cently been shown to be characteristic of square-planar cobalt(II) chelates.[24,25]

Conclusion

Nickel(II), copper(II), palladium(II), and cobalt(II) chelates have been prepared with $H_2[(sacac)_2en]$, $H_2[(sacac)_2pn]$, and *cis*-$H_2[(sacac)_2chxn]$, which are new tetradentate thioimine ligands. Zinc(II) and cadmium(II) chelates were prepared with $H_2[(sacac)_2en]$ while *trans*-$H_2[(sacac)_2chxn]$ formed only the palladium(II) chelate. All of the complexes are square-planar monomeric species. Infrared and pmr spectral data indicate that there is more charge delocalization in the sulfur-containing chelates than in their well-studied oxygen analogs. This has been attributed to some d-orbital participation on the part of the sulfur atoms which serves to drain some of the electron density from the metal ion. An alternate explanation might attribute this effect to the greater polarizability of the sulfur atom. Since the electron density around the metal ion is known to play an important role in determining the stability of $M-O_2$ bonds in oxygen adducts,[4,26] some of these new complexes are proving to be ideal species for the evaluation of inductive, π-bonding, and polarizability effects in synthetic oxygen-carrying systems. Results of thermodynamic studies on these systems will be reported in a forthcoming paper.

Acknowledgment. We wish to thank Professor Fred L. Urbach, Case Western Reserve University, for helpful comments on this work. We gratefully acknowledge support of this investigation by the Research Corp. and by the National Institutes of Health, Grant No. HL 15640.

Registry No. NaSH, 16721-80-5; $H_2[(acac)_2en]$, 6310-76-5; $H_2[(acac)_2pn]$, 16087-26-6; *cis*-$H_2[(acac)_2chxn]$, 41013-19-8; *trans*-$H_2[(acac)_2chxn]$, 42996-22-5; $H_2[(sacac)_2en]$, 40006-83-5; $H_2[(sacac)_2pn]$, 42996-17-8; *cis*-$H_2[(sacac)_2chxn]$, 42996-18-9; *trans*-$H_2[(sacac)_2chxn]$, 42946-00-9; $Ni[(sacac)_2en]$, 41258-78-0; $Ni[(sacac)_2pn]$, 42996-32-7; *cis*-$Ni[(sacac)_2chxn]$, 42996-33-8; $Cu[(sacac)_2en]$, 41192-46-5; $Cu[(sacac)_2pn]$, 42996-35-0; *cis*-$Cu[(sacac)_2chxn]$, 42996-36-1; $Pd[(sacac)_2en]$, 41391-03-1; $Pd[(sacac)_2pn]$, 42996-38-3; *cis*-$Pd[(sacac)_2chxn]$, 42996-39-4; *trans*-$Pd[(sacac)_2chxn]$, 42996-40-7; $Co[(sacac)_2en]$, 41254-15-3; $Co[(sacac)_2pn]$, 42996-42-9; $Co[(sacac)_2chxn]$, 42996-44-1; $Cd[(sacac)_2en]$, 41254-14-2; $Zn[(sacac)_2en]$, 41192-47-6.

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Contribution from the Department of Chemistry,
King's College, Strand, London WC2R 2LS, England

Transition Metal Complexes Containing Phosphorus Ligands. XII.[1] Cationic Dialkyl Phenylphosphonite and Alkyl Diphenylphosphinite Derivatives of Copper, Silver, Gold and the Platinum Metals

D. A. COUCH and S. D. ROBINSON*

Received June 20, 1973

Ligand displacement reactions performed in polar solvents afford a convenient general route to an extensive series of cationic complexes containing dialkyl phenylphosphonite, $P(OR)_2Ph$, and alkyl diphenylphosphinite, $P(OR)Ph_2$, ligands (R = Me, Et) which may be isolated as their tetraphenylborate salts. These products were characterized by elemental analysis, proton nmr spectroscopy, and conductivity measurements. Complex cations isolated and characterized in this manner include the hydrides $[RuHL'_5]^+$ and $[IrHL'_5]^{2+}$, the dinuclear species $[L_3RuX_3RuL_3]^+$, and the mononuclear cations $[RuL'_6]^{2+}$, $[IrL'_5]^+$, $[IrL_4]^+$, $[PdL_4]^{2+}$, $[PtL_4]^{2+}$, $[CuL_4]^+$, $[AgL_4]^+$, and $[AuL_4]^+$ [$L' = P(OMe)_2Ph$; $L = P(OR)_2Ph$, $P(OR)Ph_2$; R = Me, Et; X = Cl, Br]. Qualitative descriptions of the coupling patterns observed in the nmr spectra of the complex cations are given and are interpreted in terms of ligand dissociation and rearrangement processes.

Introduction

Transition metal complexes containing tertiary phosphine[2] and, more recently, tertiary phosphite[3] ligands have been extensively studied. However, the ligand properties of the related phosphonites, $P(OR)_2R'$, and phosphinites, $P(OR)R'_2$, have attracted relatively little attention, and no systematic investigation of their coordinating abilities toward the platinum metals has been reported. As part of a study of phosphorus donor ligands we have described the synthesis of cationic trialkyl phosphite complexes of gold, silver, and the platinum metals;[1] we now report a similar study on the synthesis of related complex cations containing dialkyl phenylphosphonite, $P(OR)_2Ph$, and alkyl diphenylphosphinite, $P(OR)Ph_2$, ligands (R = Me, Et).

Until recently very little was known concerning the coordinating properties of these phosphorus donor ligands, and few transition metal derivatives had been described. However a small selection of important compounds of this type have now been reported and some spectroscopic investigations have been undertaken. Complexes isolated include the salts $\{Cu[P(OR)_2Ph]_4\}Cl$,[4] the zero oxidation state nickel and palladium species, $M[P(OR)_2Ph]_4$,[4,5] and the four- and five-coordinate nickel(II) derivatives, $Ni(CN)_2[P(OR)Ph_2]_2$ and $Ni(CN)_2[P(OR)_2Ph]_3$.[6] During the course of the present study other workers have reported the complex hydrides, $FeH_2[P(OR)_2Ph]_4$,[7] $RuH_2[P(OR)_2Ph]_4$,[7] $\{RuH[P(OMe)_2Ph]_5\}\{BPh_4\}$,[8] and $CoH[P(OR)_2Ph]_4$[9] together with an ex-

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tensive series of cationic four- and five-coordinate cobalt,[10] rhodium,[11] and iridium[12,13] derivatives. No comparative study of the ligand series PPh_3, $P(OR)Ph_2$, $P(OR)_2Ph$, and $P(OR)_3$ has been reported, although Chastain, *et al.*,[6] inferred from the electronic spectra of the nickel(II) cyanide derivatives that the sequence of ligand field splitting capability increases as $PPh_3 < P(OR)Ph_2 < P(OR)_2Ph \sim P(OR)_3$. This trend was attributed to contraction and stabilization of the σ-donor orbital by the alkoxy groups; π-acceptor ability is thought to decrease as $P(OR)_2Ph > P(OR)_3$.

