Zwitterionic Complexes of Cobalt(II)

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Pseudotetrahedral zwitterionic complexes of stoicheiometry $[CoX_3^-L\text{–}L^+]$, where X = Cl, Br, or I and $L\text{–}L^+$ represents the cationic ligands $Ph_2PC_2H_4\overset{+}{N}(H)R_2$ (R = H, Me, or Et) have been prepared by the reaction of $\overset{+}{L}\text{–}LX^-$ with CoX_2. In the cases R = Me or Et, identical complexes were also prepared by the reaction of cobalt(II) halides with the unprotonated ligand in refluxing ethanol. Magnetic susceptibility, conductivity, and in particular, electronic spectral data suggest a total lack of influence of the cationic site on the ligand properties of the donor atom. Similar zwitterionic complexes of stoicheiometry $[CoBr_3^-P\text{–}\overset{+}{P}]$, where $P\text{–}\overset{+}{P}$ represents the monobenzylated derivatives of *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2PC{\equiv}CPPh_2$ were prepared in order to study the possible influence of a positive charge transmitted *via* an unsaturated organic bridge to a donor atom. A comparison of this system with the data obtained for $[Et_4N]^+[CoBr_3P\text{–}P]^-$, where the organophosphorus group is only acting in a monodentate fashion, was made.

We have been investigating the type of complexes formed by the reactions of various nitrogen–phosphorus bidentate ligands (I) with a number of transition metal systems. In the present paper we wish to report the results obtained upon reaction of (I) with cobalt(II) halides, *i.e.*, the formation of the zwitterionic complexes $[CoX_3^-(C_6H_5)_2PC_2H_4\overset{+}{N}(H)R_2]$, where X = Cl, Br, or I. The synthesis of these complexes is unexpected in the light of two pertinent facts. (i) Venanzi *et al.*[1] reported that the reaction of (II) with cobalt(II) halides yielded pseudotetrahedral complexes in which the co-ordination polyhedron is comprised of two hydrogen atoms, one phosphorus and one nitrogen atom. The ligands [(I) and (II)] and the reaction conditions employed are similar, yet, the complexes obtained are surprisingly different. (ii) Other zwitterionic complexes of the stoicheiometry $[MX_3^-L\text{–}L^+]$, where M is a divalent first row transition metal ion, X = halogen or pseudohalogen, and $L\text{–}L^+$ represents any one of a number of protonated or quaternized phosphorus and/or nitrogen

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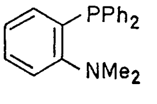
[1] R. E. Christopher, I. R. Gordon, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1968, 205.

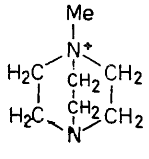
containing ligands (III—VI) have been described.[2-5] The preparation of the complexes was accomplished by reaction of MX_2 with the positively charged ligand, $L\text{-}L^+X^-$. In the present study we have prepared zwitterionic complexes by using the neutral ligands.

$R_2NC_2H_4PPh_2$
R = H, Me or Et

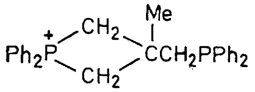
(I)



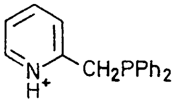
(II)



(III)



(IV)



(V)

$Ph_2P(CH_2)_n\overset{+}{P}Ph_2CH_2Ph$
$n = 1, 2$

(VI)

In addition, we wish to report the results of some investigations undertaken in an attempt to determine the effect of the positive charge on the ligand properties of the donor atom in these ligands. In all studies to date, the positively charged site, L^+, and the donor site, L, have been joined by a saturated carbon skeleton. A careful perusal of the existing literature suggested that L^+ apparently has little influence on the ligand properties of L. Whether or not this is expected is debatable.[2] Nonetheless, nothing was known at the outset of our investigation about the electronic effects of a cationic site on the donor properties of a Lewis base when the two sites are connected by an unsaturated carbon bridge. Preliminary communications of this work have appeared recently.[6,7]

RESULTS AND DISCUSSION

Physical data for the ligands and complexes prepared in this study are presented in the Table. The discussion that follows can be subdivided into three parts: the characterization of the ligands, the zwitterionic complexes containing the 'mixed' nitrogen–phosphorus cationic ligands, and the complexes containing the unsaturated organophosphorus cationic ligands.

The Cationic Ligands.—The ^1H and ^{31}P n.m.r. data for the cationic ligands is particularly significant as it convincingly establishes the site of protonation or quaternization. In the case of the reaction of $R_2NC_2H_4PPh_2$ with anhydrous $HX_{(g)}$, the amine site is selectively protonated in all three ligands. For example, the methyl resonance in the ^1H n.m.r. (Table) of $Me_2\overset{+}{N}(H)C_2H_4PPh_2X^-$ is split into a doublet due to coupling with the proton of the ammonium ion [$J(NH\text{-}CH_3) = 4{\cdot}5$—$5{\cdot}0$ Hz]. As expected the doublet collapses to a singlet upon addition of trace amounts of water because of rapid proton exchange. The ^{31}P n.m.r. spectrum (Table) of this same cationic ligand exhibits a single resonance at 21·3 p.p.m. (85% H_3PO_4 as external reference) as compared with a ^{31}P chemical shift of 20·5 p.p.m. in the non-protonated species. It is well known that protonation or quaternization of a tertiary phosphorus atom gives rise to chemical shifts downfield from phosphoric acid.[8]

Examination of the ^{31}P n.m.r. of the unsaturated organophosphorus cationic ligands indicates that in all cases only one of the tertiary phosphorus atoms is quaternized upon treatment with benzyl bromide. Two separate ^{31}P resonances are observed, one upfield near the resonance in the non-quaternized ligand and one downfield assigned to the quaternary phosphonium site.

