, 4.7; Ni, 5.7; O, 14.1; P, 12.1. Found: C, 64.2; H, 4.7; Ni, 5.4; O, 13.9; P, 11.6.

The complex is moderately soluble in benzene, tetrahydrofuran, and dichloromethane and slightly soluble in diethyl ether and *n*-heptane. The solid complex slowly decomposes in air and solutions decompose more rapidly.

Preparation of $Ni(PH_3)_2[P(OC_6H_5)_3]_2$. A 500-ml two-necked flask fitted with vacuum-line stopcock adapter and serum cap was charged with 3.0 g (0.0109 mol) of bis(1,5-cyclooctadiene)nickel[21] and 100 ml of tetrahydrofuran. The yellow mixture was frozen in liquid nitrogen and the flask was evacuated. A solution of 6.4 g (0.0206 mol) of triphenyl phosphite in 20 ml of tetrahydrofuran was added to the frozen mixture with a hypodermic syringe and phosphine (0.034 mol) was condensed in. The mixture was warmed to 25° and stirred for 2.5 hr to give a slightly gray solution. The mixture was transferred to the nitrogen box and filtered by nitrogen pressure. Addition of *n*-heptane (200 ml) to the filtrate and concentration of the solution gave a gray solid. The crude product was purified by extraction with 400 ml of diethyl ether, filtration by nitrogen pressure, addition of 300 ml of *n*-hexane to the filtrate, cooling to −78° for 4.5 hr, and collection of the resulting crystals at −78°. This procedure was repeated and the white, needlelike crystals were dried at 25° (0.1 μ) for 6 hr to give 3.6 g (44%) of $Ni(PH_3)_2[P(OC_6H_5)_3]_2$, dec pt 85°. *Anal.* Calcd for $C_{36}H_{36}NiO_6P_4$: C, 57.8; H, 4.9; Ni, 7.9; P, 16.6. Found: C, 57.7; H, 4.7; Ni, 7.6; P, 16.0.

The complex is soluble in diethyl ether, tetrahydrofuran, and benzene and slightly soluble in hexane. Solutions decompose slowly on standing under nitrogen at 25° and rapidly upon heating or air exposure. The solid complex slowly decomposes in air.

Preparation of $Ni(PH_3)_3[P(OC_6H_5)_3]$. A 500-ml three-necked flask was equipped with a vacuum-stopcock adapter, serum cap, and magnetic stirring bar. The third neck of the flask was attached through glass adapters to a medium-porosity fritted funnel which could be immersed in a cold bath. The flask was charged with 2.0 g (0.0073 mol) of bis(1,5-cyclooctadiene)nickel and 80 ml of diethyl ether. The yellow slurry was frozen in liquid nitrogen and the flask was evacuated. Phosphine (0.030 mol) was condensed in and the mixture was stirred at −30° for 20–30 min during which a gray slurry formed. The mixture was cooled to *ca.* −45° and a solution of 2.13 g (0.0068 mol) of triphenyl phosphite in 10 ml of diethyl ether was added by hypodermic syringe. The mixture was stirred at −25° for 30 min giving a colorless solution containing some black solid. The cold flask was returned to 1 atm pressure with nitrogen. The mixture was filtered at −30°, and the filtrate was collected in a flask cooled to −78° and also equipped with a low-temperature filtration apparatus. After 1.5 hr at −78°, the filtrate deposited an off-white, crystalline solid which was collected at −78°, dried at −78° in a nitrogen stream for 0.5 hr, and then dried at −25° (0.1 μ) for 1 hr. The product, a light gray crystalline solid, was bottled and stored at −40°. The product blackened after several minutes at room temperature and was not analyzed. The product was characterized as a mixture of $Ni(PH_3)_3[P(OC_6H_5)_3]$ and $Ni(PH_3)_4$ on the basis of the nuclear magnetic resonance spectra (Figures 1 and 2 and Discussion). The solutions used for the nmr spectra were prepared at −30° and filtered quickly through a cold cotton plug into an nmr tube cooled to *ca.* −40°; the nmr tube was stored at −40° prior to transfer to a precooled nmr probe. The nmr solution, however, did contain some black solid.

Preparation of $Ni(PH_3)_4$. A 500-ml three-necked flask equipped as above was charged with 1.65 g (0.0060 mol) of bis(1,5-cyclooctadiene)nickel and 80 ml of tetrahydrofuran. The yellow solution was frozen in liquid nitrogen. The flask was evacuated, and phosphine (0.0322 mol) was condensed in. The mixture was stirred at −55° for 0.5 hr and at −25° for 45 min forming a colorless solution containing some black solid. The cold flask was returned to 1 atmosphere

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Table I. Spectral Data for Phosphine and Hydridophosphide Complexes