Experimental Section

Synthesis of Complex Salts—General Comments. The synthetic methods employed in the present paper are essentially similar to those used to prepare the related trialkyl phosphite derivatives.[1] The free ligand, $P(OR)_2Ph$ or $P(OR)Ph_2$, was added to a solution or suspension of a labile transition metal precursor (usually a triphenylphosphine or olefin derivative) in the corresponding alcohol, ROH. The mixture was heated, if necessary, to achieve dissolution of the transition metal precursor and then cooled and treated with sodium tetraphenylborate. Dicationic products precipitated readily, were separated, then purified by washing with chloroform, in which they are sparingly soluble, and crystallized from dichloromethane–alcohol (ROH). The monocationic derivatives usually crystallized more slowly from the reaction solution and were purified by washing and, where necessary, by recrystallization.

Products were identified and characterized by elemental analysis, conductivity measurements, and pmr spectroscopy. The latter technique was employed to assign stereochemistry, and also gave the alkyl:aryl proton ratio, which in turn helped to verify the ligand:anion ratio. The derivatives of silver, palladium, and, to a lesser extent, gold and platinum are sensitive to air; with these exceptions all the complexes reported show good stability toward air and moisture. Some of the more unstable products could not be analyzed; their characterization is based solely on conductivity and spectroscopic measurements.

Hexakis(dimethyl phenylphosphonite)ruthenium(II) Tetraphenylborate. Dimethyl phenylphosphonite (1.0 ml) and *catena*-dibromo(bicyclo[2.2.1]hepta-2,5-diene)ruthenium (0.18 g) in methanol (10 ml) were heated under reflux until a yellow solution formed (*ca.* 4 hr). Sodium tetraphenylborate (0.32 g) in methanol (10 ml) was added, and the resultant white precipitate was recrystallized from dichloromethane–methanol as *colorless crystals* (0.52 g, 70%).

Tri-μ-chloro-hexakis(dimethyl phenylphosphonite)diruthenium(II) Tetraphenylborate. Dimethyl phenylphosphonite (1.0 ml) and *catena*-dichloro(bicyclo[2.2.1]hepta-2,5-diene)ruthenium (0.44 g) in methanol (10 ml) were heated under reflux until a clear brown solution formed (*ca.* 4–6 hr). The solution was filtered, to remove traces of precipitated metal, and then treated with sodium tetraphenylborate (0.30 g) in methanol (10 ml). The off-white precipitate was filtered off, washed with methanol, and recrystallized three times from dichloromethane–methanol to yield the required product as pale yellow crystals (0.7 g, 50%).

The following compounds were similarly prepared using the appropriate ligands and the corresponding alcoholic solvents: **tri-μ-chloro-hexakis(methyl diphenylphosphinite)diruthenium(II) tetraphenylborate** as fluffy pale yellow crystals (40%) from dichloromethane–methanol, **tri-μ-chloro-hexakis(diethyl phenylphosphonite)diruthenium(II) tetraphenylborate** as pale yellow triangular plates (32%) from dichloromethane–ethanol, **tri-μ-chloro-hexakis(ethyl diphenylphosphinite)diruthenium(II) tetraphenylborate** as pale yellow crystals (80%) recrystallized with difficulty from dichloromethane–ethanol.

The following compounds were similarly prepared from *catena*-dibromo(bicyclo[2.2.1]hepta-2,5-diene)ruthenium: **tri-μ-bromo-hexakis(diethyl phenylphosphonite)diruthenium(II) tetraphenylborate** as pale yellow crystals (50%) from dichloromethane–ethanol, **tri-μ-bromo-hexakis(ethyl diphenylphosphinite)diruthenium(II) tetraphenylborate** as yellow microcrystals (24%) from dichloromethane–ethanol.

Hydridopentakis(dimethyl phenylphosphonite)ruthenium(II) Tetraphenylborate. Dimethyl phenylphosphonite (1 ml) and chlorohydridotris(triphenylphosphine)ruthenium (0.415 g) were stirred together in methanol (10 ml) for 5 min. The pale yellow solution, which formed on standing, was treated with sodium tetraphenylborate (0.15 g) in methanol (10 ml). The resultant white precipitate was washed with methanol and crystallized from dichloromethane–methanol as white crystals (0.35 g, 61%).

Pentakis(dimethyl phenylphosphonite)iridium(I) Tetraphenylborate. Chloro(carbonyl)bis(triphenylphosphine)iridium (0.446 g), triethylamine (1.0 ml), and dimethyl phenylphosphonite (1.3 ml) were heated together under reflux in methanol (10 ml) for 30 min. Sodium tetraphenylborate (0.20 g) in hot methanol (10 ml) was added to the hot orange solution, and the mixture was then set aside for 3 days. The *pale yellow crystals* of required product (0.36 g., 46%) which gradually formed were filtered off and washed in methanol.

Tetrakis(dimethyl phenylphosphonite)iridium(I) Tetraphenylborate. Recrystallization of pentakis(dimethyl phenylphosphonite)iridium tetraphenylborate from chloroform–methanol gave the required product as *orange crystals* (50%).

Tetrakis(methyl diphenylphosphinite)iridium(I) Tetraphenylborate–Dichloromethane Adduct. Di-μ-chloro-bis(cycloocta-1,5-diene)diiridium (0.214 g) and methyl diphenylphosphinite (0.8 ml) in methanol (10 ml) were heated under reflux for 10 min, forming a deep orange solution. Sodium tetraphenylborate (0.22 g) in methanol (10 ml) was added to the cold solution, and the resultant precipitate was filtered off, washed with methanol, and then recrystallized from dichloromethane–methanol to yield the required product as *pale orange prisms* (0.77 g, 85%).

The following were similarly prepared using ethanol as solvent: **tetrakis(diethyl phenylphosphonite)iridium(I) tetraphenylborate** as orange crystals from dichloromethane–ethanol (70%), **tetrakis(ethyl diphenylphosphinite)iridium(I) tetraphenylborate** as orange crystals from dichloromethane–ethanol (80%).

Hydridopentakis(dimethyl phenylphosphonite)iridium(III) Tetraphenylborate–Dichloromethane Adduct. Chloro(carbonyl)bis(triphenylphosphine)iridium (0.32 g) and dimethyl phenylphosphonite (1.0 ml) were heated together under reflux in methanol (10 ml) for 2 hr. Sodium tetraphenylborate (0.2 g) in methanol (10 ml) was added to the hot orange solution, and the mixture was set aside overnight. The mixture of colorless and yellow crystals which formed was extracted with boiling chloroform, and the colorless insoluble residue which remained was recrystallized from dichloromethane–methanol to afford the required product as colorless crystals (0.24 g, 30%).

***trans*-Dihydridotetrakis(dimethyl phenylphosphonite)iridium(III) Tetraphenylborate.** A solution of pentakis- or tetrakis(dimethyl phenylphosphonite)iridium tetraphenylborate in dichloromethane was saturated with hydrogen until the orange color was discharged, then diluted with methanol, and set aside overnight. The *colorless crystals* of required product (80%) were filtered off, washed with methanol, and dried *in vacuo*.