Finally, it is possible to quaternize the phosphorus atom of $Me_2NC_2H_4PPh_2$ with benzyl bromide. Elemental analysis and the ^{31}P chemical shift (—31·8 p.p.m.) supports the formulation of this ligand as $[Me_2NC_2H_4\overset{+}{P}Ph_2CH_2Ph]Br^-$.

The Complexes $[CoX_3^-Ph_2PC_2H_4\overset{+}{N}(H)R_2]$ *and* $[CoBr_3^-Me_2NC_2H_4\overset{+}{P}Ph_2CH_2Ph]$, *where* X = Cl, Br, *or* I, *and* R = H, Me, *and* Et.—The reaction of cobalt(II) halides with $[Ph_2PC_2H_4\overset{+}{N}(H)R_2]X^-$ in ethanol leads to excellent yields of the expected cobalt-containing zwitterions. Surprisingly, these complexes where R = Me or Et, are also formed, albeit in yields <20%, by the reaction of the parent ligand with CoX_2 in refluxing ethanol. Apparently trace amounts of water present in the solvent causes slight hydrolysis of the metal halide generating HX which rapidly protonates the strongly basic amino-group. The use of absolute ethanol doped with a trace quantity of D_2O yields the analogous deuteriated complexes, $[CoX_3^-Ph_2PC_2H_4\overset{+}{N}(D)R_2]$. The broad $\overset{+}{N}\text{-}H$ stretching vibration at 2700 cm^{-1} in the i.r. spectrum of $[CoX_3^-Ph_2PC_2H_4\overset{+}{N}(H)R_2]$ disappears and is replaced by a strong absorption at 2100 cm^{-1} due to the $\overset{+}{N}\text{-}D$ stretch. This hydrolytic behaviour has also been noted in some analogous copper complexes.[9]

In the case of R = H, the zwitterionic complexes could be prepared only by the reaction of CoX_2 with $[Ph_2PC_2H_4\overset{+}{N}H_3]X^-$. Reaction of CoX_2 with the parent non-protonated ligand in refluxing ethanol yielded green

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[2] J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, 1970, **92**, 482.

[3] D. Berglund and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 2602.

[4] W. V. Dahlhoff, T. R. Dick, and S. M. Nelson, *J. Chem. Soc.* (*A*), 1969, 2919.

[5] C. Ercolani, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chim. Acta*, 1969, **3**, 421.

[6] R. C. Taylor and R. A. Kolodny, *Chem. Comm.*, 1970, 813.

[7] R. C. Taylor and R. A. Kolodny, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1063.

[8] 'Topics in Phosphorus Chemistry, ^{31}P Nuclear Magnetic Resonance,' M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. van Wazer, Interscience, New York, 1967, vol. 5.

[9] H. D. Caughman and R. C. Taylor, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 623.

Elemental analysis, various physical properties, and yield of the ligands and their cobalt(II) complexes

