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Cationic Complexes of Rhodium(I) and Iridium(I) with Secondary Phosphines and Related Compounds

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The reactions of $[RhCl(C_8H_{12})]_2$ and $[IrCl(C_8H_{14})_2]_2$ with a variety of secondary phosphines lead to the formation of four-coordinate cationic complexes $[M(HPR_2)_4]^+$ (M = Rh or Ir; $HPR_2 = HP(C_6H_{11})_2, HP(C_6H_{11})C_6H_5, HP(C_6H_5)_2$; M = Rh; $HPR_2 = HP(C_2H_5)_2, HP(C_2H_5)C_6H_5$). The reactions of these complexes with some small molecules (CO, H_2, HX) are described and the properties and structures of the resulting M(I) or M(III) adducts are discussed. The ligand $HP(C_2H_5)_2$ reacts with $[IrCl(C_8H_{14})_2]_2$ in methanol to give the iridium(III) hydrido derivative $[IrH(HP(C_2H_5)_2)_5]^{2+}$.

Introduction

The preparation and properties of tertiary and ditertiary phosphine complexes of rhodium and iridium have been the object of considerable interest. By contrast, the secondary phosphine derivatives have received little attention. In fact, the only examples reported in the literature appear to be the complexes $[RhCl_3(HPR_2)_3]$ (R = C_2H_5, C_6H_5),[1] $[RhCl(HP(C_6H_5)_2)_3]$,[1] $[Rh(HP(C_6H_5)_2)_4]^+$,[2] and $[Ir(CO)(HP(C_6H_5)_2)_4]^+$.[2]

In this paper we report, as a part of a systematic study on the properties of metal complexes with secondary phosphines,[3] the preparation of a series of cationic complexes of rhodium(I) and iridium(I) of general formula $[M(HPR_2)_4]^+$. The phosphine ligands employed are $HP(C_2H_5)_2$, $HP(C_2H_5)C_6H_5$, $HP(C_6H_5)_2$, $HP(C_6H_5)C_6H_{11}$ and $HP(C_6H_{11})_2$. Furthermore, the addition reactions of some small covalent molecules to the $[M(HPR_2)_4]^+$ cations have been investigated. The results can be helpful for a better understanding of the role played by the ligands in regulating the activity of the metal in $[ML_4]^+$ type complexes (M = Rh, Ir; L = phosphorus ligand[4]).

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen and the solvents were appropriately dried and distilled before use. The secondary phosphines $HP(C_6H_5)R$ (R = C_2H_5, C_6H_5, C_6H_{11}) were obtained by hydrolysis of the corresponding $LiP(C_6H_5)R$. Diethyl- and dicyclohexylphosphines were prepared following Issleib's method.[5] Di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium was prepared by the method of Chatt and Venanzi.[6] Di-μ-chloro-tetra(cyclooctene)diiridium was prepared by the method of Shaw and Singleton.[7]

Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. NMR spectra were taken using a Bruker 90 MHz instrument. Conductivity measurements were made with a LKB conductance bridge. Gas absorptions were carried out in a standard apparatus.

The physical properties and analytical data of the rhodium and iridium complexes are listed in Table I. Reaction yields ranged between 50 and 95%. Significant ir and ^1H NMR data are reported in Table II. In most cases it was impossible to detect the ^1H NMR signals due to the protons directly bound to the phosphorus; however, ir spectra of all the compounds show medium to weak bands in the 2250–2400-cm^{-1} region attributable to the P–H group of the phosphines.

Synthesis of the Complexes. $[Rh(HP(C_2H_5)_2)_4]B(C_6H_5)_4$. Diethylphosphine (9 mmol) was added to a suspension of di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium (1 mmol) in 2-propanol (15 ml). Addition of sodium tetraphenylborate gave a yellow precipitate which was recrystallized from dichloromethane-2-propanol.

$[Rh(HPR_2)_4]ClO_4$ ($R_2 = C_2H_5(C_6H_5), (C_6H_5)_2, C_6H_5(C_6H_{11}), (C_6H_{11})_2$). The phosphine (9 mmol) was added to a suspension of di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium (1 mmol) in methanol (15 ml) and the mixture was stirred until the whole original suspension had dissolved. Sodium perchlorate (1 g) in methanol (10 ml) was added and the resulting yellow precipitate was recrystallized from dichloromethane–methanol.

