TABLE V
RATE DATA ON CHLORIDE EXCHANGE WHICH INDICATE THE INFLUENCE OF CHARGE ON REACTION RATE[1]

Platinum(IV) reactant	Platinum(II) catalyst	$k_3(25°)$, M^{-2} sec^{-1}
$Pt(NH_3)_5Cl^{3+}$	$Pt(NH_3)_4^{2+}$	0.00065[a]
cis-$Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	0.0028[a]
trans-$Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	6.3
trans-$Pt(NH_3)_3Cl_3^{+}$	$Pt(NH_3)_4^{2+}$	22
trans-$Pt(NH_3)_3Cl_3^{+}$	$Pt(NH_3)_3Cl^{+}$	30

[a] Although these are labeled chloride-exchange reactions, an ammonia molecule is replaced by chloride in a slow reaction which is then followed by exchange of chloride in the new product.

TABLE VI
A CORRELATION BETWEEN EQUILIBRIUM AND RATE CONSTANTS FOR SOME REACTIONS OF PLATINUM(IV) COMPLEXES

$$trans\text{-}Pt(NH_3)_4ClX^{(3-n)+} + Cl^- \longrightarrow trans\text{-}Pt(NH_3)_4Cl_2^{2+} + X^{n-}$$

X	$K(25°)$	$k(25°)$, M^{-2} sec^{-1}	Ionic strength	Ref
Pyridine	8.2	8	0.20	7
Br^-	0.06	6.3	0.20	5
SCN^-	0.0028[a]	2.7	1.10	6
Ammonia	0.0014	0.0012	0.32	3, 4

[a] At 35.0°.

rate is expected to result from the rate-determining step 2 as the ionic strength is raised for the one reaction in which two positively charged species combine to form an activated complex with charge +3. This effect apparently overrides the reverse effect due to the preequilibrium. In the other five reactions the "ion pair" formed in step 1 is uncharged, and little ionic strength influence is expected for ion-molecule reactions. The ionic strength effect on the preequilibrium step thus determines the result for the reactions in which two +1 ions and one −1 ion react. It is not surprising that the reactions of intermediate charge type (total charge +2) exhibit intermediate (negligible) ionic strength effects.

In the reactions reported in this article the reaction rates correlate with the relative stabilities of reactants and products. Previous studies on platinum(II)-catalyzed reactions of platinum(IV) complexes (Table VI) show a similar relationship. It must be admitted, however, that although the equilibrium and rate constants in this table do fall in the same order, the magnitudes of the numbers do not correlate well. A good correlation would require appreciably faster rates for the reactions in which the neutral molecules pyridine and ammonia are displaced. The correlation which exists between equilibrium and rate constants does indicate that the activated complex for these reactions is relatively symmetrical and hence resembles to some extent both reactants and products. This, not too surprisingly, seems to be particularly valid when both entering and leaving groups are halide anions. The activated complex in a reaction in which an amine is displaced by a halide anion is inherently less symmetrical.

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Transition Metal Complexes of a Cationic Phosphine Ligand[1,2]

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A monodentate phosphine which also contains a quaternary phosphorus atom in a four-member ring was synthesized and characterized. This cationic ligand, the 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphetanium ion, abbreviated ($P\text{–}P^+$), forms the planar complexes $[Au(P\text{–}P^+)Cl_3]Cl$, $[Pd(P\text{–}P^+)_2Cl_2](ClO_4)_2$, and $Pd(P\text{–}P^+)Cl_3$ as well as the pseudotetrahedral complexes $Ni(P\text{–}P^+)X_3$ (where X_3 = Cl_3, $BrCl_2$, Br_2Cl) and $Co(P\text{–}P^+)X_3$ (where X_3 = Cl_3, Br_2Cl, I_3). The similarity of the magnetism and electronic spectral data for the $M(P\text{–}P^+)X_3$ complexes (M = Ni, Co) with those of the known pseudotetrahedral $MP(C_6H_5)_3Y_3^-$ anions (M = Ni, Co; Y = halide) indicates that the phosphine cation functions essentially as triphenylphosphine; *i.e.*, the positive charge three atoms away exerts little influence on the coordination properties of the nonquaternary phosphine group.

Introduction

Compared with the extensive number of investigations of transition metal complexes with neutral and anionic ligands, relatively few studies with positively charged ligands have been reported. In fact, the only planned efforts have been expended by Quagliano and coworkers[3-6] where they studied the coordination

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(1) This paper is based on part of the thesis submitted by D. L. Berglund to the Graduate School of The Ohio State University, March 1969, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Presented at the 1st Central Regional Meeting of the American Chemical Society, Akron, Ohio, April 1968.