Compound	Colour	M.p. (b.p.)	Yield	Analyses [a]		N.m.r. Spectra ¹H Chemical shift							³¹P	
				C	H	Solvent	δ(NH)	δ(Me)	δ(Et)	δ(NCH₂)	δ(PCH₂)	δ(Ph)	Solvent	Chemical shift
$H_2NC_2H_4PPh_2$	Pale yellow	(217, 4 mmHg)	60	75·2 (73·4)	7·35 (7·05)	Neat	1·20s			2·75m [b]	2·15m [b]	7·29m	MeOH	2·33 [e]
$Me_2NC_2H_4PPh_2$	Pale yellow	(146—149, 0·08 mmHg)	65	75·1 (74·8)	7·8 (7·85)	Neat		2·10s		2·36m	2·36m	7·35m	MeOH	20·5
$Et_2NC_2H_4PPh$ [c]	Pale yellow	(140—143, 0·05 mmHg)	75	75·0 (75·8)	8·5 (8·4)	Neat			0·87t, 2·39q [d]	2·39m	2·39m	7·21m	MeOH	20·0
$[H_3\overset{+}{N}C_2H_4PPh_2]Cl^-$	White	95—98	70	62·9 (63·4)	6·55 (6·45)	TFA	3·80m			3·80m	3·80m	7·60m [k]	MeOH	12·5 [e]
$[H_3\overset{+}{N}C_2H_4PPh_2]Br^-$	Cream	100—113	50	55·1 (54·2)	5·5 (5·5)								MeOH	21·3
$[H_3\overset{+}{N}C_2H_4PPh_2]^-$	Cream	118—119	40	47·4 (47·1)	4·85 (4·8)									
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2]Cl^-$	White	100—103	70	64·9 (65·3)	7·15 (7·2)	CD_3NO_2		2·75d [f]		3·12m	2·60m	7·46m		
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2]Br^-$	Cream	121—122	60	56·1 (56·8)	6·3 (6·25)									
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2]I^-$	Cream	123—125	50	49·2 (49·9)	5·45 (5·5)									
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2]Cl^-$	White	105—108	80	66·6 (67·2)	7·8 (7·85)	CD_3CN			1·29t, 3·06q, 3·105q	3·08m	2·64m	7·46m	MeOH	20·6
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2]Br^-$	Cream	122—124	60	59·4 (59·0)	6·7 (6·85)	CD_3NO_2			1·29t, 3·20q [d]	3·16m	2·72m	7·48m		
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2]I^-$	Cream	130—132	40	52·6 (52·3)	6·2 (6·1)	CD_3CN			1·26t, 3·18q [d]	3·12m	2·68m	7·49m		
$[Ph_2PC_2H_4\overset{+}{P}Ph_2(CH_2Ph]Br^-$	White	240—242	70	70·1 (69·6)	5·6 (5·45)	TFA					3·31d, 4·48d [l]	6·84m, 7·18m 7·77m	TFA	−8·4 [g] −26·2 −27·5
$Ph_2PC_2H_4PPh_2$						$CDCl_3$					2·12t [h]	7·26m	$CDCl_3$	12·5
cis-$Ph_2PC_2H_2PPh_2$						$CDCl_3$					[i]	7·24m	$CDCl_3$	22·8
trans-$Ph_2PC_2H_2PPh_2$						$CDCl_3$					6·74t [j]	7·28m	$CDCl_3$	7·7
$Ph_2PC_2PPh_2$						$CDCl_3$						7·23m, 7·57m	$CDCl_3$	32·0
cis-$[Ph_2PC_2H_2\overset{+}{P}Ph_2(CH_2Ph)]Br^-$	White	218—219	70	69·5 (69·8)	5·35 (5·15)	$CDCl_3$					4·99d [m]	[n]	MeOH	−12·6 ($\overset{+}{P}$); 26·0 (P)
trans-$[Ph_2PC_2H_2\overset{+}{P}Ph_2(CH_2Ph)]Br^-$	White	208—210	80	69·1 (69·8)	5·4 (5·15)	$CDCl_3$					5·25d [m]	7·0—8·1m	MeOH	−17·5($\overset{+}{P}$); −0·3(p)
$[Ph_2PC_2\overset{+}{P}Ph_2(CH_2Ph)]Br^-$	White	203—206 dec.	60	71·2 (70·1)	5·0 (4·8)	$CDCl_3$					5·31d [l]	7·16m, 7·52m, 8·22m	MeOH	−10·2($\overset{+}{P}$); 32·2(P)
$Me_2NC_2H_4\overset{+}{P}Ph_2(CH_2Ph)]Br^-$	White	90—95 dec.	50	64·8 (64·5)	6·4 (6·35)	$CDCl_3$		2·37s		3·64s	5·09m	7·0— 8·18 [m]	MeOH	−31·8
						Electronic absorption spectra [p]								
$[H_3\overset{+}{N}C_2H_4PPh_2CoCl_3^-$	Blue	100—105 dec.	20	42·3 (42·5)	4·7 (4·35)	7490 (63); 15,100 (420); 16,470 (470)								
$[H_3\overset{+}{N}C_2H_4PPh_2CoBr_3^-]$	Turquoise	115—120 dec.	30	31·7 (31·8)	3·25 (3·25)	7770 (55); 14,660 (520); 15,980 (530)								
$[H_3\overset{+}{N}C_2H_4PPh_2CoI_3^-]$	Dark green	135—140 dec.	20	25·5 (25·1)	2·7 (2·55)	7490 (39); 14,310sh; 14,790 (500)								
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2CoCl_3^-]$	Royal blue	203—205 dec.	60; 10 [q]	45·6 (45·4)	4·9 (4·95)	7940 (49); 14,680 (460); 15,090 (430); 16,810 (420)								
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2CoBr_3^-]$	Turquoise	203—206 dec.	60; 15 [q]	34·6 (34·5)	3·95 (3·8)	7440 (39); 14,080 (540); 14,430 (520); 15,190 (550)								
$[Me_2\overset{+}{N}(H)C_2H_4PPh_2CoI_3^-]$	Greenish-black	>240 dec.	30; 10 [q]	26·9 (27·5)	2·9 (3·05)	6700 (36); 13,200sh; 13,590 (1240) [t]								
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2CoCl_3^-]$ [s]	Royal blue	210—212 dec.	40; 15 [q]	47·7 (47·9)	5·95 (5·6)	7690 (51); 14,760 (440); 15,150sh; 16,840 (440)								
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2CoBr_3^-]$ [u]	Turquoise	212—214 dec.	30; 10 [q]	37·0 (36·8)	4·2 (4·3)	7460 (43); 14,100 (320); 14,440 (540); 15,220 (530)								
$[Et_2\overset{+}{N}(H)C_2H_4PPh_2CoI_3^-]$ [v]	Greenish-black	216—220 dec.	20; 5 [q]	29·4 (29·8)	3·5 (3·45)	6780 (31); 12,880sh; 13,710 (1140) [t]								
$[Me_2NC_2H_4\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$	Blue-green	80—85 dec.	10	43·1 (42·6)	4·35 (4·2)	14,120 (600); 14,940 (680); 15,660sh								
$[Ph_2PC_2\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$	Blue-green	271—274 dec.	20	51·2 (50·5)	3·65 (3·45)	14,650 (430); 15,000 (430); 16,200 (300)								
[*cis*-$Ph_2PC_2H_2\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$	Blue-green	287—289 dec.	70	50·4 (50·4)	3·65 (3·7)	14,890 (440); 15,220 (440); 16,200 (310)								
[*trans*-$Ph_2PC_2H_2\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$	Blue-green	288—291 dec.	70	51·5 (50·4)	3·8 (3·7)	14,910 (460); 15,260 (440); 16,270 (340)								
$[Ph_2PC_2H_4\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$	Blue-green	>270 dec.	70	51·0 (05·4)	3·9 (3·95)	14,500 (590); 14,850 (540); 15,400 (410)								
$[Et_4\overset{+}{N}][CoBr_3^-Ph_2C_2PPh_2]$ [w]	Blue	221—223 dec.	30	50·3 (49·5)	5·25 (4·9)	14,560 (490); 14,950 (470); 16,150 (300)								
$[Et_4\overset{+}{N}][CoBr_3^-Ph_2PC_2H_4PPh_2]$ [w]	Blue-green	228—231 dec.	60	50·4 (49·5)	5·4 (5·35)	14,710 (480); 15,020 (520); 15,330 (400)								
$[Et_4\overset{+}{N}][CoBr_3^-$*trans*-$Ph_2PC_2H_2PPh_2]$ [w]	Turquoise	231—234 dec.	60	48·7 (49·5)	5·2 (5·1)	14,990 (530); 15,100 (590); 16,210 (390)								