$[Ir(HPR_2)_4]B(C_6H_5)_4$ ($R_2 = (C_6H_5)_2, C_6H_5(C_6H_{11}), (C_6H_{11})_2$). These compounds were similarly prepared using the appropriate phosphine ligand, di-μ-chloro-tetra(cyclooctene)diiridium, and sodium tetraphenylborate.

$[IrH(HP(C_2H_5)_2)_5]Y$ (Y = ClO_4, $B(C_6H_5)_4$). Diethylphosphine (11 mmol) was added to a suspension of di-μ-chloro-tetra(cyclooctene)diiridium (1 mmol) in methanol (15 ml). A colorless solution was immediately formed, from which by adding sodium tetraphenylborate or perchlorate white crystals precipitated. The products were recrystallized from dichloromethane–methanol.

$[RhCl(HP(C_6H_{11})_2)_3]$. Dicyclohexylphosphine (4 mmol) and di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium (0.5 mmol) were heated together under reflux in *n*-hexane for 30 min. The yellow precipitate was filtered off, washed with *n*-hexane, and dried in vacuo.

$[Rh(CO)(HP(C_6H_{11})_2)_3]ClO_4$. Method (a). Carbon monoxide was passed through a solution of $[Rh(HP(C_6H_{11})_2)_4]ClO_4$ in a 1:1 mixture of dichloromethane and ethanol for 10 min. The dichloromethane was removed under reduced pressure and the yellow precipitate formed was filtered off and recrystallized from dichloromethane–ethanol.

Method (b). $[RhCl(HP(C_6H_{11})_2)_3]$ (0.2 g) was dissolved in methanol (10 ml) under a carbon monoxide atmosphere. Addition of sodium perchlorate (0.2 g) in methanol (5 ml) gave yellow crystals of the compound.

$[RhHCl(HPR_2)_4]Y$ (Y = ClO_4, $B(C_6H_5)_4$; $R_2 = (C_2H_5)_2, (C_2H_5)C_6H_5, (C_6H_5)_2, (C_6H_5)C_6H_{11}, (C_6H_{11})_2$). A suspension of $[Rh(HPR_2)_4]Y$ (1 mmol) in methanol or 2-propanol was treated with aqueous solutions of HCl (1 mmol). The mixture was stirred until the yellow original product turned white or pale-yellow. The precipitate was filtered off and washed with alcohol and diethyl ether. The compounds with $HP(C_2H_5)_2$, $HP(C_2H_5)C_6H_5$, and $HP(C_2H_5)C_6H_{11}$ were recrystallized from dichloromethane–2-propanol, while that with $HP(C_6H_{11})_2$ was recrystallized from dichloromethane–methanol. The compound with $HP(C_6H_5)_2$ is completely insoluble in the usual solvents.

$[Ir(CO)(HPR_2)_4]B(C_6H_5)_4$ ($R_2 = (C_6H_5)_2, C_6H_5(C_6H_{11})$). Method (a). *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I) (1 mmol) and the appropriate phosphine (8 mmol) were stirred in methanol (15 ml) until a clear solution was formed. Sodium tetraphenylborate (0.3 g) in methanol (10 ml) was added to the solution and a yellow precipitate formed. The product with diphenylphosphine was recrystallized from dichloromethane–ethanol, while the phenylcyclohexylphosphine derivative was purified from acetone–2-propanol.

Method (b). A suspension of $[Ir(HPR_2)_4]B(C_6H_5)_4$ in methanol was shaken in a carbon monoxide atmosphere for 30 min. The light yellow precipitates were filtered and washed with methanol and diethyl ether.

$[Ir(CO)(HP(C_2H_5)_2)_4]B(C_6H_5)_4$. Diethylphosphine (8 mmol) was added to a suspension of *trans*-chlorocarbonylbis(triphenylphosphine)iridium (1 mmol) in 2-propanol (10 ml). Sodium tetraphenylborate (0.3 g) in 2-propanol was added and the resulting precipitate was filtered off, washed with 2-propanol, and then recrystallized from dichloromethane–2-propanol.

$[Ir(CO)(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$. Dicyclohexylphosphine (5 mmol) was added to a suspension of *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.5 mmol) in methanol (15 ml). The orange solution formed was treated with sodium tetraphenylborate (0.3 mg) in methanol. The orange precipitate was filtered off and recrystallized from dichloromethane–methanol.

