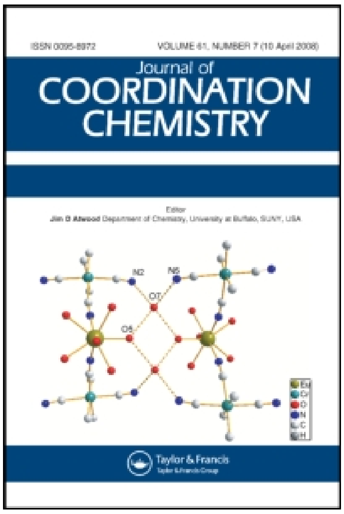

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COMPLEXES OF TRIVALENT PHOSPHORUS DERIVATIVES, XVIII. SOME COMPLEXES OF NEOPENTYLPHOSPHINES WITH RHODIUM, NICKEL, AND PALLADIUM CHLORIDES[1]

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COMPLEXES OF TRIVALENT PHOSPHORUS DERIVATIVES, XVIII. SOME COMPLEXES OF NEOPENTYLPHOSPHINES WITH RHODIUM, NICKEL, AND PALLADIUM CHLORIDES[1]

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Trineopentylphosphine reacts with hydrated rhodium(III) chloride to give yellow $\{[(Me_3CCH_2)_3P]_2RhCl_2\}_2$ in ethanol at room temperature but yellow $[(Me_3CCH_2)_3P]_2Rh(CO)Cl$ in boiling $ROCH_2CH_2OH$ ($R = CH_3$ or C_2H_5). Dineopentylphenylphosphine reacts with hydrated rhodium(III) chloride in ethanol to give red $[(Me_3CCH_2)_2PC_6H_5]_3Rh_2Cl_4$ at room temperature and orange $\{[(Me_3CCH_2)_2PC_6H_5]_2RhCl_2\}_2$ at the boiling point. Neither trineopentylphosphine nor dineopentylphenylphosphine reacts with nickel(II) chloride in ethanol solution. However, neopentyldiphenylphosphine reacts with nickel(II) chloride in ethanol solution to give purple $[Me_3CCH_2P(C_6H_5)_2]_2NiCl_2$, which gives yellow solutions in polar solvents. Trineopentylphosphine reacts with palladium(II) chloride derivatives in boiling n-butanol to give either yellow $[(Me_3CCH_2)_3P]_2PdCl_2$ or orange $[(Me_3CCH_2)_3PPdCl_2]_2$ depending upon the reaction conditions.

INTRODUCTION

Trineopentylphosphine is unusual for a purely aliphatic tertiary phosphine by being stable to air oxidation.[4] This suggests that the three relatively large neopentyl groups shield the lone pair of the trivalent phosphorus atom in trineopentylphosphine from chemical reactions. We were interested in seeing whether this unusually low reactivity of the phosphorus lone pair of trineopentylphosphine towards oxygen would be also reflected in unusual reactivity of trineopentylphosphine towards transition metal compounds possibly even giving different types of metal complexes from those obtained with other aliphatic phosphines.

This paper describes some reactions of trineopentylphosphine with rhodium, nickel, and palladium chlorides. These three transition metal systems were selected for this study since their reactions with numerous tertiary phosphines and other trivalent phosphorus and arsenic ligands have been well-documented.[5] In cases where the reactions of the metal derivatives with trineopentylphosphine appeared somewhat unusual, the corresponding reactions with dineopentylphenylphosphine[4] and neopentyldiphenylphosphine[4,6] were also investigated in order to ascertain the effects of stepwise introduction of neopentyl groups into the tertiary phosphine on the resulting transition metal chemistry.

EXPERIMENTAL SECTION

Materials

The ligands $(Me_3CCH_2)_3P$, $(Me_3CCH_2)_2PC_6H_5$, and $Me_3CCH_2P(C_6H_5)_2$ were prepared from neopentylmagnesium chloride and the appropriate phosphorus chloride by procedures described in detail elsewhere.[4] The transition metal halides were commercial products except for Na_2PdCl_4, which was prepared *in situ* from the stoichiometric quantities of NaCl and $PdCl_2$.

Preparation of the Metal Complexes (Table I)

The indicated quantities of transition metal derivative, neopentyl phosphine, and solvent (Table I) were stirred under the indicated conditions. In some cases, including most of the rhodium compounds, pure product precipitated upon cooling the reaction mixture. In the other cases where the product did not precipitate upon cooling the reaction mixture, solvent was removed in vacuum at ~25° and the residue crystallized from the indicated solvents.