[a] Calc. values in parentheses. [b] $J_{P-\alpha CH_2}$ 1·5—1·0 Hz, $J_{P-\beta CH_2}$ 6·0—6·5 Hz. [c] N, 4·8 (4·9); P, 10·8 (10·9). [d] $J_{CH_3-CH_2}$ 6·5—7·0 Hz. [e] Broad triplet with $J_{P-\beta CH_2}$ 6—7 Hz. [f] J_{NH-CH_2} 4·5 Hz. [g] The tertiary phosphorus atom in this compound is presumably protonated by trifluoroacetic acid (TFA). [h] Poorly defined triplet with J_{PCH_2} 4·0—5·0 Hz. [i] The vinyl resonance is partially obscured by the phenyl resonances. The high-field line of the expected vinyl triplet is at δ 7·04. $J_{PCH_2(Ph)}$ 15 Hz. [k] J_{NHCH_3} 4·5—5·0 Hz. [l] J_{PCH_2} 7·0 Hz, $J_{PCH_2(Ph)}$ 14 Hz. [m] J_{PCH_2} 15 Hz. [n] The phenyl region is complex with multiplets centred at δ 7·1, 7·5, 7·8, and a single resonace at δ 8·31, which latter is probably the low field line of the expected vinyl doublet. [p] In nitromethane, molar extinction coefficients in parentheses. [q] Yields refer to method of preparation, *i.e.*, Method 1; Method 2. [r] Br, 43·0 (43·0). [s] Cl, 23·0 (23·6). [t] In acetonitrile. [u] Br, 40·8 (41·0). [v] I, 52·8 (52·5). [w] 1:1 Electrolytes in nitromethane and acetonitrile.

cobalt complexes whose exact nature has not yet been determined. The anomalous behaviour of this ligand requires further study.

The elemental analyses and electronic spectral data presented in the Table support the zwitterionic formulation of the complexes. The co-ordination polyhedron around the Co^{II} ion comprises three halide ions and the phosphorus atom of the cationic ligand.

Magnetic Properties.—The room temperature magnetic moments, ranging from *ca.* 4·6 for the chlorides to *ca.* 4·8 for the iodides, are typical of d^7 Co^{II} in a tetrahedral or pseudotetrahedral (C_{3v}) ligand field.[10] The small but significant increase in the moments in the series $Cl < Br < I$ reflects the increased contribution to the moment due to spin–orbit coupling.

Electronic Absorption Spectra.—The *d–d* electronic spectral data is presented in the Table and provides the most important information about the nature of these complexes. Although the data presented in the Table is taken exclusively from solution studies, the transmittance spectra obtained in the solid state in Nujol mulls supported on filter paper are virtually superposable with the spectra in either nitromethane or acetonitrile. It was noted, however, that upon allowing the solutions to stand for periods in excess of one week, apparent replacement of the cationic ligand occurs. The solvation equilibrium (1) has been observed in

$$[MX_3^-(L\text{-}L^+)] + \text{Solvent} \rightleftharpoons [MX_3^-(\text{Solvent})] + L\text{-}L^+ \quad (1)$$

similar systems.[5,11] The slowness with which this equilibrium is established may be due to the difficulty in displacing the positively charged ligand from the anionic CoX_3^- moiety. The electronic spectrum of the solvated species is almost identical with those species formed by the nitromethane or acetonitrile solvation of CoX_4.[2,12] The solvation equilibrium also explains the slight increase in conductivity of ' aged ' nitromethane or acetonitrile solutions of $[CoX_3^-Ph_2PC_2H_4\overset{+}{N}(H)R_2]$.