(3) J. V. Quagliano, J. T. Summers, S. Kida, and L. M. Vallarino, *Inorg. Chem.*, **3**, 1557 (1964).

(4) A. K. Banerjee, L. M. Vallarino, and J. V. Quagliano, *Coord. Chem. Rev.*, **1**, 239 (1966).

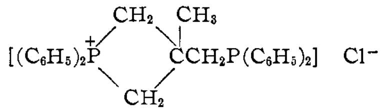
(5) V. L. Goedken, L. M. Vallarino, and J. V. Quagliano, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-119.

(6) J. V. Quagliano and L. M. Vallarino, Proceedings of the IXth International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 1966, p 216.

properties of cationic ligands that are formed by monoquaternization of simple diamines.

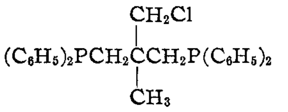
However, several isolated cases are noted where a positively charged species is bonded to a metal ion; in most of those instances the ligand became positively charged after coordination. For example, an uncoordinated phosphine or arsine group of a polydentate ligand was quaternized after the other donor atoms of the ligand were attached.[7] Drew[8] found that hydrochloric acid protonated the ethylenediamine ligands in $[Pt(en)_2]Cl_2$ and converted the complex to $Pt(enHCl)_2Cl_2$, which subsequently rearranged to $[Pt(enH)_2Cl_2][PtCl_4]$. Denning, *et al.*,[9] studied the stability constants of $[PtCl_3CH_2{=}CH(CH_2)_nNHR_2]$ in acid solutions, where the cationic olefin forms a π complex *via* the double bond. In the case of the hydrazinium ion, the nonquaternary amino group is bonded to zinc in $Zn(N_2H_5)_2(SO_4)_2$.[10]

In spite of Quagliano's studies[3-6] with cationic amine ligands, we are unaware of any systematic investigation of cationic phosphorus or arsenic ligands. This paper reports the preparation and characterization of 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphetanium[11,12] chloride



(P–P$^+$)

and some four-coordinate square-planar and pseudotetrahedral complexes in which the phosphetanium cation (P–P$^+$) coordinates *via* the nonquaternary diphenylphosphino group. The isomeric diphosphine ligand [2-(chloromethyl)-2-methyltrimethylene]bis(diphenylphosphine)



$$(C_6H_5)_2PCH_2\overset{\displaystyle CH_2Cl}{\underset{\displaystyle CH_3}{C}}CH_2P(C_6H_5)_2$$

was also prepared and a few of its complexes were characterized for comparison with those of (P–P$^+$).

Experimental Section

Reagents.—Tetrahydrofuran was dried by refluxing it with and then distilling it from lithium aluminum hydride in a nitrogen atmosphere. Gaseous ammonia was dried with a potassium hydroxide column. Water and absolute ethanol used in the ligand preparation and recrystallization were deoxygenated by bubbling nitrogen through the liquids. Acetonitrile was stirred with barium oxide to remove excess water and then stirred over and distilled from phosphorus pentoxide in an all-glass apparatus to remove basic impurities. Nitromethane was washed with 5% sodium bicarbonate and 5% sulfuric acid solutions. It was then stirred over calcium chloride and distilled in an all-glass apparatus equipped with a calcium sulfate drying tube. Other reagent grade solvents were used in the synthesis of the complexes without further purification.

Synthesis of the Ligands.—The synthesis and characterization of the phosphine cation, (P–P$^+$), was reported previously.[12] Originally the phosphetanium chloride was formed accidentally in an attempt to prepare 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C[CH_2P(C_6H_5)_2]_3$. Triphenylphosphine was cleaved by sodium in liquid ammonia to give sodium diphenylphosphide. Sodium phenyl was removed from the reaction mixture with reagent grade ammonium bromide, which was not rigorously dried and subsequently was found to contain about 0.6 mol ratio of water. Therefore, the proportionate amount of sodium diphenylphosphide was hydrolyzed so that when the organic trihalide $CH_3C(CH_2Cl)_3$ was added, only two of the three chlorides were replaced with diphenylphosphide groups. The liquid ammonia was evaporated and the reaction was completed in refluxing tetrahydrofuran, forming the chloride of (P–P$^+$).

To prepare the nonquaternized diphosphine $C_{29}H_{29}ClP_2$, the same procedure of treating $CH_3C(CH_2Cl)_3$ with a 2 mol ratio of sodium diphenylphosphide in liquid ammonia is followed,[12] except that the reaction mixture is not refluxed with tetrahydrofuran after the ammonia is evaporated.