Microanalyses on these neopentylphosphine complexes (Table II) were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and the microanalytical laboratory in the chemistry department of the University of Georgia. Melting and decomposition

TABLE I

Reactions of rhodium, nickel, and palladium chlorides with neopentyl phosphines

Metal Chloride (g., mmoles)	Phosphine[a] (g., mmoles)	Solvent (ml.)	Temp., °C	Time, Hr.	Product[ab]	Yield
$RhCl_3 \cdot 3H_2O$ (0.37, 1.4)	Neo_3P (1.39, 5.7)	EtOH (50)	25	19	$[(Neo_3P)_2RhCl_2]_2$	0.687 g. (74 %)
$RhCl_3 \cdot 3H_2C$ (0.41, 1.58)	Neo_3P (1.54, 6.34)	EtCH (50)	80	24	$[(Neo_3P)_2RhCl_2]_2$	0.863 g. (82 %)
$RhCl_3 \cdot 3H_2O$ (0.24, 0.92)	Neo_3P (0.9, 3.7)	$EtOCH_2CH_2OH$ (50)	135	24	$(Neo_3P)_2Rh(CO)Cl$	0.182 g. (30 %)
$RhCl_3 \cdot 3H_2O$ (0.34, 1.3)	Neo_2PPh (1.3, 5.2)	EtCH (50)	25	48	$(Neo_2PPh)_3Rh_2Cl_4$	0.584 g. (82%)
$RhCl_3 \cdot 3H_2C$ (0.26, 1.0)	Neo_2PPh (1.02, 4.1)	EtCH (50)	80	23	$[(Neo_2PPh)_2RhCl_2]_2$[c]	0.412 g. (61%)
$RhCl_3 \cdot 3H_2O$ (0.39, 1.5)	$NeoPPh_2$ (1.50, 5.8)	EtCH (50)	25	24	no product crystallized from yellow reaction mixture at −10°	
$RhCl_3 \cdot 3H_2C$ (0.30, 1.15)	$NeoPPh_2$ (1.17, 4.6)	EtOH (50)	80	23	no product crystallized from orange reaction mixture	
$NiCl_2 \cdot 6H_2C$ (0.24, 1.0)	Neo_3P (0.5, 2.0)	EtCH (50)	80	24	no complex formation	
$NiCl_2 \cdot 6H_2C$ (0.24, 1.0)	Neo_3P (0.5, 2.0)	$MeCO_2H$ (50)	120	24	no complex formation	
$NiCl_2$ (0.134, 1.03)	Neo_3P (0.49, 2.0)	none	160	1	no complex formation	
$NiCl_2 \cdot 6H_2O$ (0.38, 1.6)	Neo_2PPh (0.80, 3.2)	EtCH (50)	25	16	no complex formation	
$NiCl_2 \cdot 6H_2O$ (0.27, 1.1)	$NeoPPh_2$ (0.57, 2.2)	EtCH (100)	25	1	$(NeoPPh_2)_2NiCl_2$[d]	0.219 g. (30%)
$PdCl_2$ (0.22, 1.23)	Neo_3P (0.60, 2.46)	n-BuCH (50)	120	16	$(Neo_3P)_2PdCl_2$[d]	0.781 g. (95%)
Na_2PdCl_4 (0.30, 1.03)	Neo_3P (0.24, 1.0)	n-BuCH (40)	120	16	$[(Neo_3P)PdCl_2]_2$[e]	0.163g. (39%)

[a] Neo = neopentyl, Ph = phenyl.

[b] Unless otherwise indicated, the products precipitated from the reaction mixture upon cooling. In some cases partial removal of solvent in vacuum was necessary.

[c] The product was crystallized from a mixture of dichloromethane and ethanol.

[d] The product was crystallized from n-butanol.

[e] Solvent was removed from the reaction mixture at 25°/0.1 mm. The residue was crystallized from a mixture of dichloromethane and n-butanol.

points (Table II) were determined in capillaries and are uncorrected. The conductances (Table II) were determined in 0.0006 to 0.003 molar acetone solutions at room temperature using platinum electrodes and a model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio, and are quoted in ohm^{-1} cm^2/mole.