Simple ligand field considerations for a d^7 ion in a tetrahedral field indicate three *d–d* transitions are expected; ${}^4T_2(F) \longleftarrow {}^4A_2(F)$, ${}^4T_1(F) \longleftarrow {}^4A_2(F)$, and ${}^4T_1(P) \longleftarrow {}^4A_2(F)$. The symmetry of these zwitterions, however, is at most C_{3v} which should further split the orbitally degenerate excited states. Although Garrett *et al.*[13] have presented a detailed analysis of the trigonal field splittings of the quartet terms of the d^7 configuration in C_{3v} symmetry, the data in the present study is insufficient to permit accurate band assignments in the reduced symmetry. Thus, the two main regions of absorption that are observed in the present study have been assigned to the latter two transitions (hereafter called ν_2 and ν_3 respectively) under T_d symmetry. The ν_3 transition is a multicomponent absorption probably arising as a result of both spin–orbit coupling and the trigonal potential.

There are two important features worth pointing out concerning the electronic spectra of these complexes. (1) The absorption maxima for both ν_2 and ν_3 shift toward lower energies as X changes from Cl to I. This is expected based on the relative positions of the halides in the spectrochemical series. (2) The most significant result is the apparent lack of influence of the positive site on the ligand properties of the donor atom. This observation has been pointed out in other zwitterionic complexes [2–5] and appears to be quite general for all such systems in which the donor atom, L, and the cationic change, L^+, are separated by a saturated organic skeleton.

In concluding this section, comparison of the ν_3 transitions in $[CoBr_3^-Ph_2PC_2H_4\overset{+}{N}(H)Me_2]$ and $[CoBr_3^-Me_2NC_2H_4\overset{+}{P}Ph_2CH_2Ph]$, which contain the Br_3P and Br_3N chromophores, respectively, indicates the tertiary amine produces a larger ligand field splitting than the tertiary phosphine. Because the Co^{II} ion is essentially a σ-acceptor, this result is expected.

The Complexes $[CoBr_3^-P\text{-}\overset{+}{P}]$ *and* $[Et_4\overset{+}{N}][CoBr_3P\text{-}P]^-$ (*where* P–P *represents* cis- *or* trans-1,2-*bis*(*diphenylphosphino*)*ethylene and bis*(*diphenylphosphino*)*acetylene, and* $P\text{-}\overset{+}{P}$ *represents the monobenzylated derivatives of* P–P).—A careful examination of the literature prior to this study revealed a complete lack of any information concerning possible charge effects transmitted from L^+ to L *via* an unsaturated organic bridge in inorganic zwitterionic systems. An investigation of such a system might prove worthwhile. *cis*- and *trans*-1,2-Bis(diphenylphosphino)ethylene and bis(diphenylphosphino)acetylene appeared ideally suited for such a study because of their commercial availability, the ease with which they form monoquaternized salts, and the direct comparison which would be possible with the other zwitterionic systems prepared in this study and others. The presence of the unsaturated organic bridge, either the ethylenic or acetylenic group, should provide a pathway for the easy transmittance of electronic effects from L^+ to L. In disubstituted acetylenes, the ν(C≡C) stretching frequency appears in the range 2260—2190 cm^{-1}.[14] The value for ν(C≡C) in bis(diphenylphosphino)-acetylene is 2097 cm^{-1},[15] well below this range. It seems likely that this low stretching frequency is caused, at least in part, by a drift of bonding π-electron density from the carbon–carbon triple bond into the empty $d\pi$-acceptor orbitals on the phosphorus atoms. The linearity of the PCCP group greatly facilitates this process. Support for this interpretation comes from an examination of the P–C bond length in $P(C{\equiv}CPh)_3$ (1·76 Å), which is considerably shorter than the P–C

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[10] B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 37.

[11] L. Sestilli, C. Furlani, and G. Festuccia, *Inorg. Chim. Acta*, 1970, **4**, 542.

[12] S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 1961, 5105.

[13] B. B. Garrett, V. L. Goedken, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1970, **92**, 489.

[14] K. Nakanishi, ' Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, California, 1969, p. 28.

[15] A. J. Carty and A. Efraty, *Inorg. Chem.*, 1969, **8**, 543.

bond length in $\mathrm{PMe_3}$ (1·85 Å).[16] Therefore, changes in the electronic nature of one of the phosphorus atoms (by quaternization or protonation) in this ligand should influence the π-acceptor properties of the other phosphorus atom. This change in π-acceptor properties could also influence the σ-donor ability *via* a synergic interaction. This situation would be necessary in the present study because of the nature of the cobalt(II) ion, *i.e.*, it acts essentially as a σ-acceptor. Similar arguments may be extended to the other two unsaturated organophosphorus ligands.

Accordingly, a series of zwitterionic complexes of the type $[\mathrm{CoBr_3^-P{-}\overset{+}{P}}]$ were synthesized. In order to be certain that any observed electronic effect could be attributed to the cationic site alone, it was also necessary to prepare a second series of complexes of stoicheiometry $\mathrm{M^+[CoBr_3(P{-}P)]^-}$, where $\mathrm{M^+}$ is any convenient cation such as $\mathrm{Et_4\overset{+}{N}}$ and P–P is any one of the above ligands (non-quaternized) acting in a monodentate fashion.* Hopefully, the electronic spectra of analogous complexes in these two series would be sufficiently different to permit definitive statements about the effect of $\mathrm{L^+}$ on L.