***trans*-Chlorohydridotetrakis(dimethyl phenylphosphonite)iridium(III) Tetraphenylborate.** Di-μ-chloro-dichlorodihydridobis(cycloocta-1,5-diene)diiridium (0.565 g), dimethyl phenylphosphonite (1.2 ml), and benzene (10 ml) were shaken together until the complex dissolved; the solution was then evaporated under reduced pressure to yield an oil. Methanol (10 ml), dimethyl phenylphosphonite (0.5 ml), and sodium tetraphenylborate (0.5 g) in methanol (10 ml) were added successively to the residual oil; the resultant yellow precipitate was recrystallized from dichloromethane–methanol as colorless crystals. These crystals were extracted with chloroform (two 10-ml portions), and the soluble fraction was crystallized by addition of methanol to the chloroform extract. The product was identified by ir and nmr spectroscopy as *trans*-chlorohydridotetrakis(dimethyl phenylphosphonite)iridium tetraphenylborate (yield 0.53 g, 28%). The insoluble fraction was similarly identified as hydridopentakis(dimethyl phenylphosphonite)iridium(III) tetraphenylborate.

***trans*-Chlorohydridotetrakis(methyl diphenylphosphinite)iridium(III) Tetraphenylborate.** Methyl diphenylphosphinite (1.0 ml) and di-μ-chloro-dichlorodihydridobis(cycloocta-1,5-diene)diiridium (0.218 g) were heated under reflux in benzene (10 ml) for 2 min. The solution was filtered and evaporated under reduced pressure, and the residual oil was treated with methanol (10 ml) and methyl diphenylphosphinite (0.8 ml). The mixture was heated under reflux for 5 min and then treated with sodium tetraphenylborate (0.20 g) in

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Table I. Analytical and Conductivity Data for Phosphonite and Phosphinite Complexes

Complex	Analytical data, found (calcd), %		Conductivity, Λ, ohm^{-1} mol^{-1} cm^2
	C	H	
$\{Ru_2Cl_3[P(OMe)_2Ph]_6\}\{BPh_4\}$	53.15 (52.45)	5.45 (5.25)	78
$\{Ru_2Cl_3[P(OMe)Ph_2]_6\}\{BPh_4\}$	63.35 (63.65)	5.15 (5.15)	80
$\{Ru_2Cl_3[P(OEt)_2Ph]_6\}\{BPh_4\}$	55.3 (55.5)	5.8 (6.1)	81
$\{Ru_2Cl_3[P(OEt)Ph_2]_6\}\{BPh_4\}$	64.15 (64.55)	5.4 (5.5)	82
$\{Ru_2Br_3[P(OEt)_2Ph]_6\}\{BPh_4\}$	52.1 (51.75)	5.9 (5.7)	
$\{Ru_2Br_3[P(OEt)Ph_2]_6\}\{BPh_4\}$	59.8 (60.55)	5.15 (5.2)	
$\{Ru[P(OMe)_2Ph]_6\}\{BPh_4\}_2$	65.5 (65.5)	6.1 (6.1)	
$\{RuH[P(OMe)_2Ph]_5\}\{BPh_4\}$	60.6 (60.4)	6.15 (6.0)	92
$\{Ir[P(OMe)_2Ph]_4\}\{BPh_4\}$	56.15 (56.45)	5.2 (5.4)	91
$\{Ir[P(OMe)_2Ph]_5\}\{BPh_4\}$	56.5 (56.45)	5.35 (5.55)	
$\{Ir[P(OMe)Ph_2]_4\}\{BPh_4\}\cdot{}^2/_3CH_2Cl_2$	64.2 (64.35)	5.1 (5.25)	80
$\{Ir[P(OEt)_2Ph]_4\}\{BPh_4\}$	59.15 (58.95)	6.05 (6.2)	89
$\{Ir[P(OEt)Ph_2]_4\}\{BPh_4\}$	67.3 (67.1)	5.55 (5.65)	88
$\{IrH[P(OMe)_2Ph]_5\}\{BPh_4\}_2\cdot{}^2/_3CH_2Cl_2$	61.05 (61.3)	5.7 (5.65)	196
trans-$\{IrHCl[P(OMe)Ph_2]_4\}\{BPh_4\}$	64.25 (64.6)	4.9 (5.2)	83
trans-$\{IrHCl[P(OEt)_2Ph]_4\}\{BPh_4\}$	57.2 (57.35)	5.95 (6.1)	88
cis-$\{IrHCl[P(OEt)_2Ph]_4\}\{BPh_4\}$	56.75 (57.35)	5.8 (6.1)	90
trans-$\{IrHCl[P(OEt)Ph_2]_4\}\{BPh_4\}$	65.25 (65.4)	5.3 (5.55)	83
$\{Pd[P(OMe)Ph_2]_4\}\{BPh_4\}_2$	74.05 (74.6)	5.65 (5.75)	193
$\{Pd[P(OMe)_2Ph]_4\}\{BPh_4\}_2$			192
$\{Pt[P(OMe)_2Ph]_4\}\{BPh_4\}_2$	63.05 (63.45)	5.7 (5.6)	207
$\{Pt\{P(OMe)Ph_2]_4\}\{BPh_4\}_2$	71.05 (70.7)	5.5 (5.45)	209
$\{Pt[P(OEt)_2Ph]_4\}\{BPh_4\}_2$	65.45 (65.0)	6.0 (6.2)	197
$\{Pt[P(OEt)Ph_2]_4\}\{BPh_4\}_2$	70.4 (71.2)	6.2 (5.75)	189
$\{Cu[P(OMe)Ph_2]_4\}\{BPh_4\}$	72.4 (73.15)	6.0 (5.8)	
$\{Cu[P(OEt)Ph_2]_4\}\{BPh_4\}$	73.95 (73.7)	5.9 (6.2)	
$\{Ag[P(OMe)_2Ph]_4\}\{BPh_4\}$	61.0 (60.7)	5.65 (5.8)	93
$\{Ag[P(OMe)Ph_2]_4\}\{BPh_4\}$	70.9 (70.65)	5.6 (5.6)	86
$\{Ag[P(OEt)_2Ph]_4\}\{BPh_4\}$	62.3 (63.0)	6.5 (6.6)	103
$\{Ag[P(OEt)Ph_2]_4\}\{BPh_4\}$	71.3 (71.3)	5.8 (6.0)	80
$\{Au[P(OMe)_2Ph]_4\}\{BPh_4\}$	56.55 (56.2)	5.1 (5.4)	93
$\{Au[P(OMe)Ph_2]_4\}\{BPh_4\}$	66.95 (66.1)	5.0 (5.25)	70
$\{Au[P(OEt)_2Ph]_4\}\{BPh_4\}$	58.5 (58.7)	6.0 (6.15)	86
$\{Au[P(OEt)Ph_2]_4\}\{BPh_4\}$	66.8 (66.85)	5.2 (5.6)	78

methanol (10 ml); the resultant creamy white precipitate was filtered off and washed with methanol to yield the required product (0.55 g, 66%).

The following compounds were similarly prepared using ethanol in place of methanol: ***trans*-chlorohydridotetrakis(ethyl diphenylphosphinite)iridium(III) tetraphenylborate** as colorless crystals (56%), ***trans*-chlorohydridotetrakis(diethyl phenylphosphonite)iridium(III) tetraphenylborate** as colorless crystals (17%). The mother liquor from the above reaction yielded the isomeric complex ***cis*-chlorohydridotetrakis(diethyl phenylphosphonite)iridium(III) tetraphenylborate** as colorless crystals (24%).