$[IrH_2(CO)(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$. A solution of $[Ir(CO)(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$ in dichloromethane was saturated with hydrogen at room temperature. The orange color was discharged and

Table I. Properties and Analytical Data of Rhodium and Iridium Complexes

Compd	Color	Mp with dec, °C[a]	Anal. % C Calcd	% C Found	% H Calcd	% H Found	% Cl Calcd	% Cl Found	Λ_M,[b] cm^2 ohm^{-1} mol^{-1}
$[Rh(HPEt_2)_4]BPh_4$	Yellow	147	61.40	61.50	8.24	8.31			26.8
$[Rh(HPEtPh)_4]ClO_4$	Yellow	156	50.59	50.12	5.84	5.73	4.68	4.80	26.1
$[Rh(HPPh_2)_4]ClO_4$	Yellow	183	60.81	60.73	4.68	4.63	3.74	3.85	20.4
$[Rh(HPPhCy)_4]ClO_4$	Yellow	196	59.30	59.67	7.05	7.19	3.65	3.70	19.2
$[Rh(HPCy_2)_4]ClO_4$	Yellow	193	57.86	58.41	9.24	9.38	3.56	3.59	19.7
$[RhHCl(HPEt_2)_4]BPh_4$	White	168	58.67	58.62	8.00	8.14	4.33	4.25	26.4
$[RhHCl(HPEtPh)_4]BPh_4$	White	179	66.26	66.05	6.45	6.47	3.49	3.58	25.4
$[RhHCl(HPPh_2)_4]ClO_4$	White	214	58.61	58.31	4.61	4.57	7.20	7.40	*d*
$[RhHCl(HPPhCy)_4]ClO_4$	Pale-yellow	159	57.21	57.13	6.90	7.14	7.04	7.10	20.3
$[RhHCl(HPCy_2)_4]ClO_4$	White	188	55.86	55.34	9.08	9.28	6.87	6.77	20.5
$[RhCl(HPCy_2)_3]$	Yellow	216	58.92	59.60	9.49	9.31	4.84	4.91	0.2
$[Rh(CO)(HPCy_2)_3]ClO_4$	Yellow	197	53.85	53.17	8.43	8.48	4.30	4.40	22.3
$[IrH(HPEt_2)_5](ClO_4)_2$	White	234	28.51	28.69	6.70	6.96	8.42	8.37	57.9[c]
$[IrH(HPEt_2)_5](BPh_4)_2$	White	238	63.70	63.30	7.54	7.68			44.4[c]
$[Ir(HPPh_2)_4]BPh_4$	Yellow	115	68.84	68.10	5.13	5.00			22.0
$[Ir(HPPhCy)_4]BPh_4$	Orange	185	67.54	66.80	6.93	7.03			28.2
$[Ir(HPCy_2)_4]BPh_4$	Orange	240	66.29	66.54	8.65	8.77			27.9
$[Ir(CO)(HPEt_2)_4]BPh_4$	White	126	54.73	54.33	7.17	7.33			28.1
$[Ir(CO)(HPPh_2)_4]BPh_4$	Yellow	163	68.27	68.60	5.02	4.97			28.7
$[Ir(CO)(HPPhCy)_4]BPh_4$	Yellow	125	67.01	66.66	6.78	6.90			28.2
$[Ir(CO)(HPCy_2)_3]BPh_4$	Orange	199	64.54	64.91	7.91	8.10			29.4
$[Ir(CO)_2(HPCy_2)_3]BPh_4$	White	128	64.07	63.36	7.72	7.98			26.7
$[IrH_2(HPPh_2)_4]BPh_4$	White	187	68.73	68.68	5.28	5.24			27.1
$[IrH_2(HPPhCy)_4]BPh_4$	White	140	67.43	66.64	7.07	7.15			30.2
$[IrH_2(HPCy_2)_4]BPh_4$	White	280	66.21	65.50	8.79	8.91			26.4
$[IrHCl(HPPh_2)_4]BPh_4$	White	242	66.90	65.31	5.07	4.97	2.74	2.71	*d*
$[IrHCl(HPPhCy)_4]BPh_4$	White	194	65.67	65.20	6.81	6.85	2.69	2.60	28.9
$[IrHCl(HPCy_2)_4]BPh_4$	White	230	64.48	64.28	8.49	8.58	2.64	2.58	29.9
$[IrH_2(CO)(HPCy_2)_3]BPh_4$	White	154	64.25	65.23	8.04	8.20			27.2

[a] Uncorrected; the melting points of rhodium(I) and iridium(I) complexes have been determined in a sealed tube under nitrogen. [b] In 1,2-$C_2H_4Cl_2$ at 25°, for approximately 10^{-3} *M* solutions. [c] In nitrobenzene. [d] Slightly soluble.