In one case the reaction mixture was refluxed in tetrahydrofuran for 8 hr, a shorter time than the 14 hr recommended for preparation of (P–P$^+$)Cl, and a mixture of (P–P$^+$)Cl and the diphosphine was obtained. In the case of the mixture, (P–P$^+$)Cl and the diphosphine were separated by adding acetone to an ethanol solution of the mixture. The salt, (P–P$^+$)Cl, is less soluble and crystallized slowly from the mixed solvent. After four batches of crystals of (P–P$^+$)Cl were isolated from successively smaller volumes of ethanol, the remaining solvent was removed by vacuum distillation, and the viscous oil that remained was identified as the diphosphine $C_{29}H_{29}ClP_2$.[13]

Preparation of the Perchlorate Salt of (P–P$^+$).—Equivalent quantities of the phosphetanium chloride (1 mmol, 0.48 g) and lithium perchlorate (1 mmol, 0.11 g) were combined in 10 ml of refluxing ethanol. When the solution cooled to room temperature, white crystals separated; these were dried *in vacuo*. *Anal.* Calcd for $C_{29}H_{29}ClO_4P_2$: C, 64.68; H, 5.39; Cl, 6.60; P, 11.52. Found: C, 64.39; H, 5.30; Cl, 6.56; P, 11.47.

Methyl Iodide Derivatives of (P–P$^+$) and the Diphosphine.—In separate flasks a large excess of methyl iodide was added to warm (~35–40°) absolute ethanol solutions of the phosphetanium chloride and of the diphosphine. White crystals separated when the solutions cooled to room temperature. Both compounds are di-univalent electrolytes and their proton nmr spectra are consistent with addition of one and two methyl iodides, respectively.

In order to exchange the ionic chloride, the phosphetanium chloride–methyl iodide derivative then was combined with a twentyfold excess of lithium iodide dissolved in ethanol. The solution was concentrated and the phosphetanium iodide–methyl

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[7] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

[8] H. D. K. Drew, *ibid.*, 2328 (1932).

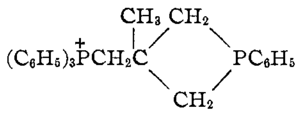
[9] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *ibid.*, *A*, 324 (1967).

[10] C. K. Prout and H. M. Powell, *ibid.*, 4177 (1961).

[11] The naming of the phosphorus cation is based on the *Chemical Abstracts* system where the compound is classified as a four-member phosphorus heterocycle. Please note that the correct spelling is phosphetanium instead of phosphetanium as originally[12] reported.

[12] D. Berglund and D. W. Meek, *J. Am. Chem. Soc.*, **90**, 518 (1968).

[13] A referee has raised the possibility that a phenyl group may have migrated during the quaternization process and formed



instead of the proposed cation where the positive charge resides on the ring phosphorus. The proton nmr spectra of (P–P$^+$)Cl and (P–P$^+$)ClO_4 in $CDCl_3$ seem to exclude the phenyl migration as the nmr spectra of both compounds show two sets of multiplets (approximately of equal intensity) centered at −126 ± 2 and −148 ± 2 cps from the internal CH_2Cl_2 standard. If a phenyl migration had occurred, the intensity ratio of the two sets of phenyl resonances would be 3:1. The lower field multiplet is assigned to the $>P^+(C_6H_5)_2$ group and the higher field resonance is assigned to the terminal $-P(C_6H_5)_2$ group. These assignments are in excellent agreement with the proton nmr spectra of $(CH_3P^+{-}P^+)I_2$ and $\{ClCH_2C(CH_3)[CH_2P^+(CH_3)(C_6H_5)_2]_2\}I_2$ in chloropentafluoro-2-propanol. These methyl iodide derivatives of (P–P$^+$) and the diphosphine have a complex phenyl resonance centered at −153 ± 1 and −147 ± 1 cps from the internal CH_2Cl_2 standard.

TABLE I

ELEMENTAL ANALYSIS DATA FOR THE COMPLEXES[a]