Tetrakis(methyl diphenylphosphinite)palladium(II) Tetraphenylborate. Dichloro(cycloocta-1,5-diene)palladium (0.210 g) was dissolved in methanol (20 ml) containing methyl diphenylphosphinite (1.0 ml), and the solution was treated with sodium tetraphenylborate (0.5 g) in methanol (10 ml). The precipitate was filtered off, washed with methanol then chloroform, and recrystallized from dichloromethane–methanol by evaporation under reduced pressure. The colorless crystals of required product (0.18 g, 15%) were given a final wash with chloroform.

Tetrakis(dimethyl phenylphosphonite)platinum(II) Tetraphenylborate. Dichloro(cycloocta-1,5-diene)platinum (0.316 g) was dissolved in methanol (10 ml) containing dimethyl phenylphosphonite (1.0 ml), and the filtered solution was treated with sodium tetraphenylborate (0.6 g) in methanol (10 ml). The resultant precipitate was extracted with hot chloroform, and the insoluble residue was crystallized from dichloromethane–methanol to yield the required product (0.035 g, 3%) as colorless crystals.

The following were similarly prepared using the appropriate ligand and the corresponding alcoholic solvent: **tetrakis(methyl diphenylphosphinite)platinum(II) tetraphenylborate** as colorless rhombic plates (21%), **tetrakis(diethyl phenylphosphonite)platinum(II) tetraphenylborate** as large pale yellow rectangular prisms (23%), **tetrakis(ethyl diphenylphosphinite)platinum(II) tetraphenylborate** as pale yellow crystals (17%).

Tetrakis(methyl diphenylphosphinite)copper(I) Tetraphenylborate. Cuprous chloride (0.10 g) and methyl diphenylphosphinite (1 ml) were heated together under reflux in methanol (10 ml) for 6 hr and then allowed to stand for 3 days. Sodium tetraphenylborate (0.35 g) in methanol (10 ml) was added to the colorless solution and the resultant white precipitate was filtered off, recrystallized from dichloromethane–methanol, and then dried *in vacuo* to yield the required product (0.73 g, 60%) as colorless crystals.

Tetrakis(ethyl diphenylphosphinite)copper(I) tetraphenylborate was similarly prepared, using the appropriate ligand in ethanol solution, as colorless crystals (62%). This product was not recrystallized.

Tetrakis(dimethyl phenylphosphonite)silver(I) Tetraphenylborate. Silver nitrate (0.105 g) was dissolved in a methanol solution (10 ml) containing dimethyl phenylphosphonite (0.8 ml). Sodium tetraphenylborate (0.21 g) in methanol (10 ml) was added and the mixture was set aside overnight. The required product, which separated as colorless crystals, was filtered off, washed with methanol, and then dried *in vacuo* (yield 0.136 g, 20%).

The following were similarly prepared using the appropriate ligand and the corresponding alcoholic solvent: **tetrakis(methyl diphenylphosphinite)silver(I) tetraphenylborate** as colorless crystals (68%) from dichloromethane–methanol, **tetrakis(diethyl phenylphosphonite)silver(I) tetraphenylborate** as colorless crystals (81%), **tetrakis(ethyl diphenylphosphinite)silver(I) tetraphenylborate** as colorless crystals (50%).

The following were similarly prepared from chloro(cyclooctene)gold using the appropriate ligand and corresponding alcoholic solvent: **tetrakis(dimethyl phenylphosphonite)gold(I) tetraphenylborate** as colorless crystals (10%) obtained with difficulty from dichloromethane–methanol, **tetrakis(methyl diphenylphosphinite)gold(I) tetraphenylborate** as colorless crystals (62%), **tetrakis(diethyl phenylphosphonite)gold(I) tetraphenylborate** as colorless crystals (42%) (this complex is particularly photosensitive), **tetrakis(ethyl diphenylphosphinite)gold(I) tetraphenylborate** as colorless crystals (28%)

See Table I for analytical and conductivity data of these compounds.

Table II. Nmr Spectra (Alkyl Protons) for Complex Cations[a]

Complex ion	ppm[c]		Hz	
	τ(Me)	τ(CH_2)	^3J(PH)	^3J(HH′)
$\{Ru_2Cl_3[P(OMe)_2Ph]_6\}^+$	6.53 (vc)		($X^d = 10.5$)	
$\{Ru_2Cl_3[P(OMe)Ph_2]_6\}^+$	7.05 (vc)		($X = 11.0$)	
$\{Ru_2Cl_3[P(OEt)_2Ph]_6\}^+$	8.70 (t)	6.23 (m)		7.0
$\{Ru_2Br_3[P(OEt)_2Ph]_6\}^+$	8.72 (t)	6.25 (m)		7.0
$\{Ru_2Cl_3[P(OEt)Ph_2]_6\}^+$	8.82 (t)	7.09 (e)		7.0
$\{Ru_2Br_3[P(OEt)Ph_2]_6\}^+$	8.70 (m)	6.95 (e)		
$\{RuH[P(OMe)_2Ph]_5\}^+$, eq	6.85 (vc)		($X = 11$)	
ax	6.93 (d)		10	
$\{Ru[P(OMe)_2Ph]_6\}^{2+}$ [b]	6.85 (vc)			
$\{Ir[P(OMe)_2Ph]_4\}^+$	6.95 (vc)		($X = 12$)	
$\{Ir[P(OMe)Ph_2]_4\}^+$	7.45 (vc)		($X = 11$)	
$\{Ir[P(OEt)_2Ph]_4\}^+$	8.95 (t)	6.67 (m)		7.0
$\{Ir[P(OEt)Ph_2]_4\}^+$ [b]	9.89 (t)	7.05 (m)		7.0
$\{IrH[P(OMe)_2Ph]_5\}^{2+}$, eq[b]	6.84 (vc)		($X = \sim 11$)	
ax	6.95 (d)		~11	
trans-$\{IrHCl[P(OMe)_2Ph]_4\}^+$ [b]	6.65 (vc)		($X = 12$)	
trans-$\{IrHCl[P(OMe)Ph_2]_4\}^+$	7.25 (e)			
trans-$\{IrHCl[P(OEt)_2Ph]_4\}^+$	8.86 (t)	6.35 (m)		7.0
cis-$\{IrH_2[P(OMe)Ph_2]_4\}^+$	7.14 (t)		($X = 12$)	
	7.08 (d)		10	
trans-$\{IrH_2[P(OEt)_2Ph]_4\}^+$	8.82 (t)	6.0–7.2 (e)		7.0
cis-$\{IrH_2[P(OEt)_2Ph]_4\}^+$	8.89 (t)			7.0
	9.05 (t)			7.0
cis-$\{IrH_2[P(OEt)Ph_2]_4\}^+$	8.73 (t)	6.5–7.2 (e)		7.0
	8.94 (t)			7.0
$\{Pt[P(OMe)Ph_2]_4\}^{2+}$ [b]	7.44 (vc)		($X = 12$)	
$\{Pt[P(OEt)_2Ph]_4\}^{2+}$ [b]	8.75 (t)	6.05 (e)		7.0
$\{Cu[P(OMe)Ph_2]_4\}^+$	6.82 (s)			
$\{Cu[P(OEt)Ph_2]_4\}^+$	8.80 (t)	6.64 (q)		7.0
$\{Ag[P(OMe)_2Ph]_4\}^+$	6.62 (d)		12.0	
$\{Ag[P(OMe)Ph_2]_4\}^+$	6.73 (d)		12.0	
$\{Ag[P(OEt)_2Ph]_4\}^+$	8.84 (t)	6.35 (m)		7.0
$\{Ag[P(OEt)Ph_2]_4\}^+$	8.91 (t)	6.58 (qn)	7.0	7.0
$\{Au[P(OMe)_2Ph]_4\}^+$	6.69 (d)		11.0	
$\{Au[P(OMe)Ph_2]_4\}^+$	6.67 (d)		13.0	
$\{Au[P(OEt)_2Ph]_4\}^+$	8.87 (t)	6.40 (e)		7.0