TABLE II

Properties of rhodium, nickel, and palladium chloride complexes of neopentylphosphines

Compound[a]	Color and Form	M.p. °C		Analyses, C	H	Cl	Mol. wt.[b]	Molar Conductance	Proton N. M R.[c], τ CH₂	CH₃
$(Neo_3P)_2RhCl_2$	yellow plates	171-173	Calcd.	54.4	10.0	10.7	662	9.0	~7.6 m	8.83, 8.94, 9.04
			Found	54.9	10.2	10.3	476 (B)			
$(Neo_3P)_2Rh(CO)Cl$	yellow plates	158-162	Calcd.[d]	56.8	10.1	5.4	654.5	1.1	~7.7 m	8.82, 9.04
			Found[d]	56.9	10.4	5.8	647 (A)			
$(Neo_2PPh)_3Rh_2Cl_4$	red solid	188-200	Calcd.	52.5	7.4	12.9	1098	16.1		9.05, 9.08, 9.12
			Found	52.2	7.6	12.8	731 (B)			
$(Neo_2PPh)_2RhCl_2$	orange plates	235-245 (dec.)	Calcd.	57.0	8.0	10.5	674	18.4		9.00, 9.05, 9.11
			Found	57.4	8.1	10.0	581 (B)			
$(NeoPPh_2)_2NiCl_2$	purple prisms	165-175 (dec.)	Calcd.	63.6	6.5	11.1		dec.		
			Found	63.5	6.6	10.7				
$(Neo_3P)_2PdCl_2$	yellow	198-201	Calcd.	54.1	10.0	10.7	666	0.3	7.91 t (4)	8.79
			Found	53.9	10.0	10.5	667 (A)			
$(Neo_3P)PdCl_2$	orange	246-250	Calcd.	42.7	7.9	16.8	421.7	1.5	7.96 d (13)	8.63
			Found	42.5	7.9	16.8	709 (B)			

[a] Neo = neopentyl, Ph = phenyl. The simplest possible formulas consistent with the stoichiometry are given.

[b] A = acetone, B = benzene. Calculated molecular weight values for the simplest possible formulas are given.

[c] d = doublet, t = triplet, m = multiplet, coupling constants in Hz are given in parentheses.

[d] Calcd. O, 2.4; Found: O, 2.2.

Spectra of the Metal Complexes

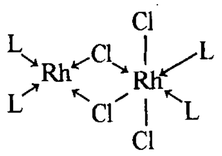
The proton n.m.r. spectra of the palladium complexes (Table II) were obtained in carbon disulfide solution and recorded at 100 MHz. on a Varian HA-100 spectrometer. The rhodium complexes were too insoluble in acetone or chloroform for satisfactory n.m.r. spectra to be obtained in these solvents. However, the neopentyl methyl resonances (Table II) of the rhodium complexes could be observed in carbon disulfide solution on a Varian T-60 spectrometer. The nickel complex $[Me_3CCH_2P(C_6H_5)_2]_2NiCl_2$ gave a blue solution in dichloromethane which appeared to be paramagnetic, since not even the signal from the tetramethylsilane internal standard was observed.

Infrared spectra were recorded on a Perkin–Elmer Model 621 spectrometer with grating optics. The ν(CO) frequency of $[(Me_3CCH_2)_3P]_2Rh(CO)Cl$ was found at 1948 cm^{-1} in dichloromethane solution. Nujol mulls of the remaining metal complexes exhibited no absorptions in the 1500–2500 cm^{-1} region which could be attributed to ν(M–H) or ν(CO) frequencies.

DISCUSSION

A striking feature of the reactions of neopentylphosphines with hydrated rhodium trichloride is the tendency to form derivatives with a chlorine:rhodium ratio of two. The absence of any infrared bands in the 1500–2500 cm^{-1} region attributable to ν(Rh–H) excludes formulations of these compounds as rhodium(III) hydrides. Furthermore, all of the compounds with a chlorine:rhodium ratio of two exhibited normal neopentyl methyl resonances in their proton n.m.r. spectra thereby excluding formulations as rhodium(II) derivatives, which would be paramagnetic and therefore would not give proton n.m.r. spectra. Accordingly all of the compounds with a chlorine:rhodium ratio of two must contain equal quantities of rhodium(I) and rhodium(III). However, molecular weight determinations on all of the rhodium–chloride complexes with a chlorine: rhodium ratio of two were closest to the expected values for formulas containing only one rhodium atom suggesting complete dissociation in solution to mixtures of monometallic rhodium(I) and rhodium(III) complexes.

The reaction between trineopentylphosphine and hydrated rhodium trichloride in ethanol at room temperature gives a yellow precipitate of stoichiometry $[(Me_3CCH_2)_3P]_2RhCl_2$ and formulated as the rhodium(I, III) derivative I ($L = (Me_3CCH_2)_3P$) analogous to the reported rhodium(I, III) complex[7] $\{[C_2H_5P(C_6H_5)_2]_2RhCl_2\}_2$ ($I{:}L = C_2H_5P(C_6H_5)_2$) obtained by the air-oxidation of a benzene solution of $[C_2H_5P(C_6H_5)_2]_3RhHCl_2$. The formation of the rhodium (I, III) derivative $\{[(Me_3CCH_2)_3P]_2RhCl_2\}_2$ from trineopentylphosphine and hydrated rhodium trichloride in boiling ethanol contrasts with the formation of the pure rhodium(I) derivative[8] $[(C_6H_5)_3P]_3RhCl$ from triphenylphosphine and hydrated rhodium trichloride in boiling ethanol. Reaction of trineopentylphosphine with hydrated rhodium trichloride under still more vigorous conditions in an alcoholic solvent (e.g. boiling 2-methoxyethanol or 2-ethoxyethanol) can result in abstraction of carbon monoxide from the solvent to give the rhodium(I) carbonyl $[(Me_3CCH_2)_3P]_2Rh(CO)Cl$, a type of reaction well documented for other tertiary phosphines including triphenylphosphine.[9]