Compound	% C		% H		% Cl		% P		% other		
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Element	Calcd	Found
$Ni(P–P^+)Cl_3$	57.52	57.48	4.79	4.86	17.60	17.43	10.25	10.16			
$Ni(P–P^+)BrCl_2$	53.62	53.84	4.47	4.53	10.94	11.65			Br	12.33	11.17
									Br + Cl	23.27	22.82
$Ni(P–P^+)Br_2Cl$	50.14	50.50	4.18	4.31	5.12	4.97	8.93	8.82	Br	23.05	23.24
$[CH_3(P^+–P^+)][NiI_4]$	35.26	35.61	3.13	3.41					I	49.76	51.96
$Co(P–P^+)Cl_3$	57.52	55.70	4.79	4.80	17.60	17.14	10.25	10.36	Co	9.75	9.82
									N[b]	0.00	0.50
$[Co(P–P^+)Br_2Cl] \cdot CH_3NO_2$	47.68	47.62	4.24	4.43	4.70	4.96	8.21	8.22	Br	21.19	21.85
									N	1.85	1.77
$Co(P–P^+)I_3$	39.59	38.71	3.30	3.18	0.00	0.36	7.05	6.83	I	43.34	41.54
$[Au(P–P^+)Cl_3]Cl$	44.67	44.50	3.72	3.90	18.23	18.42	7.96	7.93			
$Pd(P–P^+)Cl_3$	53.37	53.15	4.45	4.66	16.35	16.59	9.51	9.47			
$[Pd(P–P^+)_2Cl_2](ClO_4)_2$	55.46	56.85	4.62	4.69	11.31	10.90	9.88	9.69			
$Ni(C_{29}H_{29}ClP_2)Br_2$[c]	50.14	50.60	4.18	4.38	5.12	4.80	8.93	9.02	Br	23.05	22.50

[a] The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] This complex was prepared from cobaltous nitrate. [c] The formula $C_{29}H_{29}ClP_2$ represents the diphosphine ligand $ClCH_2C(CH_3)[CH_2P(C_6H_5)_2]_2$.

iodide salt, $[CH_3(P^+–P^+)]I_2$, crystallized. *Anal.* Calcd for $C_{30}H_{32}I_2P_2$: C, 50.85; H, 4.52; I, 35.88; P, 8.76. Found: C, 51.06; H, 4.78; I, 35.59; P, 8.50.

General Preparation of the Complexes.—Warm ethanol solutions of the phosphetanium chloride (1 mmol, 0.48 g, in 5 ml) and the appropriate metal salt (1 mmol in 10 ml) were mixed under a nitrogen atmosphere. The resulting solution was refluxed for 15 min and then cooled slowly to room temperature. The solid materials were collected on a sintered-glass funnel, recrystallized, and dried 24 hr *in vacuo* at room temperature. The specific recrystallization solvents are given below and the elemental analysis data for the complexes are listed in Table I.

$Ni(P–P^+)Cl_3$, $Ni(P–P^+)BrCl_2$, and $Ni(P–P^+)Br_2Cl$.—The nickel(II) complexes were recrystallized from 2 ml of methanol by adding 18 ml of acetone. The $Ni(P–P^+)BrCl_2$ compound was also isolated when solutions of $(P–P^+)Cl$ and "$NiBrClO_4$" were mixed. The white $(P–P^+)ClO_4$ compound precipitated almost immediately; this salt was removed, and the turquoise filtrate was concentrated to 5 ml to give $Ni(P–P^+)BrCl_2$.

$Co(P–P^+)Cl_3$, $Co(P–P^+)Br_2Cl$, and $Co(P–P^+)I_3$.—The $Co(P–P^+)Cl_3$ complex was prepared from a reaction mixture containing $Co(NO_3)_2$ and $(P–P^+)Cl$, where the extremely soluble $(P–P^+)NO_3$ remained in solution. The $Co(P–P^+)Cl_3$ complex was recrystallized from a mixture of 2 ml of methanol and 18 ml of acetone. This chloride may also be prepared easily from cobaltous chloride and the phosphetanium chloride in ethanol. The bromide was recrystallized from hot nitromethane and formed the solvate $[Co(P–P^+)Br_2Cl] \cdot CH_3NO_2$. The $Co(P–P^+)I_3$ complex was prepared from $(P–P^+)I$ and CoI_2 and recrystallized from ethanol.

$[Au(P–P^+)Cl_3]Cl$ and $Pd(P–P^+)Cl_3$.—The gold complex crystallized from 50 ml of ethanol and acetone over a period of 5 days; the palladium compound crystallized from 75 ml of methanol at −10° over a period of 4 days.

$[Pd(P–P^+)_2Cl_2](ClO_4)_2$.—An ethanol solution of 1 mmol of $(P–P^+)Cl$ was added to a filtered solution of 0.5 mmol of Na_2PdCl_4. Ethanol was added to bring the total volume to 100 ml and the solution was refluxed for 1 hr before the solution was added to 15 mmol of $LiClO_4$ in ethanol. The mixture was concentrated and cooled to room temperature and the resulting solid was recrystallized from hot acetone.

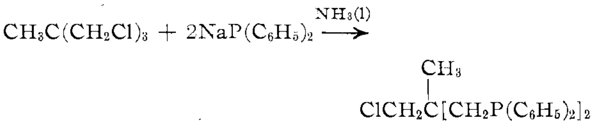
$[CH_3(P^+–P^+)][NiI_4]$.—The iodide salt of the divalent cation, $[CH_3(P^+–P^+)]I_2$, was added to an ethanol solution of nickel iodide. After adding 20 ml of acetone to the refluxing mixture, a red color developed; on continued refluxing the deep red material separated.