	Infrared (Nujol)		¹H nmr			
Complex	Freq, cm^{-1}	Assignment	τ, ppm	Multiplicity (J, Hz)	Assignment	Solvent
$MnBr(CO)_3(PH_3)_2$	2392 s	ν_{PH}	5.74[a]	Doublet of multiplets (J_{PH} = ±339.5, $J_{P'H}$ = ±12.5, $\|J_{PP'}\|$ = 54)	PH_3	$CDCl_3$
	2358 m					
	2015 w[b]	ν_{CO}[c]				
	2049 s					
	2033 sh[b]					
	1992 s					
	1946 s					
	1015 s	δ_{PH}				
	991 s					
$Ni(PH_3)[P(OC_6H_5)_3]_3$	2347 m	ν_{PH}	7.71[d]	Doublet (J = 300) of quartets (J = 18)	PH_3	C_6D_6
	2309 s					
	1019 s	δ_{PH}	2.97	Multiplet	C_6H_5	
$Ni(PH_3)_2[P(OC_6H_5)_3]_2$	2336 m	ν_{PH}	7.45[a]	Doublet ($J \approx 316$) of triplets (J = 19)	PH_3	C_6D_6
	2304 m					
			2.78	Multiplet	C_6H_5	
$Ni(PH_3)[P(C_6H_5)_3]_3$	2273 s	ν_{PH}	e			
	1025 sh	δ_{PH}				
	1015 s					
$Ni(PH_3)_2[P(C_6H_5)_3]_2$	2278 sh	ν_{PH}	6.54[a]	Doublet ($J \approx 290$) of multiplets	PH_3	C_6D_6
	2262 s					
	1083 s	δ_{PH}	2.83	Multiplet	C_6H_5	
	1077 sh					
	1053 s					
$[Ir(PH_3)(DPPE)_2]Cl$[f]			8.02[g–i]	Multiplet	PCH_2CH_2P	CD_2Cl_2
			8.11	Doublet (J = 300) of quintets (J = 6)	$IrPH_3$	
			8.30	Doublet (J = 192)	Free PH_3	
			6.76, 9.00	. . .	$(C_2H_5)_2O$ impurity	
[*cis*-$IrH(PH_2)(DPPE)_2]Cl$[f]	2331 w	ν_{PH}	21.7[d,h,i]	Doublet (J = 118) of quartets (J = 15)	IrH	CD_2Cl_2
	2294 m					
	2268 sh					
	2114	ν_{IrH}	9.95	Doublet (J = 180) of quintets (J = 5)	$IrPH_2$	
			7.02	Multiplet	PCH_2CH_2P	
			6.65, 8.90	. . .	$(C_2H_5)_2O$ impurity	
[*cis*-$IrH(PH_2)(DPPE)_2][B(C_6H_5)_4]$[f]	2353 m	ν_{PH}	Same as for chloride salt			
	2268 s					
	2119 s	ν_{IrH}				
[*trans*-$IrH(PH_2)(DMPE)_2]Cl$[f]	2252 m	ν_{PH}				
	1957 m	ν_{IrH}				
[*trans*-$IrH(PH_2)(DMPE)_2][B(C_6H_5)_4]$[f]	2260 m	ν_{PH}	23.23[d]	Septet (J = 16)	IrH	CD_2Cl_2
	1960 m	ν_{IrH}	10.38	Doublet (J = 174) of quintets (J = 7)	$IrPH_2$	
			8.36	Multiplet	DMPE[f]	
			2.88	Multiplet	C_6H_5	

[a] The spectrum was recorded at 60 MHz. [b] These absorptions correspond to the $MnBr(CO)_4(PH_3)$ impurity. [c] The spectrum was obtained using a $CHCl_3$ solution. [d] The spectrum was recorded at 220 MHz. [e] The ¹H nmr spectrum was not obtained due to low solubility. [f] DPPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; DMPE = $(CH_3)_2PCH_2CH_2P(CH_3)_2$. [g] The spectrum was recorded at 100 MHz. [h] Chemical shifts were measured from internal CH_2Cl_2 and referred to $Si(CH_3)_4$ assuming $\tau(CH_2Cl_2)$ 4.72. [i] The aromatic region was not recorded.

with nitrogen, the mixture was filtered at −30°, and the colorless filtrate was collected at −78°. After 1 hr at −78°, off-white needle-like crystals had formed and they were collected at −78°, washed with cold pentane, dried in a stream of cold nitrogen at −78°, and then dried at −55° (0.1 μ) for 1 hr. The product was bottled and stored at −40°. The solid blackened at *ca.* −10° and was not analyzed. Characterization of the product as $Ni(PH_3)_4$ is based on the method of preparation and the ¹H nmr spectrum (Figure 2 and Discussion). The solutions used for the proton spectra were prepared at −30° and filtered quickly through a cold cotton plug into an nmr tube cooled to *ca.* −40°. The nmr solution contained a trace of black solid.

Preparation of $Ni(PH_3)[P(C_6H_5)_3]_3$. A red-brown slurry of 4.4 g (0.0040 mol) of $Ni[P(C_6H_5)_3]_4$[22] in 60 ml of diethyl ether was degassed on a vacuum line and frozen in liquid nitrogen, and 0.0045 mol of phosphine was condensed in. The mixture was stirred at 25° for 15 min during which a yellow, crystalline solid was formed. The mixture was then stirred at 0° for 15 min and filtered. The yellow solid was dried at 25° (0.01 μ) for 2 hr to give 2.4 g (69%) of $NiPH_3[P(C_6H_5)_3]_3$, dec pt 78°. *Anal.* Calcd for $C_{54}H_{48}NiP_4$: C, 73.6; H, 5.5; Ni, 6.7; P, 14.1. Found: C, 73.0; H, 5.6; Ni, 6.5; P, 13.0.

The complex decomposes on air exposure as a solid or in solution; solutions decompose slowly at 25° even in the absence of air. The complex has low solubility in benzene and tetrahydrofuran, is slightly soluble in diethyl ether, and is insoluble in *n*-hexane.