Table II. Ir and High-Field NMR spectra

Compd	Infrared (Nujol) ν_{MH}, cm^{-1}	ν_{CO}, cm^{-1}	^{1}H NMR (CH_2Cl_2) τ (MH)	Multiplicity (*J*), Hz
$[Rh(CO)(HPCy_2)_3]ClO_4$		1985		
trans-$[RhHCl(HPEt_2)_4]BPh_4$	2090		26.85	Doublet ($J_{RhH} = 19$) of quintets ($J_{PH} = 13$)
trans-$[RhHCl(HPPhEt)_4]BPh_4$	2060		26.33	Multiplet
$[RhHCl(HPPh_2)_4]ClO_4$	2080		*a*	
cis-$[RhHCl(HPPhCy)_4]BPh_4$	2010		18.95	Broad doublet ($J_{PH} \sim 180$)
trans-$[RhHCl(HPCy_2)_4]ClO_4$	2110		27.07	Multiplet
$[Ir(CO)(HPEt_2)_4]BPh_4$		1925		
$[Ir(CO)(HPPh_2)_4]BPh_4$		1940		
$[Ir(CO)(HPPhCy)_4]BPh_4$		1920		
$[Ir(CO)(HPCy_2)_3]BPh_4$		1985		
$[Ir(CO)_2(HPCy_2)_3]BPh_4$		2005, 1945		
$[IrH_2(CO)(HPCy_2)_3]BPh_4$	2140, 2060	1995	22.08	Doublet ($J_{PH} = 112$) of triplets ($J_{PH} = 17$)
			22.13	Quartet ($J_{PH} = 17$)
cis-$[IrH_2(HPPh_2)_4]BPh_4$	2090, 2060		20.95	Symmetrical second-order pattern, 6 lines
cis-$[IrH_2(HPPhCy)_4]BPh_4$	2070, 2020		22.23	Symmetrical second-order pattern, 6 lines
cis-$[IrH_2(HPCy_2)_4]BPh_4$	2090, 2080		23.66	Symmetrical second-order pattern, 6 lines
$[IrH(HPEt_2)_5](BPh_4)_2$	2120		24.10	Doublet ($J_{PH} = 110$) of quintets ($J_{PH} = 15$)
$[IrHCl(HPPh_2)_4]BPh_4$	2080		*a*	
trans-$[IrHCl(HPPhCy)_4]BPh_4$	2210		29.50	Quintet ($J_{PH} = 12.5$)
trans-$[IrHCl(HPCy_2)_4]BPh_4$	2240		31.17	Quintet ($J_{PH} = 11$)

[a] Slightly soluble.

by addition of methanol colorless crystals of the required product were formed.

$[Ir(CO)_2(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$. A suspension of the orange $[Ir(HP(C_6H_{11})_2)_4]B(C_6H_5)_4$ in methanol was allowed to react with carbon monoxide for 30 min. The colorless product formed was filtered off, washed with methanol and diethyl ether, and dried in vacuo.

$[IrH_2(HPR_2)_4]B(C_6H_5)_4$ (R_2 = $(C_6H_5)_2$, $C_6H_5(C_6H_{11})$, $(C_6H_{11})_2$). A solution of $[Ir(HPR_2)_4]B(C_6H_5)_4$ in dichloromethane was treated with hydrogen until the orange color was discharged. Addition of methanol results in the formation of a white precipitate, which was recrystallized from dichloromethane–methanol.

$[IrHCl(HPR_2)_4]B(C_6H_5)_4$ (R_2 = $(C_6H_5)_2$, $C_6H_5(C_6H_{11})$, $(C_6H_{11})_2$). To a solution of $[Ir(HPR_2)_4]B(C_6H_5)_4$ (0.5 mmol) in dichloromethane (10 ml), HCl (0.5 mmol) in methanol (10 ml) was added. This solution became colorless and by adding an excess of methanol colorless crystals of the product were formed.