It was anticipated that a comparison of the ligand field spectra (ν_3 transition in strict T_d symmetry) for analogous complexes in the two series would reveal differences which could be directly related to the electronic influence of the cationic site on the donor properties of the tertiary phosphorus atom. Surprisingly, the electronic spectra for analogous complexes, *e.g.* $[\mathrm{CoBr_3^-Ph_2PC{\equiv}C\overset{+}{P}Ph_2CH_2Ph}]$ and $[\mathrm{Et_4N}]^+[\mathrm{CoBr_3Ph_2PC{\equiv}CPPh_2}]^-$, are virtually superposable. The negligible influence of the cationic site is also reflected in a comparison of the ν(C≡C) stretching frequencies in these same two complexes, $\Delta\nu = 6\ \mathrm{cm^{-1}}$.[7] Although the unsaturated organophosphorus ligands do produce a somewhat larger ligand field, *e.g.* compare $[\mathrm{CoBr_3^-Ph_2PC_2H_4\overset{+}{P}Ph_2CH_2Ph}]$ and $[\mathrm{CoBr_3^-Ph_2PC_2H_4\overset{+}{N}(H)R_2}]$ with $[\mathrm{CoBr_3^-Ph_2PC{\equiv}C\overset{+}{P}Ph_2CH_2Ph}]$, this is probably because of the influence of the unsaturated organic bridge which increases the basicity and hence the ligand field strength of the tertiary phosphine.

Apparently the particular zwitterionic system and the physical methods chosen are too insensitive to allow any definitive conclusions to be made. Further work is continuing on some octahedral complexes where the effect may be more pronounced and consequently more amenable to study.[17]

EXPERIMENTAL

All manipulations involving the preparation, quaternization, and protonation of the ligands were performed under a dry nitrogen atmosphere. The cobalt complexes were sufficiently stable in solution and in the solid state to be handled in air (except where noted). Triphenylphosphine (Eastern), anhydrous cobalt(II) halides (Research Organic/Inorganic Chemical), bis(1,2-diphenylphosphino)-ethane (Arapahoe), *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene (Pressure Chemical), bis(diphenylphosphino)-acetylene (Strem), the amine chloride hydrochlorides (Aldrich), and ethyleneimine (Dow) were commercial products. The free amine chlorides were prepared from their hydrochlorides by the procedure outlined by the Michigan Chemical Corp.[18] All solvents were spectral grade and used without further purification (except where noted). Solution and solid state electronic transmittance spectra of the complexes were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained in dichloromethane, nitromethane, or acetonitrile using a set of matched 1 cm quartz cells. Solid state spectra were obtained as Nujol mulls supported on filter paper according to the technique of Lee, Griswold, and Kleinberg.[19] The ^{1}H n.m.r. spectra of the ligands were obtained at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane as internal reference. The ^{31}P spectra were obtained at 40·5 MHz on the same instrument operating in the HR mode. Phosphoric acid (85%) was used as the external reference. Conductivity measurements were performed at room temperature with an Industrial Instruments RC-16-B2 conductivity bridge using a cell with cell constant $k = 0{\cdot}1792\ \mathrm{cm^{-1}}$. Measurements were made on 10^{-3}—10^{-4}M solutions of the complexes in nitromethane and acetonitrile. Both solvents were carefully dried over pre-dried (300 °C) 4 Å molecular sieves. The conductivity data was treated according to the method reported by Feltham and Hayter.[20] All the cobalt complexes prepared in this study (with the exception of the tetraethylammonium salts) are weak electrolytes in both solvents (see Discussion). The tetraethylammonium salts had conductivities in both solvents corresponding to 1 : 1 electrolytes. Magnetic susceptibility measurements were carried out at room temperature with a magnetic susceptibility balance of the Faraday type. I.r. spectra of Nujol mulls of KBr pellets were recorded on a Perkin-Elmer 621 Grating spectrometer calibrated with polystyrene. Microanalyses were determined by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.; Pascher Mickroanalytisches Laboratorium, Bonn, Germany; and by Mr. M. Kshatriya of this Department. The latter analyses were run on a Perkin-Elmer 240 C, H, and N Analyser.

Preparation of the Ligands.—Although the preparation of the 'mixed' nitrogen-phosphorus ligands have been reported elsewhere,[21,22] *i.e.*, the reaction of appropriate 2-halogenoethyldialkylamines with diphenylphosphorus Grignard reagent,[23] a more convenient method, based on the work of Issleib and Rieschel,[24] is reported here.

(2-Dialkylaminoethyl)diphenylphosphine, $\mathrm{R_2NC_2H_4PPh_2}$,

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* In the case of the tetraethylammonium salt of $[\mathrm{CoBr_3P{-}P}]^-$, the desired complex containing *cis*-1,2-bis(diphenylphosphino)-ethylene could not be isolated, presumably because of the strong tendency for chelation.

[16] V. D. Mootz and G. Sasmannshausen, *Z. anorg. Chem.*, 1967, **355**, 200.

[17] R. L. Keiter, L. Cary, and R. C. Taylor, unpublished results.

[18] Technical Bulletin CBR 1410 (1964), Michigan Chem. Corp., Chicago.

[19] R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 1278.

[20] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

[21] G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, 1967, **6**, 1929.

[22] R. C. Taylor, G. R. Dobson, and R. A. Kolodny, *Inorg. Chem.*, 1968, **7**, 1886.