[a] Solvent $CDCl_3$ unless otherwise indicated. [b] Solvent CD_2Cl_2. [c] Key: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; vc, virtual coupling pattern; m, multiplet; e, envelope. [d] X = separation of outer satellites; see Figures 1 and 2.

Results and Discussion

Ruthenium Complex Cations. The phosphonite and phosphinite ligands L [L = $P(OR)_2Ph$, $P(OR)Ph_2$; R = Me, Et] reacted slowly with $[RuCl_2(C_7H_8)]_n$ in boiling methanol (R = Me) or ethanol (R = Et) to afford the binuclear tri-μ-chloro cations $[L_3RuCl_3RuL_3]^+$ which were isolated as pale yellow crystalline tetraphenylborate salts. The bromo complex $[RuBr_2(C_7H_8)]_n$ reacted with $P(OEt)_2Ph$ and $P(OEt)Ph_2$ in ethanol to give the corresponding tri-μ-bromo cations $[L_3RuBr_3RuL_3]^+$ but reacted with $P(OMe)_2Ph$ in methanol to afford the hexacoordinated dication $\{Ru[P(OMe)_2Ph]_6\}^{2+}$ in good yield. The latter complex cation presumably owes its formation to the smaller steric requirements of the $P(OMe)_2Ph$ ligands. All attempts to prepare osmium phosphonite and phosphinite derivatives were frustrated by lack of a suitable labile precursor.

Conductivity data for the series of dinuclear ruthenium cations were consistent with their formulation as 1:1 electrolytes of the proposed stoichiometry, and nmr spectra (alkyl:aryl proton ratios) confirmed a ligand:anion ratio of 6:1 in each instance. (See Table II for nmr data.) The methyl protons of each of the complex dications $[L_3RuX_3RuL_3]^{2+}$ [L = $P(OMe)_2Ph$, $P(OMe)Ph_2$; X = Cl, Br] are equivalent and give rise to a symmetrical virtual coupling nmr pattern (Figure 1). With one exception (see below), the pmr spectra of the corresponding ethyl phosphonite and phosphinite complex cations [L = $P(OEt)_2Ph$, $P(OEt)Ph_2$] each contain a well-resolved triplet (methyl protons) and a complex, symmetrical envelope (methylene protons). These nmr results, together with the analytical and conductivity data, serve to establish the binuclear structure proposed for the complex cations. The methyl protons of the ethyl diphenylphosphinite complex $\{Ru_2Br_3[P(OEt)Ph_2]_6\}\{BPh_4\}$ give rise to a complex nmr pattern instead of the expected triplet, and the exact nature of the complex cation therefore remains the subject of some speculation. It is possible, however, that the anomalous nmr pattern may simply reflect the presence of rotational restrictions imposed by the combination of bulky bromide and ethyl diphenylphosphinite ligands.

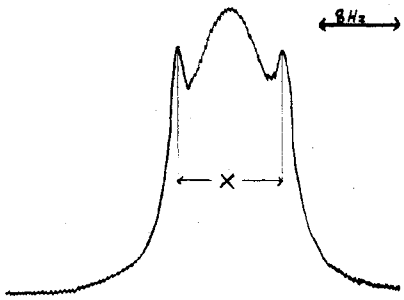

Figure 1. Proton nmr spectrum (methyl region) for complex dications $[L_3RuX_3RuL_3]^+$ [L = $P(OMe)_2Ph$, $P(OMe)Ph_2$; X = Cl, Br].

The methyl resonance of the cation $\{Ru[P(OMe)_2Ph]_6\}^{2+}$ comprises a symmetrical virtual coupling pattern, consistent with the presence of six equivalent $P(OMe)_2Ph$ ligands.

It is interesting to note that the phosphines PEt_2Ph and $PEtPh_2$, of stereochemical form very similar to that of $P(OMe)_2Ph$ and $P(OMe)Ph_2$, respectively, have previously been reported to give binuclear trihalide-bridged ruthenium and osmium complex cations analogous to those described above.[14] This observation supports our belief that steric factors are primarily responsible for determining the stoichiometry of the complex cations formed in these systems.

Our efforts to prepare cationic hydrido complexes of the form $\{RuHL_5\}^+$ were only partially successful. The complex $\{RuH[P(OMe)_2Ph]_5\}\{BPh_4\}$ was obtained as an air-stable white crystalline solid; however, attempts to prepare similar derivatives containing the larger ligands $P(OMe)Ph_2$, $P(OEt)Ph_2$, and $P(OEt)_2Ph$ failed, presumably because five ligands of this size cannot be comfortably accommodated about a single ruthenium ion. The methyl protons of the equatorial ligand set in the complex cation $\{RuH[P(OMe)_2Ph]_5\}^+$ give rise to a virtual coupling nmr pattern (24 protons) comprising a broad strong center member and two pairs of symmetrically placed satellites. Similar patterns are discussed in part XI[1] and have previously been reported for several systems containing four $P(OMe)_nPh_{3-n}$ ligands ($n = 1$–3) in a planar configuration.[11,12,15] The methyl protons of the axial $P(OMe)_2Ph$ ligand give rise to a doublet $[^3J(PH)]$ with no visible evidence of interligand phosphorus–hydrogen coupling. The high-field nmr pattern comprises a doublet of quintets consistent with the presence of a hydride ligand coupled to one trans and four equivalent cis phosphorus nuclei. This simple first-order spectrum contrasts sharply with the very complex patterns observed for the high-field reconances in the cationic hydrides $\{RuH[P(OR)_3]_5\}^+$ [1] and $\{IrH[P(OMe)_2Ph]_5\}^{2+}$ (see below).

Iridium Complex Cations. The iridium(I) and -(III) precursors $IrCl(CO)(PPh_3)_2$, $[IrCl(C_8H_{12})]_2$, and $[IrHCl_2(C_8H_{12})]_2$ reacted with the phosphonite and phosphinite ligands (L) to afford a variety of four- and five-coordinate iridium(I) complexes $[IrL_x][BPh_4]$ ($x = 4, 5$) and six-coordinate iridium(III)-hydrido derivatives $[IrHL_5][BPh_4]_2$, $[IrH_2L_4][BPh_4]$, and $[IrHClL_4][BPh_4]$.