Preparation of $Ni(PH_3)_2[P(C_6H_5)_3]_2$. Phosphine was bubbled slowly through a red-brown slurry of 4.5 g (0.0041 mol) of $Ni[P(C_6H_5)_3]_4$ in 80 ml of diethyl ether at 0–5° for 1.5 hr.

The resulting yellow slurry was flushed briefly with nitrogen and filtered at −10°, and the yellow, crystalline solid was washed with diethyl ether and dried at 25° (0.1 μ) for 16 hr to give 1.8 g (68%) of $Ni(PH_3)_2[P(C_6H_5)_3]_2$, dec pt 95°. *Anal.* Calcd for $C_{36}H_{36}NiP_4$: C, 66.3; H, 5.6; Ni, 9.0; P, 19.1. Found: C, 66.1; H, 5.7; Ni, 9.1; P, 18.3.

Upon exposure to air the solid compound decomposes after several hours while solutions decompose within minutes. It is soluble in benzene and tetrahydrofuran and insoluble in diethyl ether and *n*-hexane.

The complex may also be prepared by the reaction of excess phosphine with $Ni(C_2H_4)[P(C_6H_5)_3]_2$.

Preparation of $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ (X = Cl,

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$B(C_6H_5)_4$). 1. **Characterization by ^{1}H Nmr.** An nmr tube containing an orange solution of 0.110 g (1.07 × 10^{-4} mol) of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$[23,24] and 1 drop of CH_2Cl_2 in 0.6 ml of CD_2Cl_2 was cooled in liquid nitrogen and evacuated, phosphine (1.18 × 10^{-4} mol) was condensed in, and the tube was sealed. The contents were mixed at −78° to give a bright yellow solution, and the tube was quickly transferred to the nmr probe which had been precooled to −70°. The ^{1}H nmr spectrum was recorded at 100 MHz (Figure 4a and Table I). A similar spectrum was obtained using $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$.[23,24] The resonance centered at τ 8.11 indicates the formation of $\{IrPH_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}^+X^-$.

2. **Attempted Isolation of $\{IrPH_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$.** In a two-necked, 500-ml flask equipped with a vacuum-line adapter, serum stopper, and magnetic stirrer, a solution of 1.5 g (0.0012 mol) of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ in 25 ml of dichloromethane was frozen in liquid nitrogen and degassed under vacuum, and phosphine (0.0055 mol) was condensed in. On warming to −78°, the orange solution rapidly became bright yellow. After the solution was stirred at −78° for 0.5 hr, 200 ml of diethyl ether was added *via* a hypodermic syringe, and the resulting yellow precipitate was collected at −78°. Although stable at −78°, the yellow solid rapidly became orange upon warming to *ca.* −40°. The infrared spectrum of the orange product was identical with that of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$. The thermally unstable yellow product is formulated as the PH_3 complex $\{IrPH_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$.

Preparation of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$. A two-necked, 500-ml round-bottom flask fitted with a vacuum-line adapter, serum cap, and magnetic stirring bar was charged with 3.0 g (0.00292 mol) of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$ and 75 ml of acetonitrile. The orange solution was frozen in liquid nitrogen, the flask was evacuated, and phosphine (0.0116 mol) was condensed in. When the mixture was warmed to 25°, the orange color rapidly faded to pale yellow. After the solution was stirred to 25° for 0.5 hr, 200 ml of diethyl ether was added *via* a hypodermic syringe, and the resulting cream-colored precipitate was collected, washed with diethyl ether, and dried at 25° (0.5 μ) for 3 hr to give 2.35 g (76%) of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$, dec pt 198°. *Anal.* Calcd for $C_{52}H_{51}ClIrP_5$: C, 58.2; H, 4.9; Cl, 3.4; P, 14.6. Found: C, 57.5; H, 5.0; Cl, 3.6; P, 13.9.

The complex is soluble in polar organic solvents such as acetonitrile, dichloromethane, or methanol, but the solutions are pale orange and slowly decompose, preventing purification of the initial precipitate. The solid is insoluble in nonpolar organic solvents and did not appear changed after standing in air for 16 hr.

Preparation of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]\}[B(C_6H_5)_4]$. A two-necked, round-bottom flask equipped with a vacuum-line adapter, serum cap, and magnetic stirrer was charged with 4.0 g (0.00306 mol) of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ and 50 ml of dichloromethane. The solution was frozen in liquid nitrogen, the flask was evacuated, and phosphine (0.00622 mol) was condensed in. On warming to 25°, the solution successively changed from bright orange (−78°) to bright yellow (−78°) to pale orange (*ca.* −40°) to pale yellow (25°). After the solution was stirred at 25° for 5 min, the clear, almost colorless solution was cooled to 0°, 200 ml of diethyl ether was added with a hypodermic syringe, and the resulting off-white precipitate was collected, washed with diethyl ether, and dried at 85° (0.5 μ) for 1.5 hr to give 3.9 g (95%) of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$, dec pt 195–198°. *Anal.* Calcd for $C_{76}H_{71}BP_5Ir$: C, 68.0; H, 5.3; P, 11.5. Found: C, 67.8; H, 5.5; P, 11.2.

The complex is soluble in acetonitrile and dichloromethane, but the solutions slowly decompose and the initial product could not be recrystallized. The solid complex appeared to be unchanged after 16 hr of exposure to air.

The use of PD_3 in this reaction gave the corresponding deuteride, $\{cis\text{-}IrD(PD_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$. The infrared spectrum (Nujol) showed ν_{PD} at 1656 (m) cm^{-1} and ν_{IrD} at 1613 cm^{-1} ($\nu_{PH}/\nu_{PD} = 1.37$; $\nu_{IrH}/\nu_{IrD} = 1.32$).