Results and Discussion

Rhodium Derivatives. Treatment of a suspension of $[RhCl(C_8H_{12})]_2$ in methanol or 2-propanol with secondary phosphines (Rh–HPR_2 = 1:4.5) rapidly gave orange-red solutions from which the yellow products $[Rh(HPR_2)_4]Y$ (Y = ClO_4, $B(C_6H_5)_4$) were isolated on addition of sodium perchlorate or tetraphenylborate. If a large excess of the ligands $HP(C_2H_5)_2$ and $HP(C_2H_5)C_6H_5$ was used, red semicrystalline oils, probably $[Rh(HPR_2)_5]Y$, were obtained. $[Rh(HPR_2)_4]Y$ complexes were characterized by elemental analysis and were found to be 1:1 electrolytes in 1,2-dichloroethane.

Manometric measurements show that all of these four-coordinate rhodium(I) complexes, except the dicyclohexylphosphine derivative, readily and reversibly reacted with hydrogen, in 1,2-dichloroethane at ambient condition. No pure hydrido derivatives have been isolated in the solid state; however, ir spectra of the solutions, which show a broad band in the 1950–1980-cm^{-1} region, are consistent with the formation of *cis*-$[RhH_2(HPR_2)_4]^+$ cations.[4b,8] These complexes have been also found to slowly catalyze the hydrogenation of cyclohexene. The lack of reactivity of the dicyclohexylphosphine derivative is probably related to the relatively high steric hindrance of this ligand.

The complexes $[Rh(HPR_2)_4]Y$ were found to react with hydrochloric acid to give white or pale-yellow products which analyzed as $[RhHCl(HPR_2)_4]Y$ ($Y = ClO_4$, $B(C_6H_5)_4$). The ir spectrum of $[RhHCl(HP(C_6H_5)C_6H_{11})_4]B(C_6H_5)_4$ contains a broad diffuse band at 2000 cm^{-1}, consistent with the presence of hydride trans to the phosphorus ligand.[9,10] In agreement with this arrangement, the metal–hydride resonance in the ^1H NMR spectrum appears as a broad doublet at τ 18.95, with separation of about 180 Hz. By contrast, the ir spectra of the other $[RhHCl(HPR_2)_4]Y$ complexes show a sharp peak in the 2060–2110-cm^{-1} region, which suggests that H is trans to Cl.[8-10] The trans stereochemistry is confirmed for the compound $[RhHCl(HP(C_2H_5)_2)_4]B(C_6H_5)_4$ by a high-field ^1H NMR spectrum which exhibits a well-resolved doublet of quintets at τ 26.85 ($J_{Rh-H} = 19$ Hz, $J_{P-H} = 13$ Hz). The metal–hydride signal appears as a not resolved multiplet at about τ 27 (Table II) for the complexes $[RhHCl(HPR_2)_4]^+$ ($HPR_2 = (C_2H_5)C_6H_5$, $(C_6H_{11})_2$). The HCl adduct of the complex with diphenylphosphine has been previously reported by Sanders,[2] who suggested a binuclear structure $[Rh_2HCl_2(HP(C_6H_5)_2)_6]^+$. However, owing to the low solubility of the compound, this structure cannot be confirmed by NMR measurements.

When solutions of the complexes $[Rh(HPR_2)_4]Y$ were treated with CO (1 atm, 25°C) ready formation of carbonyl derivatives occurred. From the solutions, however, analytically pure samples were obtained only in the case of the dicyclohexylphosphine derivative, while, in the other cases, yellow semicrystalline oils were recovered. Therefore, the reaction between CO and the $[Rh(HPR_2)_4]^+$ complexes was investigated in 1,2-dichloroethane solution, by measuring the amount of CO absorbed and the ir spectra of the solutions. $[Rh(HP(C_6H_{11})_2)_4]^+$ absorbs about 1 mol of CO per mol of Rh, with formation of the monocarbonyl adduct $[Rh(CO)(HP(C_6H_{11})_2)_3]^+$ ($\nu_{CO} = 2000$ cm^{-1}). This complex has been isolated in the solid state also by reacting an ethanol solution of $[RhCl(HP(C_6H_{11})_2)_3]$ with CO in the presence of $NaClO_4$. In the case of $[Rh(HP(C_6H_5)_2)_4]^+$, less than 1 mol of CO per mol of Rh was absorbed and the ir spectra of the 1,2-dichloroethane solutions show a strong band at 1960 cm^{-1}, which disappears on bubbling nitrogen through the solution. The position of the band is consistent with the formation of the monocarbonyl derivative $[Rh(CO)(HP(C_6H_5)_2)_4]^+$.[8,10] The ir spectra of the solutions containing the carbonyl adducts with the phosphines $HP(C_6H_5)C_6H_{11}$, $HP(C_6H_5)C_2H_5$, and $HP(C_2H_5)_2$ (more than 1 mol of CO per mol of Rh was absorbed) show bands at 2005–2015 cm^{-1} and 1940–1950 cm^{-1}, which can be attributed respectively to four-coordinate $[Rh(CO)(HPR_2)_3]^+$ and five-coordinate $[Rh(CO)(HPR_2)_4]^+$ species. Moreover, less intense bands appear at 1970–1985 cm^{-1}, probably due to the formation of some amount of dicarbonyl derivatives $[Rh(CO)_2(HPR_2)_3]^+$. When nitrogen is bubbled through the solutions, the band at 1970–1985 cm^{-1} disappears, while those at 2005–2015 and 1940–1950 cm^{-1} gain in intensity. It should be noted that, in disagreement with our results, Sanders claimed that $[Rh(HP(C_6H_5)_2)_4]^+$ does not react with carbon monoxide or hydrogen.[2]