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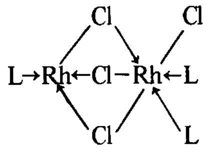


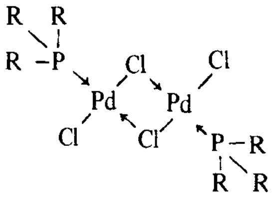
II

The reaction of dineopentylphenylphosphine with hydrated rhodium trichloride in ethanol at room temperature gave an immediate red precipitate of stoichiometry corresponding to a rather unusual rhodium(I, III) complex $[(Me_3CCH_2)_2PC_6H_5]_3$-Rh_2Cl_4, which could have structure II although such a structure would force the tetracoordinate rhodium(I) to have tetrahedral rather than the more normal square planar geometry. When the mixture of dineopentylphenylphosphine and hydrated rhodium trichloride in ethanol is boiled, this initial red precipitate dissolves, the solution gradually becomes lighter, and then a yellow-orange precipitate separates. The yellow-orange precipitate has the stoichiometry $[(Me_3CCH_2)_2PC_6H_5]_2RhCl_2$. It probably is an analogue of the trineopentylphosphine–rhodium complex of similar stoichiometry described above, with the structure I ($L = (Me_3CCH_2)_2PC_6H_5$).

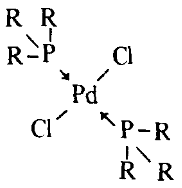
The reaction of neopentyldiphenylphosphine with hydrated rhodium trichloride in ethanol either at room temperature or the boiling point gave mixtures which failed to deposit solid compounds upon cooling in contrast to the corresponding reactions with $(Me_3CCH_2)_3P$, $(Me_3CCH_2)_2PC_6H_5$, and $(C_6H_5)_3P$. This system was not investigated in detail.

The reaction between trineopentylphosphine and nickel chloride failed to give any evidence for complex formation even at elevated temperatures when anhydrous nickel chloride and no solvent were used. Apparently the low reactivity of trineopentylphosphine is manifested towards nickel(II) chloride as well as oxygen. Even dineopentylphenylphosphine failed to form a complex upon reaction with nickel(II) chloride in ethanol solution indicating that two neopentyl groups on a trivalent phosphorus are sufficient to inhibit its reaction with nickel chloride. On the other hand, neopentyldiphenylphosphine reacted with nickel(II) chloride to give a yellow solution which deposited purple crystals of the expected stoichiometry $[Me_3CCH_2P(C_6H_5)_2]_2NiCl_2$. Redissolving these purple crystals in polar solvents regenerated the yellow solution. The purple crystals gave a bluish solution in dichloromethane which deposited an insoluble cream precipitate upon standing. This bluish solution exhibited no proton n.m.r. spectrum, even of the tetramethylsilane internal standard, thereby suggesting the purple form to be paramagnetic. These observations suggest an equilibrium between a purple paramagnetic tetrahedral form and a yellow presumably diamagnetic square planar form for $[Me_3CCH_2P(C_6H_5)_2]_2NiCl_2$ similar to equilibria between tetrahedral and square planar nickel halide complexes of the type L_2NiCl_2 reported for other alkyldiarylphosphines.[10,11]

Reactions of palladium(II) chloride derivatives with trineopentylphosphine required relatively vigorous conditions (boiling n-butanol). Either a simple mono-metallic derivative $[(Me_3CCH_2)_3P]_2$-$PdCl_2$ or a less soluble bimetallic derivative $[(Me_3CCH_2)_3PPdCl_2]_2$ (III: $R = (CH_3)_3CCH_2$) could be isolated depending upon the phosphine: palladium ratio. The proton n.m.r. spectrum of $[(Me_3CCH_2)_3P]_2PdCl_2$ exhibited a triplet for the neopentyl methylene protons arising from virtual coupling[12] indicative of a strong phosphorus–phosphorus interaction thereby suggesting formulation of this palladium complex as the *trans*-isomer IV.



III



IV

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