A similar reaction of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}PF_6$ with phosphine in tetrahydrofuran gave a white precipitate. The infrared spectrum showed ν_{PH} at 2300 cm^{-1} and ν_{IrH} at 2150 cm^{-1}. The product was assumed to be $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}PF_6$ but was not further characterized because of its unfavorable solubility characteristics.

Reactions of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ (I). 1. Thermal Decomposition of the Solid. A 0.5-g portion of I was heated at 180° (0.2 μ) for 3 hr. The white solid slowly became bright orange. The infrared spectrum (Nujol) of the orange residue (0.47 g) was identical with that of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$.

2. **Thermal Decomposition in Solution.** Nitrogen was slowly bubbled through a refluxing solution of 0.5 g of I in 26 ml of acetonitrile for 30 min. The initially yellow solution became bright orange, and, upon cooling, orange crystals formed which were identified as $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ by infrared analysis. Loss of phosphine occurred at a slower rate when the solution was not flushed with nitrogen.

3. **Reaction with Hydrogen.** Hydrogen was bubbled slowly through a refluxing solution of 0.5 g of I in 25 ml of acetonitrile. The yellow solution became colorless, and upon cooling a white crystalline solid formed. This solid was identified as $\{IrH_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ by comparison of the Nujol infrared spectrum with that of an authentic sample.[23,24]

4. **Reaction with Carbon Monoxide.** Carbon monoxide was bubbled slowly through a refluxing solution of 0.5 g of I in 25 ml of acetonitrile. The initially yellow solution became colorless and then yellow. Upon cooling, a pale yellow crystalline solid formed which was identified as $\{Ir(CO)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$ by comparison of the Nujol infrared spectrum with that to an authentic sample.[23,24]

5. **Reaction with D_2O.** A yellow solution of 0.5 g of I and 1 ml of D_2O in 10 ml of acetonitrile was stirred at 25° for 0.5 hr. The resulting pale orange solid was collected and dried in a nitrogen stream at 25°. The infrared spectrum (Nujol) of this solid showed ν_{PH} at 2280 (w), ν_{PD} at 1660 (m), and ν_{IrH} at 2130 (m) cm^{-1}. No absorption corresponding to ν_{IrD} was observed, suggesting that exchange of only the PH protons had occurred. Evaporation of the filtrate left an orange solid which was identified by infrared analysis as $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$.

Preparation of $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$. In a vacuum-line reaction, phosphine (0.0163 mol) was condensed into a degassed, frozen solution of 3.0 g (0.0054 mol) of $\{Ir(CO)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$[25] in 20 ml of acetonitrile. The solution was stirred at 25° for 10 min and frozen in liquid nitrogen, and noncondensable gas was removed. After the cycle was repeated twice, no noncondensable gas was observed, and the colorless mixture was warmed to 25°. Addition of 200 ml of diethyl ether with a hypodermic syringe formed a white precipitate which was collected and purified by reprecipitation from an acetonitrile solution with diethyl ether to give 2.0 g (67%) (after drying at 25° (0.5 μ) for 3 hr) of white $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$, mp 185–189°. *Anal.* Calcd for $C_{12}H_{35}ClP_5Ir$: C, 25.7; H, 6.3; Cl, 6.3; P, 27.5. Found: C, 26.7; H, 6.3; Cl, 6.6; P, 25.5.

The complex is soluble in acetonitrile, ethanol, methanol, acetone, and dichloromethane and insoluble in diethyl ether, benzene, and hexane. It is moderately stable in air.

When PD_3 was used in a similar reaction, the product showed a new infrared band at 1634 cm^{-1} (ν_{PD}) while the bands at 2247 (ν_{PH}) and 1953 (ν_{IrH}) cm^{-1} were greatly reduced in intensity. The Ir–D stretching frequency was not observed because of the interference of ligand bands at *ca.* 1400 cm^{-1}.

Preparation of $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}[B(C_6H_5)_4]$. To a solution of 1.0 g (0.00178 mol) of $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$ in 10 ml of ethanol was added a solution of 2.0 g (0.0058 mol) of $NaB(C_6H_5)_4$ in 10 ml of ethanol. The resulting white precipitate was collected and purified from dichloromethane–ethanol by evaporation, and the white, crystalline product was dried at 25° (0.5 μ) for 16 hr to give 0.8 g (53%) of $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}[B(C_6H_5)_4]$. *Anal.* Calcd for $C_{36}H_{55}BP_5Ir$: C, 51.1; H, 6.6; P, 18.3. Found: C, 50.1; H, 6.4; P, 17.9.

Reactions of $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$. The complex was recovered unchanged after treatment with N_2, CO, or H_2 in refluxing acetonitrile or D_2O in acetonitrile at 25° or upon heating at 175° (0.1 μ) for 4 hr.

Results and Discussion

Nickel and Manganese Complexes. The series of new complexes $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$ (x = 1–4) was prepared by

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(23) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 88, 5324 (1966).

(24) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).