Finally, all the $[Rh(HPR_2)_4]^+$ complexes have been found to react rapidly with oxygen in 1,2-dichloroethane solutions at ambient condition. However, no evidence for the formation of $[RhO_2(HPR_2)_4]^+$ adducts has been obtained but about 2 mol of O_2 per mol of rhodium was absorbed, with decomposition of the complexes and formation of oxidation products of the phosphines.

Iridium Derivatives. When $[IrCl(C_8H_{14})_2]_2$ was allowed to react with an excess of the phosphines $HP(C_6H_5)_2$, $HP(C_6H_5)C_6H_{11}$, and $HP(C_6H_{11})_2$ in methanol, orange solutions were formed. Addition of $NaB(C_6H_5)_4$ precipitated yellow-orange crystals of the expected $[Ir(HPR_2)_4]B(C_6H_5)_4$ complexes. By contrast, reaction of $[IrCl(C_8H_{14})_2]_2$ in methanol with $HP(C_2H_5)_2$ gave a colorless solution, from which white crystals were obtained by adding $NaB(C_6H_5)_4$ or $NaClO_4$. The compound was shown to be a hydrido derivative of the type $[IrH(HP(C_2H_5)_2)_5]Y_2$ by elemental analyses, ir, and ^1H NMR spectra. The ir spectra exhibit, along with the ligands and the uncoordinated anion modes, a sharp peak at 2120 cm^{-1}, which can be assigned to a metal–hydrogen stretching vibration. High-field NMR spectra in CH_2Cl_2 show a well-resolved doublet of quintets centered at τ 21.1, which is assigned to the hydrogen bound to iridium, coupled to a trans phosphorus nucleus ($J_{P-H} = 110$ Hz) and to four equivalent cis phosphorus nuclei ($J_{P-H} = 15$ Hz). Moreover, the alkyl–aryl proton *ratio* for the complex $[IrH(HP(C_2H_5)_2)_5](B(C_6H_5)_4)_2$ agrees with the proposed stoichiometry. A similar hydrido complex is formed in the reaction between $[IrCl(C_8H_{14})_2]_2$ and $HP(C_2H_5)C_6H_5$, but analytically pure samples were not obtained.

Probably the formation of $[IrH(HP(C_2H_5)_2)_5]^{2+}$ cation occurs via a five-coordinate intermediate $[Ir(HP(C_2H_5)_2)_5]^+$, which is rapidly protonated to a hydrido derivative of Ir(III). It should be noted that with less basic phosphorus ligands, such as trialkyl phosphites, the five-coordinate $[Ir(P(OR)_3)_5]^+$ (R = CH_3, C_2H_5) species do not yield spontaneously the hydrido derivatives. However, we found that, if the reaction between $[IrCl(C_8H_{11})_2]_2$ and $P(OR)_3$ in methanol is carried out in the presence of a slight excess of $HClO_4$, the complexes $[IrH(P(OR)_3)_5](ClO_4)_2$ are easily obtained. Moreover, we have observed a similar behavior in the series of cobalt(I) derivatives. Whereas the $[Co(P(OR)_3)_5]^+$ complexes are fairly stable in alcohol solutions, the $[Co(HPR_2)_5]^+$ ones slowly give hydrido derivatives of cobalt(III) of the type $[CoH(HPR_2)_5]^{2+}$.[11]