$[Ni(C_{29}H_{29}ClP_2)Br_2]$.—An ethanol solution of the oily diphosphine ligand, $C_{29}H_{29}ClP_2$, was combined with a solution of nickel bromide. The reaction mixture was refluxed 15 min and then cooled to room temperature; the orange compound was isolated and recrystallized from acetone.

Magnetism, Conductance, and Spectral Measurements.—These physical methods of characterization were performed as previously reported.[14] The observed magnetic susceptibility values were corrected for the diamagnetism of the ligands; the correction for $(P–P^+)$ is 306×10^{-6} cgsu and the value for the unquaternized ligand $C_{29}H_{29}ClP_2$ is 323×10^{-6} cgsu.[15]

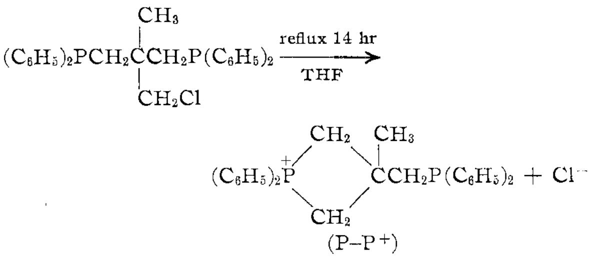
Results and Discussion

Cationic Phosphine Ligand.—The 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphetanium cation,[11] abbreviated $(P–P^+)$, was formed from [2-(chloromethyl)-2-methyltrimethylene]bis(diphenylphosphine); the latter was prepared in liquid ammonia by the reaction



$$CH_3C(CH_2Cl)_3 + 2NaP(C_6H_5)_2 \xrightarrow{NH_3(l)} ClCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}[CH_2P(C_6H_5)_2]_2 \qquad (1)$$

An intramolecular quaternization reaction of the diphosphine was accomplished by 14 hr of refluxing in tetrahydrofuran (eq 2). In one instance a reflux period



(2)

of 8 hr gave a mixture of the diphosphine and the phosphetanium chloride.

The ionic nature of the phosphetanium chloride is indicated by (1) the conductance (71 cm²/ohm mol) in nitromethane, (2) the two types of diphenylphosphino groups in the proton nmr spectrum, (3) the im-

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[14] T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **6**, 1395 (1967).

[15] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 403.

mediate precipitation of silver chloride when the compound is treated with silver nitrate, (4) the rapid exchange of the chloride for other anions, and (5) the addition of only 1 mol of methyl iodide. The iodide of this dipositive cation, $[CH_3(P^+{-}P^+)]I_2$, was treated with nickel(II) iodide, and the resulting compound was identified as $[CH_3(P^+{-}P^+)][NiI_4]$.[16] The latter compound is quite distinguishable from the $Ni(P{-}P^+)I_3$ complex, so that $CH_3(P^+{-}P^+)$ functions simply as a dipositive cation, whereas the $(P{-}P^+)$ cation behaves as a positively charged phosphine ligand.

A general method for preparing quaternary phosphonium compounds is to heat a tertiary phosphine with an alkyl halide.[17] The intramolecular quaternization used here to prepare $(P{-}P^+)Cl$ does not appear to be a typical procedure for synthesizing four-member phosphorus heterocycles.[18-20] However, this reaction gives good yields of $(P{-}P^+)Cl$ and should have synthetic utility for other phosphetanium compounds.

Complexes.—In order to evaluate the coordination properties of the phosphorus cation, several four-coordinate nickel(II), cobalt(II), palladium(II), and gold(III) complexes of $(P{-}P^+)$ were characterized. The $(P{-}P^+)$ cation functions as a monodentate ligand and bonds *via* the unquaternized diphenylphosphino group. In contrast to complexes of the cationic amine ligands that were studied by Quagliano, *et al.*,[3-6] these phosphine complexes are soluble in several polar organic solvents and they are not noticeably sensitive to atmospheric moisture. Infrared spectra indicate that the $-P(C_6H_5)_2$ group does not tend to oxidize under the conditions used for synthesis of the complexes.

Square-Planar Complexes.—The $[Au(P{-}P^+)Cl_3]Cl$, $[Pd(P{-}P^+)Cl_3]$, and $[Pd(P{-}P^+)_2Cl_2](ClO_4)_2$ complexes are diamagnetic and their electronic absorption spectra are characteristic of a square-planar geometry (Table II).