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the reaction of phosphine with suitable zerovalent nickel complexes. Excess phosphine displaced one triphenyl phosphite from $Ni[P(OC_6H_5)_3]_4$ in refluxing tetrahydrofuran to give $Ni(PH_3)[P(OC_6H_5)_3]_3$. Further substitution of triphenyl phosphite did not appear to occur in this reaction. The other members of the series were prepared by reaction of phosphine with bis(1,5-cyclooctadiene)nickel and the appropriate stoichiometric amount of triphenyl phosphite. The synthesis of $Ni(PH_3)_4$ by a similar procedure was reported[17] prior to the publication of this work. The complex was characterized by Raman spectroscopy. Tetrakis(phosphine)nickel(0) is the first example of a metal complex containing only phosphine ligands, although another tetrakis(phosphine) complex, $Cr(CO)_2(PH_3)_4$, has been described.[7]

The $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$ ($x = 1$-4) complexes are white or off-white crystalline solids, soluble in common organic solvents. However, the thermal stability decreases markedly with increasing substitution of phosphine. Thus, $Ni(PH_3)[P(OC_6H_5)_3]_3$ can be recrystallized from boiling *n*-heptane, $Ni(PH_3)_2[P(OC_6H_5)_3]_2$ decomposes in hot *n*-hexane, and $Ni(PH_3)_3[P(OC_6H_5)_3]$ and $Ni(PH_3)_4$ decompose in solution or in the solid state below room temperature. The low thermal stability of the tris- and tetrakis-phosphine complexes prohibited characterization by elemental analysis and their formulation is based upon the method of preparation and the observed ^1H and ^{31}P magnetic resonance spectra.

Phosphine also displaced triphenylphosphine from $Ni[P(C_6H_5)_3]_4$ in diethyl ether at room temperature to give $Ni(PH_3)[P(C_6H_5)_3]_3$ or $Ni(PH_3)_2[P(C_6H_5)_3]_2$ depending upon whether 1 equiv or an excess of phosphine, respectively, was used. These complexes are yellow, crystalline solids which decompose rapidly upon heating in benzene solution; they also decompose upon air exposure either as solids or in solution.

The infrared and proton magnetic resonance spectra of the new nickel complexes (Table I and Figures 1 and 2) confirm the presence of the phosphine ligands. The 220-MHz proton spectrum of the phosphine ligand in $Ni(PH_3)[P(OC_6H_5)_3]_3$ is a first-order doublet of quartets arising from P-H coupling ($J = 300$ Hz) within the PH_3 group combined with coupling ($J = 18$ Hz) of the PH protons with the three phosphorus nuclei of the triphenyl phosphite ligands. The 60-MHz proton spectra of the phosphine ligands in $Ni(PH_3)_2[P(OC_6H_5)_3]_2$ and $Ni(PH_3)_2[P(C_6H_5)_3]_2$ were poorly resolved and the spectra appeared as doublets of multiplets; chemical shift data are given in Table I. The 220-MHz proton spectrum of the phosphine ligands in $Ni(PH_3)_2[P(OC_6H_5)_3]_2$ (Figure 1a) more clearly showed the multiplet structure. The complex pattern arises from coupling of the PH_3 groups to give an $X_3AA'X'_3$ spectrum[26,27] combined with coupling with the phosphite phosphorus nuclei. The 220-MHz proton spectrum of the phosphine ligands in $Ni(PH_3)_3[P(OC_6H_5)_3]$ (Figure 1b) is similarly complex and arises from virtual coupling of the three phosphine groups with further splitting by the phosphite phosphorus nucleus. The spectrum also shows the presence of $Ni(PH_3)_4$; displacement of PH_3 from $Ni(PH_3)_4$ by triphenyl phosphite is apparently incomplete under the reaction conditions. No resonances other than those due to aromatic and phosphine protons were observed indicating that complete displacement of 1,5-cyclooctadiene had occurred.

The product from the reaction of excess phosphine with bis(1,5-cyclooctadiene)nickel is formulated as $Ni(PH_3)_4$ on the basis of the 220-MHz proton resonance spectrum (Figure 2). The symmetrical doublet of complex multiplets arises from virtual coupling of the four phosphine groups. Similarly complex spectra were observed for the phosphine protons in $Cr(CO)_2(PH_3)_4$.[27] The only other proton resonance observed in the solution was that of free phosphine (from decomposition) indicating that 1,5-cyclooctadiene was completely displaced in the reaction. Although the number of phosphine groups coordinated to the nickel atom cannot be deduced from the proton spectrum, a four-coordinate structure is consistent with those of other zerovalent nickel complexes.