A complex of the type $[IrH(P)_5]^{2+}$ has been reported to be formed also in the reaction between $[IrCl(CO)(P(C_6H_5)_3)_2]$ and $P(OCH_3)_2C_6H_5$ in boiling ethanol.[12]

Oxidative addition of hydrogen and hydrogen chloride occurs on the complexes $[Ir(HPR_2)_4]B(C_6H_5)_4$ to yield iridium(III) derivatives, $[IrH_2(HPR_2)_4]B(C_6H_5)_4$ and $[IrHCl(HPR_2)_4]B(C_6H_5)_4$, respectively. For the $[IrH_2(HPR_2)_4]^+$ adducts a cis arrangement is suggested by ir spectra, which show two bands in the Ir–H stretching region. The metal–hydride resonance in the ^1H NMR spectra appears as a symmetrical second-order pattern containing six resolved lines and is again consistent with a mutually cis arrangement of the two hydride groups.[12] A trans structure for $[IrHCl(HPR_2)_4]^+$ ($HPR_2 = HP(C_6H_5)C_6H_{11}$, $HP(C_6H_{11})_2$) is inferred from the high frequency (2200-cm^{-1} region) of the metal–hydrogen stretching vibration and from the appearance of the hydride resonance as a symmetric quintet (Table II).

It was not possible to obtain ^1H NMR spectra for the complex $[IrHCl(HP(C_6H_5)_2)_4]^+$, owing to its limited solubility. However, the iridium–hydrogen stretching vibration falls at 2080 cm^{-1}, thus suggesting a trans arrangement of the hydride groups toward the phosphine.

Carbon monoxide readily reacted with the $[Ir(HPR_2)_4]^+$ complexes in methanol suspension, to produce the five-coordinate carbonyl derivatives $[Ir(CO)(HPR_2)_4]^+$ (HPR_2 = $HP(C_6H_5)_2$, $HP(C_6H_5)C_6H_{11}$) or $[Ir(CO)_2(HP(C_6H_{11})_2)_3]^+$. Carbonyl complexes of Ir(I) with secondary phosphines can also be obtained by reacting $[IrCl(CO)(P(C_6H_5)_3)_2]$ with an excess of secondary phosphine in methanol in the presence of $NaB(C_6H_5)_4$. By this route, the compounds $[Ir(CO)(HPR_2)_4]B(C_6H_5)_4$ (HPR_2 = $HP(C_2H_5)_2$, $HP(C_6H_5)_2$, and $HP(C_6H_5)C_6H_{11}$) and $[Ir(CO)(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$ have been isolated. The latter complex, which can take up further carbon monoxide to yield $[Ir(CO)_2(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$, easily gives oxidative addition reactions. I.e., the reaction with hydrogen yields *cis*-$[IrH_2(CO)(HP(C_6H_{11})_2)_3]^+$ (ν_{IrH} at 2140 and 2160 cm^{-1}), whose ^1H NMR spectra, in the high-field region, show a complex signal which arises from overlapping of a doublet of triplets (hydride trans to phosphine) on a quintet (hydride trans to carbonyl group). Additional splitting of the signals by H–H coupling (J_{H-H} = 2 Hz) is also observed.

Finally, the orange $[Ir(HPR_2)_4]^+$ complexes irreversibly take up oxygen in the solid state, giving cream-colored products, which probably are 1:1 adducts. However, the $Ir–O_2$ bands, in the 800–900-cm^{-1} region[13] could not be detected owing to the strong absorptions of the ligands and of the tetraphenylborate anion. Recrystallization of the crude products is accompanied by extensive decomposition and pure samples have not been obtained.

