Qualitative Study. Nagakura[5] noticed that the decomposition of solutions in heptane happens quickly, except at very low concentrations. In benzene and dioxane, solutions seem more stable up to concentrations of the order of 10^{-3} M, but in both cases, as well as in more polar solvents (ethyl ether), a precipitate appears at sufficiently high concentrations. When there is a large excess of amine, white crystals appear, and, in the case of an excess of iodine, a brown oily precipitate is formed. The analysis of the latter seems difficult, but the white crystals have been identified as triethylamine hydroiodide ($Et_3N \cdot HI$). The compound is very soluble in water and a titration of I^- ions and total iodine gave 53 and 54 wt %. Theoretically, $Et_3N \cdot HI$ contains 55.4% iodide. Besides, a synthetic salt has the same point of decomposition when heated and the dielectric properties of solutions of these two compounds in chloroform are the same (see below).

The solubility of pure triethylamine hydroiodide in heptane and cyclohexane was found to be very low. Benzene and dioxane can dissolve more than 10^{-3} mole/l.; this is sufficient to greatly affect the dielectric measurements.

A study on a WTW Type DM.01 dipolemeter showed that the permittivity of dilute solutions in heptane and cyclohexane is stable during few minutes; afterward, it decreases when precipitation occurs. In the case of dioxane, the permittivity increases during a first stage, which can be short at high concentration, and decreases when the precipitation begins.

Qualitatively, we can conclude that a complex between Et_3N and I_2 is formed instantaneously after mixing and is slowly decomposed to give $Et_3N \cdot HI$ among the products of this decomposition. Solutions in dioxane seem more stable because of the solubility of these compounds. It is not impossible that, in the solution, $Et_3N \cdot HI$ gives complexes as $Et_3N \cdot HI_3$

Dipole Moment of Triethylamine Hydroiodide. Measurements on solutions of $Et_3N \cdot HI$ in dioxane (*ca* 10^{-3} M) gave $\mu = 10.6$ D, but the low solubility makes the accuracy of the measurements rather bad. Runs carried out on solutions in chloroform using Onsager's relation, extended to mixtures of polar substances,[6] gave $\mu = 11.6$ D. In these experiments, concentrations up to about 15×10^{-3} M could be studied without any trouble from the conductivity, but this result can hardly be compared with the former because of an eventual solvation of $Et_3N \cdot HI$ which may introduce a slight difference on the value of μ. The same value of μ is obtained using the white precipitate mentioned above instead of synthetic hydroiodide.

Dipole Moment of Triethylamine–Iodine Complex. Dielectric measurements are in good agreement with the formation of a 1:1 complex, but the study is only possible with an excess of amine and in very dilute solutions. We worked on solutions ranging from 10 to 20×10^{-3} M at room temperature. Under these conditions, solutions in cyclohexane or heptane are stable for a few minutes. The measurement of dipole moment requires knowledge of the equilibrium constant K of the reaction

$$Et_3N + I_2 \rightleftharpoons Et_3N \cdot I_2$$

The determination of K is possible but not accurate because of the rather restrictive operating conditions. We obtained in cyclohexane at 25° $K = 2.5 \pm 2 \times 10^3$ l./mole and in heptane at 19.5° $K = 3 \pm 2 \times 10^3$ l./mole. The values are comparable with 6.32×10^3 and 4.69×10^3 l./mole obtained in heptane at 20 and 25° by Nagakura.[5] Using the values of K given by Nagakura, we obtained for the dipole moment of the complex the values given in Table I.

Table I

	μ, D			
	Run 1	Run 2	Run 3	Run 4
In heptane at 19.5°	5.6	5.5	5.5	5.7
In cyclohexane at 25°	5.0	5.9	5.9	
In dioxane (lit. values)	11.3[3]		12.4[1]	

These results are in good agreement with the dipole moments of complexes formed between iodine and amines given by Kortüm[4] and Kobinata.[2] The large values found by Toyoda[1] and Tsubomura[3] cannot be attributed to an ionic structure of complex but rather to the presence of $Et_3N \cdot HI$ formed by a secondary reaction.

Pierre Boule
Laboratoire de Chimie Théorique
Université de Nancy, Nancy, France
Received November 29, 1967

---

[5] S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

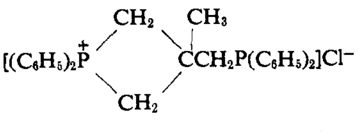
[6] J. Barriol and A. Weisbecker, *J. Chim. Phys.*, 623 (1965).