The Fourier-mode, proton-noise-decoupled ^{31}P nmr spec-

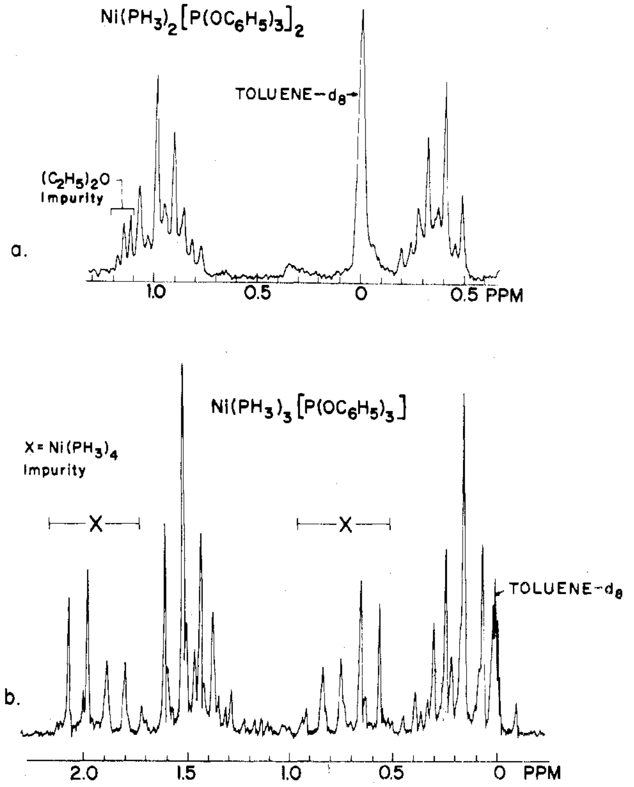

Figure 1. The 220-MHz ^1H nmr spectra of the phosphine ligands in $Ni(PH_3)_2[P(OC_6H_5)_3]_2$ (a) and $Ni(PH_3)_3[P(OC_6H_5)_3]$ (b) in toluene-d_8 at −40°. Figure 1a was recorded using a Fourier-mode attachment. The chemical shifts are referred to the methyl group of toluene-d_8. Both solutions contained some nickel metal and chemical shifts relative to external $(CH_3)_4Si$ were not obtained.

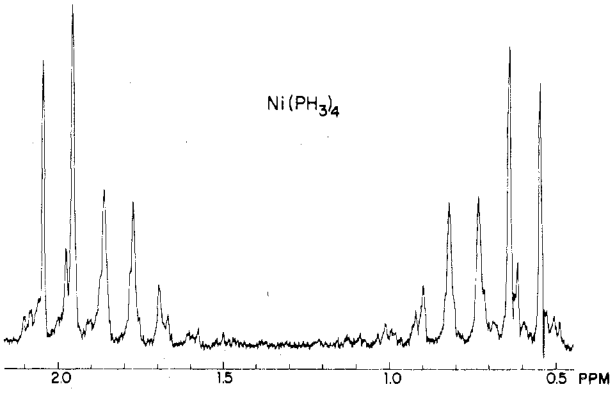

Figure 2. The 220-MHz ^1H nmr spectrum of $Ni(PH_3)_4$ in toluene-d_8 at −40°. The chemical shifts are referred to the methyl group of toluene-d_8. The solution contained a trace of nickel metal and chemical shifts relative to external $(CH_3)_4Si$ were not obtained.

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(26) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, 15, 157 (1968).

(27) E. Moser, E. O. Fischer, W. Bathelt, W. Gretner, L. Knauss, and E. Louis, *J. Organometal. Chem.*, 19, 377 (1969).

tra[28] of the $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$ (x = 0-4) complexes are summarized in Table II. The multiplet patterns observed for the complexes with x = 1-3 confirm the assigned compositions, and, in the case of $Ni(PH_3)_3[P(OC_6H_5)_3]$, are the basis for characterization of the product since no elemental analyses could be obtained. The spectra also support the presence of $Ni(PH_3)_4$ as an impurity in $Ni(PH_3)_3[P(OC_6H_5)_3]$ in agreement with the proton nmr spectrum (Figure 1b).

At room temperature in benzene solution, $Ni(PH_3)[P(C_6H_5)_3]_3$ reacted with carbon monoxide to give $Ni(CO)_2[P(C_6H_5)_3]_2$ and with triphenyl phosphite to give $Ni[P(OC_6H_5)_3]_4$; triphenylphosphine did not react and appeared to stabilize the phosphine complex. Under similar conditions, $Ni(PH_3)[P(OC_6H_5)_3]_3$ did not react with triphenyl phosphite while triphenylphosphine displaced phosphine to give a mixture of nickel(0) complexes. The phosphine protons of $Ni(PH_3)[P(OC_6H_5)_3]_3$ did not undergo deuterium exchange in mixtures of D_2O or CH_3OD in tetrahydrofuran at room temperature even in the presence of triethylamine. However, after 1-hr reflux the product recovered from a mixture of $Ni(PH_3)[P(OC_6H_5)_3]_3$, CH_3OD, and triethylamine in tetrahydrofuran showed a new infrared band at 1680 cm^{-1}, indicating that some H-D exchange of the phosphine protons had occurred.

The orange, crystalline complex $MnBr(CO)_3(PH_3)_2$ was obtained by the reaction of excess phosphine with $MnBr(CO)_5$ in refluxing tetrahydrofuran. The reaction conditions were similar to those reported for the synthesis of $MnBr(CO)_4(PH_3)$,[3] and the product which is obtained appears to be determined by the procedure used for isolation and purification. In the case of the mono-phosphine complex, an attempt was made to sublime the crude product[29] which may have decomposed the bis-phosphine product; the sublimation step was omitted in the procedure described here. A similar reaction has been used to prepare $MnI(CO)_4PH_3$ and $MnI(CO)_3(PH_3)_2$ from phosphine and $MnI(CO)_5$.[12]

The 60-MHz proton resonance spectrum of the phosphine ligands in $MnBr(CO_3)(PH_3)_2$ is compared in Figure 3 with the computer-simulated spectrum calculated[30] assuming a virtually coupled $X_3AA'X'_3$ spectrum. The computer simulation is nearly identical with the observed spectrum; the parameters used in the calculation are summarized in Table I. The nmr pattern requires magnetically equivalent phosphine ligands, and this, along with the observation of three carbonyl stretching frequencies (Table I), establishes the octahedral stereochemistry of $MnBr(CO)_3(PH_3)_2$ as having cis phosphine groups with the bromide ligand trans to a carbonyl.