TABLE II

CONDUCTANCE AND ELECTRONIC SPECTRAL DATA FOR THE SQUARE-PLANAR COMPLEXES

Complex	Color	Absorption max, cm^{-1}: Solid state (Nujol mulls)	Absorption max, cm^{-1}: Soln (ϵ)[a]	Λ_M, $cm^2/ohm\ mol$
$Ni(C_{29}H_{29}ClP_2)Br_2$[b]	Orange	20,750 24,750	20,700 (962) 25,000 (668)	10[c]
$Pd(P{-}P^+)Cl_3$	Orange	25,300 sh[d]	27,050 sh (1130)	18[e]
$[Pd(P{-}P^+)_2Cl_2](ClO_4)_2$	Orange	24,800	27,100 (1260)	186[f]
$[Au(P{-}P^+)Cl_3]Cl$	Gold	24,500	26,500 sh (483)	131[f]

[a] ϵ, the molar absorptivity at the absorption maximum. [b] The formula $C_{29}H_{29}ClP_2$ represents the diphosphine ligand, $ClCH_2C(CH_3)[CH_2P(C_6H_5)_2]_2$. [c] Approximately 10^{-3} *M* nitromethane solution. [d] sh indicates a shoulder on a much more intense absorption. [e] Approximately 10^{-3} *M* dimethylformamide solution. [f] Approximately 10^{-3} *M* acetonitrile solution.

The orange nickel(II) complex of the unquaternized diphosphine, $C_{29}H_{29}ClP_2$, is a diamagnetic nonelectrolyte in nitromethane and its electronic spectrum indicates a square-planar structure. Since this ligand functions as a typical chelating diphosphine,[21] its coordination behavior was not investigated further.

Pseudotetrahedral Complexes.—The four-coordinate nickel(II) and cobalt(II) complexes of $(P{-}P^+)$ are intensely blue or bluish green, are paramagnetic, and are moderate electrolytes in nitromethane. Since the $(P{-}P^+)$ ligand simultaneously incorporates a cation, the $M(P{-}P^+)X_3$ complexes should exhibit low conductance values if the halides remain strongly coordinated. The conductivity values (Table III) in nitromethane suggest that a significant amount of dissociation occurs. In fact, the values increase in the series Cl < Br < I, consistent with the weaker ligand field strength of the heavier halides. The electronic absorption spectra taken in nitromethane solution (Table IV) also reflect the solvation process, as the spectra in solution are shifted slightly to higher energy relative to the solid-state spectra.

TABLE III

PHYSICAL CHARACTERIZATION DATA FOR THE PSEUDOTETRAHEDRAL COMPLEXES

Compound	Color	Conductivity Λ_M,[a] $cm^2/ohm\ mol$	μ_{eff}, BM[b]
$Ni(P{-}P^+)Cl_3$	Blue	16	3.61
$Ni(P{-}P^+)BrCl_2$	Turquoise	33	3.71
$Ni(P{-}P^+)Br_2Cl$	Bluish green	63	3.59
$[CH_3(P^+{-}P^+)][NiI_4]$	Deep red	160	3.44[c]
$Co(P{-}P^+)Cl_3$	Blue	28	4.64
$[Co(P{-}P^+)Br_2Cl]\cdot CH_3NO_2$	Blue	34	4.65
$Co(P{-}P^+)I_3$	Bluish green	51	4.78

[a] Λ_M, molar conductance obtained on approximately 10^{-3} *M* nitromethane solutions. [b] These moments have not been corrected for temperature-independent paramagnetism. [c] Value is slightly field dependent.

The symmetry of the metal–ligand environment in the $M(P{-}P^+)X_3$ (M = Ni, Co) complexes is approximately C_{3v} and even lower in those cases where two different halides are coordinated. The reduction of symmetry from T_d to C_{3v} and C_s should result in significant changes in the energy levels of the d electrons. Consequently, one would expect the orbital contribution to the magnetic moments to be smaller than for T_d complexes and the "d–d" electronic transitions to T states to be split into two and three components for C_{3v} and C_s symmetries, respectively. In fact, the observed magnetic moments (Table III) of the $Ni(P{-}P^+)X_3$ complexes are somewhat lower than the range of 3.8–4.0 BM that is usually observed for T_d Ni(II) complexes, but the moments are appreciably higher than the "spin-only" value of 2.83 BM and reflect the pseudotetrahedral structures. The electronic absorption spectra (Table IV) are also consistent with a pseudotetrahedral arrangement of one phos-

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TABLE IV
ELECTRONIC ABSORPTION MAXIMA (CM^{-1}) FOR THE PSEUDOTETRAHEDRAL COMPLEXES