Treatment of $IrCl(CO)(PPh_3)_2$ or $[IrCl(C_8H_{12})]_2$ with the ligands, L, in boiling alcoholic solvents, followed by addition of sodium tetraphenylborate, afforded the stable orange complexes $[IrL_4][BPh_4]$ $[L = P(OR)Ph_2, P(OEt)_2Ph]$ or the yellow complex $[IrL'_5][BPh_4]$ $[L' = P(OMe)_2Ph]$. This latter species, on recrystallization from chloroform–methanol, lost one molecule of ligand to afford the tetrakis derivative $[IrL'_4][BPh_4]$. In several of the above reactions addition of triethylamine served to remove traces of HCl and thereby prevent formation of iridium(III) hydrides. In the absence of triethylamine, $IrCl(CO)(PPh_3)_2$ reacted with dimethyl phenylphosphonite under similar conditions to produce a modest yield of $\{IrH[P(OMe)_2Ph]_5\}\{BPh_4\}_2$. The failure to obtain analogous products $[IrHL_5][BPh_4]_2$ with the other, more bulky, ligands may again be attributed to steric problems.

Reactions of the ligands, L, with the iridium(III)-cycloocta-1,5-diene complex $[IrHCl_2(C_8H_{12})]_2$ in boiling benzene, followed by evaporation of the solutions under reduced pressure, gave oils which appeared to contain isomeric forms of the hydridic complexes $IrHCl_2L_3$ [ν(IrH) *ca.* 2080 cm^{-1} (hydride trans to phosphorus?) and *ca.* 2200 cm^{-1} (hydride trans to chloride?)]. These oils reacted with excess ligand, L, in boiling alcohol to give the hydridic species *cis-* and *trans-*$[IrHClL_4][BPh_4]$. The dihydride *trans-*$\{IrH_2[P(OMe)_2Ph]_4\}\{BPh_4\}$ was also isolated from a reaction of this type.

Oxidative addition of dihydrogen and hydrogen chloride to the complexes $[IrL_4][BPh_4]$ provided an alternative route to the iridium(III) derivatives $[IrH_2L_4][BPh_4]$ and $[IrHClL_4][BPh_4]$. Some of these products were isolated and characterized (see Experimental Section); others were identified in solution by high-field nmr spectroscopy (see Table III).

Steric and electronic effects observed for these iridium complexes appear to follow the expected course; for iridium(I) complexes the preference for a coordination number of 5 rather than 4 decreases as $P(OR)_3 > P(OR)_2Ph > P(OR)Ph_2 > PPh_3$, while the tendency to yield iridium(III) species decreases in the reverse order. Only the smallest ligand in the present group, $P(OMe)_2Ph$, gave both four- and five-coordinate iridium(I) derivatives, the remainder yielded only four-coordinate complexes $[IrL_4][BPh_4]$.

The methyl protons of the complex cations $\{Ir[P(OMe)_2Ph]_4\}^+$ and $\{Ir[P(OMe)Ph_2]_4\}^+$ give rise to a symmetrical pattern (Figure 2) with the broad inner satellites partially submerged by the strong center peak. This pattern is consistent with the presence of four $P(OMe)_nPh_{3-n}$ ligands in a square-planar configuration. The nmr spectra of the corresponding ethyl phosphonite and phosphinite complexes $\{Ir[P(OEt)_2Ph]_4\}^+$ and $\{Ir[P(OEt)Ph_2]_4\}^+$ each contain a triplet (methyl protons) and a multiplet (methylene protons). The methyl proton resonance, observed in the spectrum of $\{Ir[P(OEt)Ph_2]_4\}^+$, occurs 1.2 ppm to high field of the corresponding free ligand resonance. This phenomenon has previously been observed[12] and has been tentatively attributed to a "neighbor anisotropy effect"[16] involving the phenyl groups or to the close proximity of the methyl groups to the central metal ion.

The methyl protons of the hydridic cation $IrH[P(OMe)_2Ph]_5{}^{2+}$ give rise to a complex pattern which appears to consist of a doublet [axial $P(OMe)_2Ph$] and a symmetrical pattern typical of four $P(OMe)_nPh_{3-n}$ ligands in a square-planar configuration. However, these signals overlap, and their exact form remains a matter for conjecture. The high-field nmr signal comprises a second-order pattern with ten well-resolved lines visible. This and other similar high-field patterns are the subject of further investigations.

The nmr resonances (Table II) arising from methyl and ethyl moieties present in the complex cations *cis-* and *trans-*$[IrH_2L_4]^+$ and *trans-*$[IrHClL_4]^+$ $[L = P(OR)_2Ph, P(OR)Ph_2$; $R = Me, Et]$ are consistent with the structures proposed for these species. The high-field nmr patterns (Table III) observed for the cations *trans-*$[IrH_2L_4]^+$ and *cis-* and *trans-*$[IrHClL_4]^+$ are first order and also serve to confirm the stereochemistry proposed for each complex. However the cations *cis-*$[IrH_2L_4]^+$ each give rise to a symmetrical second-order pattern containing six resolved lines (Figure 3); these latter spectra are the subject of further investigation.

Palladium and Platinum Complex Cations. The palladium-cycloocta-1,5-diene complex $PdCl_2(C_8H_{12})$ reacted with excess $P(OMe)Ph_2$ in methanol to form a clear, colorless solution from which the complex salt $\{Pd[P(OMe)Ph_2]_4\}\{BPh_4\}_2$ precipitated on addition of sodium tetraphenylborate. Apparently related products were obtained using the other

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(14) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961).

(15) L. M. Haines, *Inorg. Chem.*, 10, 1693 (1971).

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 176.

Table III. Ir and High-Field Nmr Spectra of Cationic Hydrides

Complex ion	ν(MH), cm^{-1}	τ(MH), ppm	Coupling pattern^b
$\{RuH[P(OMe)_2Ph]_5\}^+$	~1900	18.93	d, $J(PH)_t = 89.0$; qn, $J(PH)_c = 19.0$
$\{IrH[P(OMe)_2Ph]_5\}^{2+}$	2080	22.0^a	Complex 2nd-order pattern, 10 peaks
trans-$\{IrHCl[P(OMe)_2Ph]_4\}^+$	2200	28.1^a	qn, $J(PH)_c = 13$
trans-$\{IrHCl[P(OMe)Ph_2]_4\}^+$	2210	27.65	qn, $J(PH)_c = 13$
trans-$\{IrHCl[P(OEt)_2Ph]_4\}^+$	2200	28.4	qn, $J(PH)_c = 13$
trans-$\{IrHCl[P(OEt)Ph_2]_4\}^+$	2200	27.93	qn, $J(PH)_c = 13$
cis-$\{IrHCl[P(OEt)_2Ph]_4\}^+$	2085	20.8	d, $J(PH)_t = 178$; d, $J(PH)_c = 16$ t, $J(PH)_c = 12$
trans-$\{IrH_2[P(OMe)_2Ph]_4\}^+$	1805	19.33	qn, $J(PH)_c = 16.5$
trans-$\{IrH_2[P(OEt)_2Ph]_4\}^+$		19.3	qn, $J(PH)_c = 16.5$
cis-$\{IrH_2[P(OMe)_2Ph]_4\}^+$		22.7	Symmetrical 2nd-order pattern, 6 lines^c
cis-$\{IrH_2[P(OMe)Ph_2]_4\}^+$		22.1	Symmetrical 2nd-order pattern, 6 lines^c
cis-$\{IrH_2[P(OEt)_2Ph]_4\}^+$		22.8	Symmetrical 2nd-order pattern, 6 lines^c
cis-$\{IrH_2[P(OEt)Ph_2]_4\}^+$		22.3	Symmetrical 2nd-order pattern, 6 lines^c

^{a} Spectra taken in CD_2Cl_2; all others taken in $CDCl_3$. ^{b} Key: d, doublet; t, triplet; qn, quintet. Subscripts: c, cis; t, trans. J values in hertz. ^{c} See Figure 3.