Iridium Complexes. The reaction of phosphine with an orange solution of $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ (X = Cl or $B(C_6H_5)_4$) in dichloromethane at −78° gave a deep yellow solution from which yellow crystals were isolated at −78° upon addition of diethyl ether. Upon warming to room temperature, the yellow crystals became orange and the original iridium(I) complex was obtained. The yellow solid was identified as the phosphine complex $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ from the 100-MHz proton nmr spectrum at −70° (Table I and Figure 4a). Coordinated phosphine appears at τ 8.11 as a doublet (J_{PH_3} = 300 Hz) of poorly resolved quintets (J = 6 Hz); the quintet structure arises from coupling of the PH_3 protons with the four magnetically equivalent phosphorus nuclei of the tertiary phosphine ligands.

Table II. Fourier-Mode, Proton-Noise-Decoupled ^{31}P Nmr Spectra of $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$[a]

	δ,[b] ppm		
x	$P(OC_6H_5)_3$	PH_3	J, Hz
0	130.3 (s)		
1	138.9 (d)	−163.7 (q)	9
2	145.1 (t)	−160.1 (t)	20.5
3	151.8 (q)	−159.6 (d)[c]	36
4		−156.1 (s)	

[a] The spectra were obtained using toluene solutions at −40°. [b] The chemical shifts are relative to external H_3PO_4. [c] This spectrum also showed a singlet at δ −156.1 due to the $Ni(PH_3)_4$ impurity.

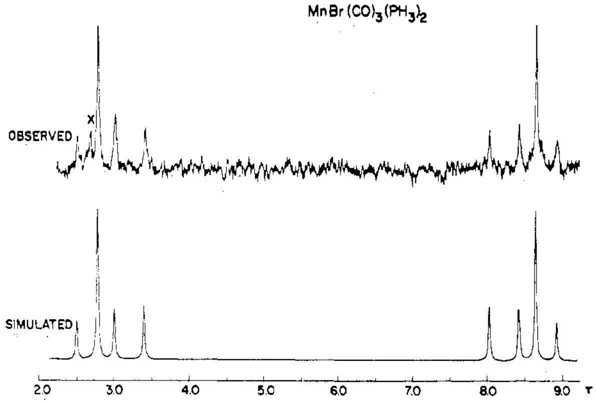

Figure 3. Observed and computer-simulated ^1H nmr spectra of $MnBr(CO)_3(PH_3)_2$. The observed spectrum was obtained at 60 MHz using a $CDCl_3$ solution with an internal $Si(CH_3)_4$ reference; X indicates a $CHCl_3$ impurity.

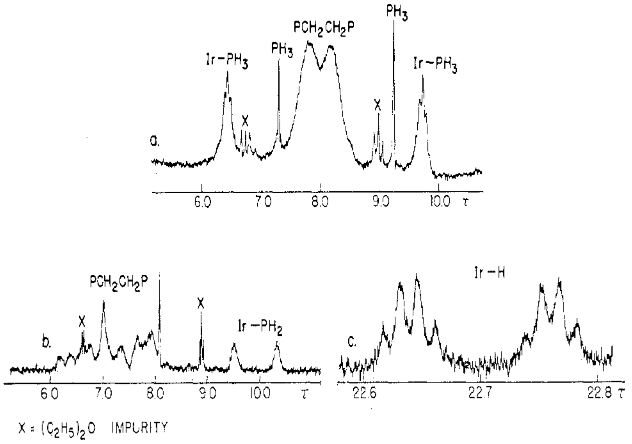

Figure 4. Proton nmr spectra of CD_2Cl_2 solutions of $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$ at −70° and 100 MHz (a) and $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$ at 220 MHz in the low-field (b) and high-field (c) region. Chemical shifts are calculated from internal CH_2Cl_2 assuming τ (CH_2Cl_2) 4.72.

When a dichloromethane solution of $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ was warmed to room temperature in a closed system, the color first changed from bright yellow to orange and then to pale yellow. Addition of diethyl ether gave an off-white precipitate of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ which is formed by oxidative addition of a P-H bond to the iridium(I) cation. The infrared and 220-MHz proton nmr spectra and chemical reactivity are consistent with a six-coordinate iridium(III) cation containing cis hydride and nonbridging PH_2 ligands.

In the proton resonance spectrum of $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ (Table I and Figure 4b, c)

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[28] The ^{31}P spectra were obtained by Dr. Paul Meakin.

[29] F. Klanberg, private communication.

[30] The computer-simulated spectrum was obtained by Dr. Paul Meakin.

the doublet centered at τ 9.95 is assigned to a nonbridging PH_2 ligand. The value of $J_{PH} = 180$ Hz for the PH_2 ligand is larger than that observed for the PH_2 ligand in the $[Mo(PH_2)(CO)_5]^-$ ion (160 Hz)[31] or for $NaPH_2$ in liquid ammonia (139 Hz)[32] but is significantly lower than that observed for the bridging PH_2 ligand in the $[(CO)_5MoPH_2Mo(CO)_5]^-$ ion (249 Hz)[31] or for complexed PH_3 (Table I). An increase in P-H coupling upon coordination of the PH_2 group is expected in accord with that found for PH_3. Each of the PH_2 doublets observed in Figure 3b is a quintet ($J =$ 5 Hz) because of coupling with the tertiary phosphine nuclei. This fine structure establishes the coordination of all four tertiary phosphorus atoms to the iridium. The iridium-hydride resonance is observed as a doublet of quartets at τ 21.7 and the splitting pattern is interpreted as arising from coupling of the hydride hydrogen with a trans tertiary phosphine phosphorus atom ($J = 118$ Hz) and smaller coupling with three cis tertiary phosphine phosphorus atoms ($J =$ 15 Hz). The coupling of the hydride with the phosphorus nucleus of the cis PH_2 group is assumed to be very small or zero. The absence of coupling between the hydride and PH_2 group may be due to the nature of the H-Ir-PH_2 angle; an angular dependence of geminal coupling has been suggested for CH_2[33] and PH_2[34] groups. The assignment of infrared absorptions to ν_{PH_2} and ν_{IrH} (Table I) was confirmed by the use of PD_3 in the reaction; the expected values for ν_{PD_2} and ν_{IrD} were observed.