Complex	Solid state (Nujol mulls)	CH$_3$NO$_2$ soln (ϵ)[a]
Ni(P–P$^+$)Cl$_3$	8,930 sh[b]	8,980 sh[b]
	9,480	9,430 (20)
	10,280	10,260 (20)
	15,380	15,420 (83)
	16,700	16,770 (78)
	~27,750 sh	
Ni(P–P$^+$)BrCl$_2$	9,170	9,260 (104)
	10,050	10,020 (104)
	15,150 sh	15,150 (129)
	16,130	16,130 sh (125)
	~27,750 sh	
Ni(P–P$^+$)Br$_2$Cl	9,080	9,080 (74)
	10,000	
	14,930 sh	14,820 sh (184)
	15,950	15,990 (212)
	27,300 sh	~27,750 (1170)
Co(P–P$^+$)Cl$_3$	4,830	4,830 (59)
	7,140 sh	~8,000 b[c] (45)
	8,130 b[c]	
	14,300	14,570 (421)
	15,070	15,160 (423)
	16,770	16,820 (418)
	27,100 sh	
[Co(P–P$^+$)Br$_2$Cl]·CH$_3$NO$_2$[d]	6,340 b	6,230 (42)
	7,300 b, sh	7,460 b (36)
	14,700 sh	14,500 (574)
	15,040	14,800 sh (555)
	15,770	15,800 (399)
	16,130 sh	16,100 sh (365)
Co(P–P$^+$)I$_3$	5,720 b, sh	5,150 sh (91)
		5,520 (96)
		6,760 b, sh (28)
	13,070	13,500 sh (698)
	14,170	13,950 (802)
		14,400 sh (674)
		24,700 (2140)
[CH$_3$(P$^+$–P$^+$)][NiI$_4$]	7,090	
	7,750 sh	8,260 (72)
	8,260	8,770 (62)
	10,990	
	12,120	13,890 (251)
	13,510	14,600 (254)
	19,160	18,830 (1380)
	26,740	21,510 sh (1260)

[a] ϵ, molar absorptivity at band maxima in parentheses. [b] sh, shoulder on a much more intense absorption. [c] b, broad maxima. [d] Nitromethane adduct was obtained when the bromide complex was recrystallized from nitromethane.

phorus and three halide donors around nickel(II) or cobalt(II). Cotton, *et al.*,[22–24] established that the MP(C$_6$H$_5$)$_3$X$_3^-$ anions (where M = Co, Ni) exhibit magnetic and spectral properties very similar to T$_d$ Co(II) and Ni(II) complexes, and the C$_{3v}$ structure of NiP(C$_6$H$_5$)$_3$I$_3^-$ has been confirmed recently by X-ray crystallography.[25]

The experimental magnetic susceptibility values of the cobalt(II) compounds were corrected for diamagnetism[15] of the (P–P$^+$) ligand and for temperature-independent paramagnetism (TIP) of Co(II). The values of the ligand field parameter Δ, which were calculated from the observed spectral data (Table V), were used to calculate the TIP corrections according to the relationship TIP = 2.09/Δ.[26] The susceptibility corrections and the calculated moments are given in Table VI. The trend in the magnetic moment values (Tables III and VI) is consistent with an increasing orbital contribution to the "spin-only" value as the ligand field strength of the halides decreases.[22,26] By comparing the magnetic data of the Co(P–P$^+$)X$_3$ complexes with those reported by Cotton, *et al.*,[22,26] for the tetrahedral CoX$_4^{2-}$ and CoP(C$_6$H$_5$)$_3$X$_3^-$ series, it is apparent that the Co(P–P$^+$)X$_3$ complexes are pseudotetrahedral.

TABLE V
SUMMARY OF THE SPECTRAL AND MAGNETIC DATA FOR THE COBALT COMPLEXES

	Co(P–P$^+$)Cl$_3$	Co(P–P$^+$)Br$_2$Cl	Co(P–P$^+$)I$_3$
ν_3, cm^{-1} [a]	15,810	15,280	14,040
ν_2, cm^{-1} [a]	6860	6220	4580
Δ(calcd), cm^{-1}	3980	3590	2610
B', cm^{-1}	716	715	719
β (B'/B)[b]	0.74	0.74	0.74
μ_{eff}, BM	4.50	4.50	4.59
λ', cm^{-1}	−159	−144	−119

[a] ν_3 and ν_2 are treated as the transitions $^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$, respectively, in T$_d$ symmetry; however, in C$_{3v}$ symmetry the T$_1$ states would be split into A$_2$ and E states and this factor may account for some of the multiple bands in the ν_2 and ν_3 regions. [b] B = 967 cm^{-1} for the Co(II)-free ion.