[23] A. Job and G. Dussolier, *Compt. rend.*, 1927, **184**, 1454.

[24] K. Issleib and R. Rieschel, *Chem. Ber.*, 1965, **98**, 2086.

where R = Me *or* Et. A 3 l, three-neck round bottom flask equipped with a nitrogen bleed, water cooled reflux condenser, mechanical stirrer, and pressure equalizing dropping funnel was charged with triphenylphosphine (131 g, 0·5 mol), lithium metal chips (6·9 g, 1·0 mol), and tetrahydrofuran (900 ml). The mixture was stirred overnight or until all the lithium was gone. Tertiary butyl chloride (47 g, 0·5 mol) was added dropwise over 1 h to the deep blood-red solution in order to destroy the phenyllithium produced in the reaction. After refluxing for 1 h, freshly distilled 2-chloroethyldialkylamine, $R_2NC_2H_4Cl$ (R = Me or Et) (0·5 mol), in anhydrous ether (100 ml) was added dropwise during 2 h. The resultant milky solution was refluxed an additional hour, cooled, and carefully hydrolysed with saturated aqueous ammonium chloride solution (500 ml). The organic layer was separated and dried over anhydrous potassium carbonate. After removal of most of the solvent by rotary evaporation, the oily residue was fractionally distilled yielding 65—70% of the ligand as a pale straw coloured oil.

(2-*Aminoethyl*)*diphenylphosphine*, $H_2NC_2H_4PPh_2$. The preparation of this ligand has been described previously by Issleib and Haferburg.[25] The following modification was used. The apparatus described above was charged with triphenylphosphine (262 g, 1·0 mol), metallic lithium chips (13·9 g, 2·0 mol), and tetrahydrofuran (900 ml). After stirring overnight, t-butyl chloride (92 g, 1·0 mol) was added dropwise during 1 h. The resultant solution was refluxed for 1 h before adding ethylenimine (43 g, 1·0 mol). After complete addition, the reflux was continued for 2 h. The milky solution was allowed to cool and then hydrolysed with deaerated water (400 ml). The organic layer was separated and dried over anhydrous potassium carbonate. After removal of solvent by rotary evaporation, the residue was fractionally distilled yielding 141 g (61%) of the desired product as a light yellow oil.

Preparation of Cationic Ligands.—The ammonium halide salts of all three ' mixed ' ligands were prepared by the same method, *i.e.* dissolution of the ' mixed ' ligand in ether followed by passage of anhydrous HX gas through the solution. Immediate precipitation of the ammonium salt occurred in all cases. In general, the ammonium salts are quite hygroscopic and must be handled in a dry atmosphere. They can be stored conveniently in a vacuum desiccator (calcium chloride as desiccant). Prepared in this manner were 2-*diphenylphosphinoethylammonium halide*, (2-*diphenylphosphinoethyl*)*dimethylammonium halide*, and (2-*diphenylphosphinoethyl*)*diethylammonium halide*.

(2-*Dimethylaminoethyl*)*benzyldiphenylphosphonium Bromide*.—Benzyl bromide (1·0 g, 5·8 mmol) in anhydrous ether (10 ml) was mixed with (2-dimethylaminoethyl)diphenylphosphine (1·5 g, 5·8 mmol) in ether (25 ml). The flask was stoppered and allowed to stand at room temperature for 6 h. The white hygroscopic solid which precipitated, was filtered off, washed with cold ether, and dried *in vacuo*. The salt was stored in a vacuum desiccator ($CaCl_2$ desiccant).

cis- *and* trans-(2-*Diphenylphosphinoethenyl*)*benzyldiphenylphosphonium Bromide*.—To *cis*- or *trans*-$Ph_2PCH = CHPPh_2$ 1·0 g, 0·5 mmol) dissolved in acetone–ethanol (1 : 1, 50 ml), was added a solution containing benzyl bromide (1·0 g, 0·58 mmol) in acetone (10 ml). After standing at room temperature for several days, the white crystalline product precipitated. The salt was filtered, washed with cold ether, and dried *in vacuo*. Additional product was obtained by cooling the filtrate to −10 °C. Yields were of the order of 75%.

(2-*Diphenylphosphinoethyl*)*benzyldiphenylphosphonium Bromide*.—This salt was prepared by the procedure reported by Quagliano *et al.*[5]

(2-*Diphenylphosphinoethynyl*)*benzyldiphenylphosphonium Bromide*.—Bis(diphenylphosphino)ethynylene (2·0 g, 0·5 mmol) dissolved in acetone–ether (1 : 1, 50 ml) was added to a solution of benzyl bromide (2·0 g, 1·16 mmol) in acetone (20 ml). The solution was refluxed for ½ h, cooled, and the volume of solvent reduced to 15 ml. Crystallization of the salt occurred upon storing overnight at −10 °C. The product was filtered off, washed with cold ether, and dried *in vacuo*.

Preparation of the Cobaltous Complexes, Method 1.—(*a*) $[H_3\overset{+}{N}C_2H_4PPh_2CoCl_3^-]$ *and* $[H_3\overset{+}{N}C_2H_4PPh_2CoBr_3^-]$. A hot ethanolic solution solution (25 ml) containing the appropriate 2-diphenylphosphinoethylammonium halide (2 mmol) was added to a solution containing the corresponding anhydrous cobalt(II) halide (2 mmol) dissolved in hot ethanol (25 ml). After a short reflux (10 min), the solution was filtered hot. Crystallization occurred upon cooling in an ice-bath. The complexes were recrystallized from hot ethanol and dried *in vacuo*. Both complexes are hygroscopic and must be stored in a desiccator ($CaCl_2$ desiccant).