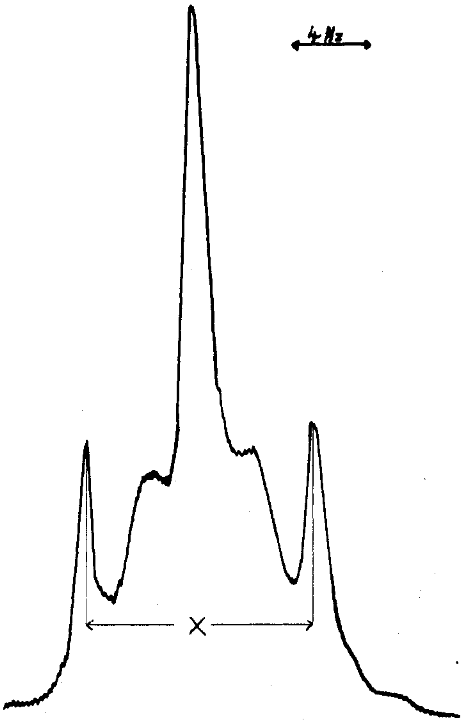

Figure 2. Proton nmr spectrum (methyl protons) for complex cations $[IrL_4]^+$ [L = $P(OMe)_2Ph$, $P(OMe)Ph_2$].

phosphorus ligands (L) but these underwent decomposition within a few hours and were not fully characterized.

In contrast the platinum(II) cations $[PtL_4]^{2+}$ were readily prepared from $PtCl_2(C_8H_{12})$ and excess ligand and were characterized as white or pale yellow air-stable crystalline tetraphenylborate salts. Evidence for the formation of palladium(II) and platinum(II) monocations $[MClL_3]^+$ was observed but none was isolated.

The palladium and platinum dicationic salts $[ML_4][BPh_4]_2$ are sparingly soluble in common nmr solvents, and the palladium derivatives are unstable in solution; in general they did not provide nmr spectra of acceptable quality.

Copper, Silver and Gold Complex Cations. Silver nitrate reacted with the phosphonite and phosphinite ligands, L, in the appropriate alcohol to give colorless solutions from which the cations $[AgL_4]^+$ were isolated as their tetraphenylborate salts. The corresponding gold(I) complexes $[AuL_4][BPh_4]$ were similarly prepared from $AuCl(C_8H_{14})$. Synthesis of these complexes completes the triad of complex cations $\{M[P(OR)_2Ph]_4\}^+$ (M = Cu, Ag, Au). We have also prepared and characterized the copper(I) cations $\{Cu[P(OR)Ph_2]_4\}^+$ thus completing the triad $\{M[P(OR)Ph_2]_4\}^+$. The copper, silver, and gold complexes are all white crystalline solids; several of them are photosensitive.

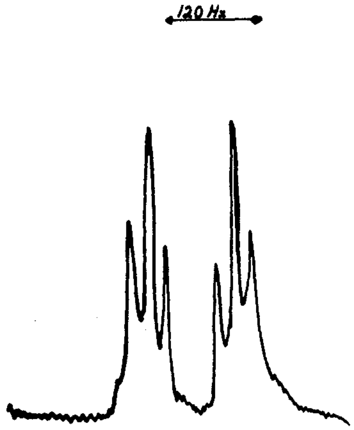

Figure 3. High-field proton nmr spectra for complex cations *cis*-$[IrH_2L_4]^+$ [L = $P(OMe)_2Ph$, $P(OMe)Ph_2$].

The nmr spectra (alkyl protons) of the silver and gold complex cations show clearly resolved intraligand phosphorus–proton coupling [$^3J(PH)$]; those of the copper cations do not display this coupling. Interligand phosphorus-hydrogen coupling [$^5J(PH)$] is absent from all of these spectra (see Table II). The absence of detectable interligand $^5J(PH)$ coupling interactions may indicate that the couplings $J(PMP)$ are very small, as is the case in many other tetrahedral MP_4 systems.[17] However, the overall coupling behavior is more probably attributable to ligand rearrangement and dissociation phenomena. A detailed investigation of these systems is in progress and will be reported elsewhere.

Acknowledgment. We thank the SRC for financial support.

Registry No. $\{Ru_2Cl_3[P(OMe)_2Ph]_6\}\{BPh_4\}$, 42741-18-4; $\{Ru_2Cl_3[P(OMe)Ph_2]_6\}\{BPh_4\}$, 42789-21-9; $\{Ru_2Cl_3[P(OEt)_2Ph]_6\}$-$\{BPh_4\}$, 42741-19-5; $\{Ru_2Cl_3[P(OEt)Ph_2]_6\}\{BPh_4\}$, 42741-20-8; $\{Ru_2Br_3[P(OEt)_2Ph]_6\}\{BPh_4\}$, 42741-21-9; $\{Ru_2Br_3[P(OEt)Ph_2]_6\}$-$\{BPh_4\}$, 42741-22-0; $\{Ru[P(OMe)_2Ph]_6\}\{BPh_4\}_2$, 42741-23-1; $\{RuH[P(OMe)_2Ph]_5\}\{BPh_4\}$, 37766-60-2; $\{Ir[P(OMe)_2Ph]_4\}\{BPh_4\}$, 42741-25-3; $\{Ir[P(OMe)_2Ph]_5\}\{BPh_4\}$, 42741-26-4; $\{Ir[P(OMe)Ph_2]_4\}$-$\{BPh_4\}$, 38333-57-2; $\{Ir[P(OEt)_2Ph]_4\}\{BPh_4\}$, 42741-28-6; {Ir[P-