TABLE VI
CORRECTED MAGNETIC SUSCEPTIBILITY DATA FOR THE COBALT COMPLEXES

	Co(P–P$^+$)Cl$_3$	Co(P–P$^+$)Br$_2$Cl	Co(P–P$^+$)I$_3$
Diamagnetic correction, cgsu × 10^6	389	439	470
TIP, cgsu × 10^6	525	582	801
χ_M^{cor}, cgsu × 10^6	8459	8467	8789
μ_{eff}, BM	4.50	4.50	4.59

To investigate the possible influences of the positively charged phosphetanium group on the phosphine donor, one should have a ligand with very similar structural and inductive properties. In the present study either CH$_3$P(C$_6$H$_5$)$_2$ or C$_2$H$_5$P(C$_6$H$_5$)$_2$ would be ideal; unfortunately, no pseudotetrahedral Co(II) or Ni(II) complexes of either ligand have been reported. However, Cotton, *et al.*,[22–24] have studied the pseudotetrahedral MP(C$_6$H$_5$)$_3$X$_3^-$ complexes. Since both the M(P–P$^+$)X$_3$ and MP(C$_6$H$_5$)$_3$X$_3^-$ types of complexes have a common set of donor atoms, *i.e.*, one aryl phosphine and three halides, coordinated in a pseudotetrahedral geometry, one can deduce the effect of the positive charge in (P–P$^+$) by a direct comparison of the magnetic and electronic properties in the two series of complexes. The data in Tables IV–VI show a remarkable correlation with the data for the corresponding MP(C$_6$H$_5$)$_3$X$_3^-$ anions. Thus, the (P–P$^+$) cation functions essentially as

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triphenylphosphine, so the presence of the positive phosphetanium group three carbon atoms away does not appreciably influence the coordination properties of the diphenylphosphino group.

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Metal Complexes as Ligands. VIII.[1] Square-Planar Binuclear Copper(II) Complexes with Ring-Substituted Salicylaldimines

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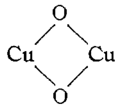
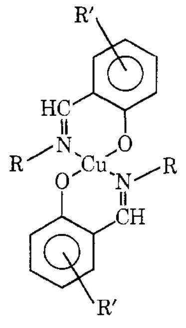
A series of copper(II) complexes with ring-substituted, bidentate salicylaldimine ligands and the corresponding binuclear copper halide derivatives has been prepared and studied. The spectral and magnetic properties of the parent mononuclear complexes and of their binuclear derivatives are interpreted in terms of an essentially planar environment about the copper atoms. No significant dependence of the stereochemistry upon the bulkiness of the substituent on the nitrogen atom of the salicylaldimine group is observed. These results contrast with those for the analogous complexes with no ring substituents, in which there is a strong dependence of the stereochemistry on the bulkiness of the nitrogen substituent in the parent mononuclear complexes and a similar but smaller dependence in the binuclear derivatives. The role of magnetic and infrared data as an analytical tool for the binuclear complexes is discussed.

Introduction

Many metal complexes with bi-, tri-, or tetradentate salicylaldimines react with other metal salts such as halides, nitrates, or perchlorates, to form various bi- and trinuclear complexes containing similar and dissimilar metals.[1-5] When both metal atoms in a binuclear complex or all three metals in a trinuclear complex are paramagnetic, antiferromagnetic interactions are usually observed.[1-7] In particular, when the copper(II) complexes of bidentate salicylaldimines (1, R′ = H) are treated with copper(II) chloride,[5,8] bromide,[1] or nitrate,[9] binuclear complexes are formed (2, R′ = H, X = Cl, Br, or ONO_2), with a *trans* arrangement of the ligands about the skeleton; these complexes exhibit pairwise antiferromagnetic interactions in all cases investigated.[5,7] A strong trend from planar toward tetrahedral configuration as the nitrogen substituent R becomes more bulky has been observed in the parent complexes 1, R′ = H,[10,11] while a similar but much lesser trend was found in the binuclear complexes 2, R′ = H.[5,7,8]





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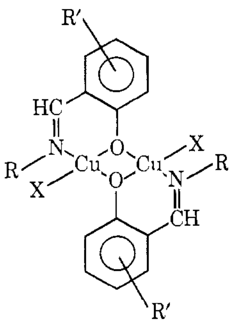

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We now report on the reaction of copper(II) halides with ring-substituted salicylaldimine complexes 1 (R′ = 5-Cl, 5-Br, 3,5-$(Cl)_2$, 5-NO_2, 5,6-benzo) and compare the properties of the binuclear complexes formed with their analogs having no substituents (R′ = H) in the phenyl rings of the salicylaldimine group.

Experimental Section

The organic ligands and their copper(II) complexes (1) were prepared by standard methods described in the literature[12-17] using the appropriate primary amines and 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-

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