A hydridophosphide complex, $\{$*trans*-$IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$, was also obtained in the reaction of $Ir(CO)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Cl$ with phosphine. The use of PD_3 gave the corresponding deuterio complex, and the tetraphenylborate salt was obtained by reaction of the chloride with sodium tetraphenylborate in ethanol. The 220-MHz proton resonance spectrum of the tetraphenylborate salt is summarized in Table I. The PH_2 protons appear as a doublet of quintets establishing coordination of the four tertiary phosphine phosphorus atoms. The hydride resonance (τ 23.23) is an apparent septet ($J = 16$ Hz) and is explained by an octahedral geometry with the hydride ligand trans to the PH_2 group. The septet is thus a doublet of overlapping quintets with $J(\text{H-P}_{trans}) = 32$ Hz and $J(\text{H-P}_{cis}) =$ 16 Hz. The solution decomposes slowly and a weak resonance of an unknown hydride impurity was observed at τ 22.60.

Reductive elimination of phosphine from $\{$*cis*-$IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ ($X = B(C_6H_5)_4$) is facile and occurs upon heating the solid complex at 180° under vacuum or in refluxing acetonitrile. The product in each case was $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$. Phosphine was also displaced by carbon monoxide or hydrogen in acetonitrile and the products, $\{Ir(CO)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ and $\{Ir(H_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$, respectively, are identical with those previously obtained from reactions of the iridium(I) cation.[23,24] In contrast, $\{$*trans*-$IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$ was recovered unchanged after treatment with nitrogen, carbon monoxide, or hydrogen in refluxing acetonitrile or upon heating at 175° under vacuum. When $\{$*cis*-$IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}$ was treated with D_2O in acetonitrile at 25°, the infrared spectrum of the recovered product indicated that H-D exchange of the PH_2 protons only had occurred. The $(CH_3)_2PCH_2CH_2P(CH_3)_2$ analog was recovered unchanged from a similar reaction.

In the reaction of phosphine with $RhCl[P(C_6H_5)_3]_3$, the product was originally formulated[3] as $RhCl(PH_3)[P(C_6H_5)_3]_2$, but an infrared absorption at 2150 cm^{-1} was assigned as being due primarily to an Rh-H vibration. This reaction was repeated using PD_3, and the appearance of new infrared absorptions at 1690 cm^{-1} (ν_{PD}) and 1525 cm^{-1} (ν_{RhD}) confirms the presence of an Rh-H bond. In view of the results described above for iridium(I), the rhodium product is reformulated as a rhodium(III) hydridophosphide complex, $\{RhH(PH_2)Cl[P(C_6H_5)_3]_2\}_n$. The most likely value of n is 2, and the complex may contain chloride or phosphide bridges. The low solubility prevented further characterization of this complex.

The reaction of phosphine with $IrCl(CO)[P(C_6H_5)_3]_2$ was also reinvestigated, and although a pure product was not obtained, it appears certain that a hydridophosphide complex of iridium(III) was formed rather than the phosphine complex originally postulated.[3] The formation of PH_2 groups accompanied by formation of metal hydrides or loss of hydrogen (as H_2 or HX) is a more probable explanation for the cluster compounds previously reported to be phosphine complexes.[3]

Registry No. $MnBr(CO)_3(PH_3)_2$, 38708-63-3; $MnBr(CO)_4(PH_3)$, 20753-25-7; $Ni(PH_3)[P(OC_6H_5)_3]_3$, 38708-65-5; $Ni(PH_3)_2[P(OC_6H_5)_3]_2$, 38708-66-6; $Ni(PH_3)_3[P(OC_6H_5)_3]$, 38708-67-7; $Ni(PH_3)_4$, 37513-28-3; $Ni(PH_3)[P(C_6H_5)_3]_3$, 38708-69-9; $Ni(PH_3)_2[P(C_6H_5)_3]_2$, 38708-70-2; $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ ($X = Cl$), 38708-71-3; $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ ($X = B(C_6H_5)_4$), 38811-47-1; $\{IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}Cl$, 38703-57-0; *cis*-$\{IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}[B(C_6H_5)_4]$, 38703-58-1; *cis*-$\{IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}PF_6$, 38703-59-2; *trans*-$\{IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl$, 38703-60-5; *trans*-$\{IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}[B(C_6H_5)_4]$, 38703-61-6; $\{RhH(PH_2)Cl[P(C_6H_5)_3]_2\}_n$, 38832-80-3.

Acknowledgments. The author is indebted to Dr. Paul Meakin for assistance in the interpretation of the nmr spectra and to Drs. E. L. Muetterties, G. W. Parshall, and U. Klabunde for many helpful discussions.

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