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$\{\mathrm{Ir[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42741-29-7; $\{\mathrm{IrH[P(OMe)_2Ph]_5}\}\{\mathrm{BPh_4}\}_2$, 42741-30-0; *trans*-$\{\mathrm{IrHCl[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42741-31-1; *trans*-$\{\mathrm{IrHCl[P(OEt)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42741-32-2; *cis*-$\{\mathrm{IrHCl[P(OEt)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42741-33-3; *trans*-$\{\mathrm{IrHCl[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42741-34-4; $\{\mathrm{Pd[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-35-5; $\{\mathrm{Pd[P(OMe)_2Ph]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-36-6; $\{\mathrm{Pt[P(OMe)_2Ph]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-37-7; $\{\mathrm{Pt[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-38-8; $\{\mathrm{Pt[P(OEt)_2Ph]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-39-9; $\{\mathrm{Pt[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}_2$, 42741-40-2; $\{\mathrm{Cu[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42741-41-3; $\{\mathrm{Cu[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42740-91-0; $\{\mathrm{Ag[P(OMe)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42740-92-1; $\{\mathrm{Ag[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42740-93-2; $\{\mathrm{Ag[P(OEt)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42740-94-3; $\{\mathrm{Ag[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42789-22-0; $\{\mathrm{Au[P(OMe)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42740-85-2; $\{\mathrm{Au[P(OMe)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42740-86-3; $\{\mathrm{Au[P(OEt)_2Ph]_4}\}\{\mathrm{BPh_4}\}$, 42740-87-4; $\{\mathrm{Au[P(OEt)Ph_2]_4}\}\{\mathrm{BPh_4}\}$, 42740-88-5; *trans*-$\{\mathrm{IrHCl[P(OMe)_2Ph]_4}\}^+$, 42740-95-4; *cis*-$\{\mathrm{IrH_2[P(OMe)Ph_2]_4}\}^+$, 42740-96-5; *trans*-$\{\mathrm{IrH_2[P(OEt)_2Ph]_4}\}^+$, 42740-97-6; *cis*-$\{\mathrm{IrH_2[P(OEt)_2Ph]_4}\}^+$, 42740-98-7; *cis*-$\{\mathrm{IrH_2[P(OEt)Ph_2]_4}\}^+$, 42740-99-8; *trans*-$\{\mathrm{IrH_2[P(OMe)_2Ph]_4}\}^+$, 42741-00-4; *cis*-$\{\mathrm{IrH_2[P(OMe)_2Ph]_4}\}^+$, 42741-01-5; *catena*-dibromo(bicyclo[2.2.1]hepta-2,5-diene)ruthenium, 42740-81-8; *catena*-dichloro(bicyclo[2.2.1]hepta-2,5-dieneruthenium, 42740-82-9; chlorohydridotris(triphenylphosphine)ruthenium, 19631-00-6; chloro(carbonyl)bis(triphenylphosphine)iridium, 14871-41-1; di-μ-chlorobis(cycloocta-1,5-diene)diiridium, 12112-67-3; hydrogen, 1333-74-0; di-μ-chloro-dichlorodihydridobis(cycloocta-1,5-diene)diiridium, 12148-12-8; dichloro(cycloocta-1,5-diene)palladium, 12107-56-1; dichloro(cycloocta-1,5-diene)platinum, 12080-32-9.

Contribution from the Institute of Inorganic Chemistry,
University of Basel, CH-4056 Basel, Switzerland

Ternary Complexes in Solution. XVI.[1] Influence of the Size of the Chelate Rings on the Stability of Mixed-Ligand Copper(II) Complexes Containing Aliphatic Ligands

HELMUT SIGEL,* RENE CARACO, and BERNHARD PRIJS

Received July 11, 1973

The influence of the ring size on the stability of ternary $\mathrm{Cu^{2+}}$ complexes was studied (25°; $I = 0.1$). The differences, $\Delta \log K = \log K^{\mathrm{CuA}}{}_{\mathrm{CuAB}} - \log K^{\mathrm{Cu}}{}_{\mathrm{CuB}}$, which correspond to the equilibrium $\mathrm{CuA + CuB \rightleftharpoons CuAB + Cu}$, and the constants, $\log X$, concerning the equilibrium $\mathrm{CuA_2 + CuB_2 \rightleftharpoons 2\,CuAB}$, were compared for aliphatic ligands forming five- and six-membered chelates: for A = ethylenediamine and B = oxalate ($\log X = 0.94$), glycinate (1.03), and 1,2-propylenediamine (0.31) (five membered) or malonate (2.31), β-alaninate (0.88), and 1,3-propylenediamine (1.00) (six membered); for A = 1,3-propylenediamine and B = oxalate (3.14), glycinate (2.37), ethylenediamine (1.00), and 1,2-propylenediamine (1.13) or malonate ($\log X = 2.55$) and β-alaninate (1.70). It is concluded that in general mixed ligand complexes containing a five- as well as a six-membered chelate ring are favored in comparison with those containing either two five- or two six-membered rings. Furthermore, it appears that ternary complexes containing two six-membered chelates are somewhat more stable than the corresponding complexes containing two five-membered rings. Additionally, two earlier results are confirmed: (i) if the formation of a ternary complex leads to a neutralization of charge, its formation is favored, and (ii) comparisons of mixed-ligand systems containing either ethylenediamine or 2,2′-bipyridyl reveal the stability increasing effect of the latter ligand and the discriminating qualities of the $\mathrm{Cu^{2+}}$–2,2′-bipyridyl 1:1 complex.

Systematic studies of mixed-ligand $\mathrm{Cu^{2+}}$ complexes revealed[2] that among the driving forces which lead to the formation of ternary $\mathrm{Cu^{2+}}$ complexes in solution are statistical factors,[3-5] steric hindrance in one of the binary parent complexes,[6,7] and neutralization of charge by forming the ternary complex.[8,9] Ternary complexes of especially high stability are formed by an aromatic amine and a second ligand with O as donor atoms.[1,10,11] The reason for this increased stability is due to cooperative effects and π-bond formation in these systems.[11,12]

As the stability of binary chelate complexes is strongly dependent upon the size of the ring,[13] the same may be surmised for mixed-ligand complexes. In fact, this is confirmed by a recent study where one of the ligands was *aromatic.*[14] These systems contained either two five-membered chelate rings or one five- and one six-membered ring. For the sake of an unequivocal generalization it is necessary to do a similar investigation with *aliphatic* ligands only. The ternary complexes studied now contain either two six-, a five- and a six-, or two five-membered rings. The stability constants of the following two series of complexes were determined or taken from earlier work: (i) the ethylenediamine–$\mathrm{Cu^{2+}}$–L system and (ii) the 1,3-propylenediamine–$\mathrm{Cu^{2+}}$–L system, where L = oxalate (ox) or malonate (mal), glycinate (gly) or β-alaninate (β-al), and ethylenediamine (en), 1,2-propylenediamine (1,2-prop), or 1,3-propylenediamine (1,3-prop).

Experimental Section

Materials. Ethylenediamine and glycine were from Fluka AG, Buchs, Switzerland. β-Alanine and 1,3-propylenediamine were obtained from the British Drug Houses, Ltd., Poole, England. Disodium oxalate or malonate were from Merck AG, Darmstadt, Germany. From ethylenediamine and 1,3-propylenediamine the respective dihydrochlorides were prepared. *Anal.* Calcd for $\mathrm{C_2H_{10}N_2Cl_2}$ (en·2HCl): C, 18.06; H, 7.58; N, 21.06; Cl, 53.30. Found: C, 18.28; H, 7.76; N, 21.06; Cl, 53.29. *Anal.* Calcd for $\mathrm{C_3H_{12}N_2Cl_2}$ (1,3-

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