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Registry No. $[Rh(HPEt_2)_4]BPh_4$, 57109-24-7; $[Rh(HPEtPh)_4]ClO_4$, 57109-26-9; $[Rh(HPPh_2)_4]ClO_4$, 33990-36-2; $[Rh(HPPhCy)_4]ClO_4$, 57109-28-1; $[Rh(HPCy_2)_4]ClO_4$, 57109-29-2; *trans*-$[RhHCl(HPEt_2)_4]BPh_4$, 57109-31-6; *trans*-$[RhHCl(HPPhEt)_4]BPh_4$, 57109-33-8; $[RhHCl(HPPh_2)_4]ClO_4$, 57109-35-0; *cis*-$[RhHCl(HPPhCy)_4]ClO_4$, 57109-37-2; *cis*-$[RhHCl(HPPhCy)_4]BPh_4$, 57109-38-3; *trans*-$[RhHCl(HPCy_2)_4]ClO_4$, 57109-40-7; $[RhCl(HPCy_2)_3]$, 55017-05-5; $[Rh(CO)(HPCy_2)_3]ClO_4$, 57109-42-9; $[IrH(HPEt_2)_5](ClO_4)_2$, 57109-44-1; $[IrH(HPEt_2)_5](BPh_4)_2$, 57109-45-2; $[Ir(HPPh_2)_4]BPh_4$, 57109-47-4; $[Ir(HPPhCy)_4]BPh_4$, 57109-49-6; $[Ir(HPCy_2)_4]BPh_4$, 57109-51-0; $[Ir(CO)(HPEt_2)_4]BPh_4$, 57109-53-2; $[Ir(CO)(HPPh_2)_4]BPh_4$, 33990-20-4; $[Ir(CO)(HPPhCy)_4]BPh_4$, 57109-55-4; $[Ir(CO)(HPCy_2)_3]BPh_4$, 57109-57-6; $[Ir(CO)_2(HPCy_2)_3]BPh_4$, 57109-59-8; *cis*-$[IrH_2(HPPh_2)_4]BPh_4$, 57109-61-2; *cis*-$[IrH_2(HPPhCy)_4]BPh_4$, 57109-63-4; *cis*-$[IrH_2(HPCy_2)_4]BPh_4$, 57109-65-6; $[IrHCl(HPPh_2)_4]BPh_4$, 57109-67-8; *trans*-$[IrHCl(HPPhCy)_4]BPh_4$, 57109-69-0; *trans*-$[IrHCl(HPCy_2)_4]BPh_4$, 57109-71-4; *cis*-$[IrH_2(CO)(HPCy_2)_3]BPh_4$, 57109-73-6; $[RhCl(C_8H_{12})]_2$, 12092-47-6; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I), 15318-31-7; HCl, 7647-01-0.

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Molecular Structure of *trans*-Methyliodo[difluoro[3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)]borate]rhodium(III)

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The structure of *trans*-methyliodo[difluoro[3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)]borate]rhodium(III), $Rh(CH_3)I[C_2(DO)(DOBF_2)]$, has been determined from three-dimensional x-ray diffraction data collected by counter methods using θ–2θ scans. The octahedrally coordinated Rh ion lies in the plane of the four N atoms of the macrocyclic ligand. The methyl and iodide occupy axial positions with bond distances Rh–C = 2.090 (4) Å and Rh–I = 2.813 (0) Å. The overall ligand conformation resembles the "chair" conformation of cyclohexane with the BF_2 bridge bent toward the axial methyl and the propylene bridge toward the iodide. The shortest axial methyl C–F distance of 3.11 Å is close to the sum of the van der Waals radii. The ^1H NMR spectrum in CD_2Cl_2 exhibits spin coupling of the axial methyl protons with ^{19}F in the BF_2 bridge (J_{H-F} = 2.3 Hz), consistent with a weak CH···F interaction. The dark orange crystals of $Rh(CH_3)I[C_2(DO)(DOBF_2)]$ conform to the space group $P2_1/n$ with $a = 9.424$ (4) Å, $b = 17.36$ (1) Å, $c = 12.40$ (1) Å, and $\beta = 94.18$ (5)°; $Z = 4$; $\rho_{calcd} = \rho_{obsd} = 1.84$ g/cm³. The structure was refined anisotropically by full-matrix least squares using 2977 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ to give $R_1 = 0.031$ and $R_2 = 0.038$.

Introduction

The coordinatively unsaturated, square-planar complex of rhodium(I) with tetradentate 3,3'-(trimethylenedinitrilo)bis(2-butanone oximate),[2] [$(DOH)_2$pn], **1a**, is one of the most reactive neutral d^8 complexes toward oxidative addition[3] reactions yet isolated.[4] Primary and secondary alkyl halides readily form rhodium(III) adducts in high yield (eq 1). Steric constraints imposed by the rigid macrocycle are thought to enforce trans addition. Recent kinetic studies have revealed a marked neighboring-group effect for α,ω-dihaloalkyls during oxidative addition reactions with rhodium(I) complexes of 3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate), [$C_2(DOH)_2$pn], and its BF_2-bridged derivative[5] **1b**. Since 1,4-dibromocyclohexane fails to afford any product other than