(*b*) $[H_3\overset{+}{N}C_2H_4PPh_2CoI_3^-]$. A hot n-butanol solution (15 ml) of 2-diphenylphosphinoethylammonium iodide (2 mmol) was added to anhydrous cobalt(II) iodide (2 mmol) in hot n-butanol (25 ml). Dark green crystals of the complex separated upon cooling in an ice-bath. Attempts to recrystallize the complex from a variety of solvents were unsuccessful.

(*c*) $[Me_2\overset{+}{N}(H)C_2H_4PPh_2CoX_3^-]$ *where* X = Cl *or* Br. A hot ethanolic solution (50 ml) containing the appropriate 2-diphenylphosphinoethyldimethylammonium halide (2 mmol) was added to the corresponding anhydrous cobalt(II) halide (2 mmol) dissolved in ethanol (25 ml). After a short reflux (15 min), the solution was filtered hot. The product which precipitated upon cooling, was filtered and washed with a small portion of cold ethanol. The complexes were recrystallized from hot ethanol and dried *in vacuo*.

The iodo-complex, $[Me_2\overset{+}{N}(H)C_2H_4PPh_2CoI_3^-]$, was prepared in an analogous fashion using n-butanol as the reaction and recrystallization solvent.

The corresponding zwitterionic cobalt complexes of 2-diphenylphosphinoethyldiethylammonium halides were prepared by the same method outlined above.

Method 2.—The zwitterionic cobalt complexes containing either $Me_2\overset{+}{N}(H)C_2H_4PPh_2$ or $Et_2\overset{+}{N}C_2H_4PPh_2$ were also prepared by the following procedure. A hot ethanolic solution (25 ml) of $Me_2NC_2H_4PPh_2$ or $Et_2NC_2H_4PPh_2$ (2 mmol) was added to a solution containing the appropriate cobalt(II) halide (2 mmol) in hot ethanol (25 ml). After refluxing for 30 min, the solution was filtered hot and allowed to cool. The crystalline product was filtered off, washed with cold ethanol, and recrystallized from hot ethanol. The corresponding iodides were prepared in n-butanol. Yields were generally much lower for this method.

(*d*) $[Me_2NC_2H_4\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-]$. To a solution containing $[Me_2NC_2H_4\overset{+}{P}Ph_2(CH_2Ph)]Br^-$ (2 mmol) in boiling

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[25] I. Issleib and D. Haferburg, *Z. Naturforsch.*, 1965, **20b**, 916.

ethanol (50 ml) was added a solution containing anhydrous cobalt(II) bromide (2 mmol) in hot ethanol (25 ml). Precipitation of the product occurred while the solution was still hot. Cooling yielded an additional crop of crystals which were collected, washed with cold ethanol, and dried *in vacuo*. The complex is extremely hygroscopic.

(*e*) $[\mathrm{Ph_2PC{\equiv}C\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-}]$. Cobalt(II) bromide (1 mmol) was dissolved in hot ethanol (25 ml) and added to a solution containing $[\mathrm{Ph_2PC{\equiv}C\overset{+}{P}Ph_2(CH_2Ph)}]\mathrm{Br^-}$ (1 mmol) dissolved in hot ethanol–acetone (1 : 1, 25 ml). Upon cooling, the complex precipitated as royal blue crystalline plates. After filtering and washing with cold ethanol, the product was dried *in vacuo*.

(*f*) $[\mathrm{Ph_2PC_2H_4\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-}]$ was prepared by the procedure of Quagliano *et al.*[5]

(*g*) [cis- *or* trans-$\mathrm{Ph_2PCH{=}CH\overset{+}{P}Ph_2(CH_2Ph)CoBr_3^-}$]. To the *cis*- or *trans*-isomer of the cationic ligand (2 mmol) in acetone–ethanol (1 : 1, 50 ml) was added anhydrous cobalt(II) bromide (2 mmol) in hot ethanol (35 ml). After heating for 10 min, the solution was filtered hot and then cooled to −10 °C. After several hours, crystals of the desired product precipitated. The complex was recrystallized from acetone–ethanol (1 : 1).

(*h*) $[\mathrm{Et_4\overset{+}{N}}][\mathrm{CoBr_3^-Ph_2PC{\equiv}PPh_2}]$. Anhydrous cobalt(II) bromide (1 mmol) dissolved in hot ethanol (35 ml) was added with stirring to an equimolar mixture (1 mmol) of tetraethylammonium bromide and bis(1,2-diphenylphosphino)acetylene in acetone–ethanol (1 : 1, 50 ml). After heating for 5 min at reflux temperature, the solution was filtered hot. Crystals of the desired product were deposited upon cooling. The complex was washed with cold acetone and dried *in vacuo*. $[\mathrm{Et_4\overset{+}{N}}][\mathrm{CoBr_3^-}$*trans*-$\mathrm{Ph_2PCH{=}CHPPh_2}]$ was prepared in an analogous manner.

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