Coordination by a Positively Charged Phosphorus Ligand[1]

Sir:

In marked contrast to the extensive number of investigations with neutral and negatively charged ligands, relatively little work has been reported with positively charged ligands. In fact, the only concerted effort in this area has been undertaken recently by Quagliano, *et al.*,[2–6] in which they investigated the coordination properties of a few diamine ligands where one of the nitrogen atoms was either protonated or alkylated. However, there has been no systematic investigation on the coordination properties of a compound that possesses a quaternary phosphorus or arsenic atom.

This paper reports the preparation and characterization of 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphitanium chloride



$$[(C_6H_5)_2\overset{+}{P}(CH_2)_2C(CH_3)CH_2P(C_6H_5)_2]Cl^-$$

and some pseudo-tetrahedral cobalt(II) complexes in

---

[1] The authors thank the National Science Foundation for financial support of this research (Grant No. GP-5729).

[2] J. V. Quagliano, S. Kida, and J. Fujita, *J. Am. Chem. Soc.*, **84**, 724 (1962).

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

[6] 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.

which the phosphitanium cation[7] coordinates *via* the nonquaternary diphenylphosphino group.

The positive phosphorus ligand was prepared by treating a solution of sodium diphenylphosphide, NaP$(C_6H_5)_2$ (0.22 mole), with 0.1 mole of 2-chloromethyl-2-methyl-1,3-dichloropropane, $CH_3C(CH_2Cl)_3$, in liquid ammonia for 2 hr before evaporating the solvent; subsequently, 300 ml of tetrahydrofuran was added and the reaction mixture was refluxed for 14 hr before hydrolyzing with aqueous ammonium chloride. The organic layer was separated and dried over sodium sulfate for 12 hr. The solvent and all volatile products were removed by vacuum distillation (<1 mm at 170°), leaving a gummy material. Extraction of the gum with absolute ethanol and recrystallization from ethanol–acetone yielded white crystals, mp 268–272°.

Anal. Calcd for $C_{29}H_{29}ClP_2$: C, 73.26; H, 6.11; Cl, 7.47; P, 13.05. Found: C, 73.17; H, 6.32; Cl, 7.39; P, 12.68.

To demonstrate the coordination properties of the phosphorus cation, the pseudo-tetrahedral cobalt halide complexes $[Co(P{-}P^+)Cl_3]$, $[Co(P{-}P^+)Br_2Cl \cdot CH_3NO_2]$, and $[Co(P{-}P^+)I_3]$ were isolated. For example, 0.5 mmole of the phosphitanium chloride was treated with 0.5 mmole of cobalt bromide, $CoBr_2 \cdot 6H_2O$, in 5 ml of warm ethanol. The deep blue material was recrystallized from nitromethane; the resulting blue crystals contained a nitromethane molecule.

Anal. Calcd for $C_{30}H_{32}Br_2ClCoNO_2P_2$: C, 47.68; H, 4.24; Br, 21.19; Cl, 4.70; P, 8.21; N, 1.85. Found: C, 47.62; H, 4.43; Br, 21.85; Cl, 4.96; P, 8.22; N, 1.77.

Identification of the phosphitanium cation, $[C_{29}H_{29}P_2]^+$, was obtained from infrared and nmr spectra and by the observations that the compound is a univalent electrolyte in nitromethane, readily precipitates AgCl when treated with silver nitrate, and immediately exchanges the chloride for other anions. This positively charged phosphorus ligand forms a series of complexes with the general formula $[M(P{-}P^+)X_3]$ (where M = Co, Ni, Pd, Au; X = Cl, Br, I).[8] Generally, the crystalline $[M(P{-}P^+)X_3]$ complexes are not affected by atmospheric moisture, in constrast to the sensitivity of the cationic amine ligands.[2–5]

The $[Co(P{-}P^+)X_3]$ complexes are similar to the pseudo-tetrahedral $[Co(PPh_3)X_3]^-$ anions in terms of the coordinating atoms.[9,10] However, the $P{-}P^+$ complexes are essentially nonelectrolytes because the phosphitanium ligand simultaneously incorporates the cation. The presence of both the anionic and cationic units in a molecular complex has a formal analogy to an inorganic zwitterion system.

The multiple-peak electronic transitions (Table I) at ~7000 and ~15,000 cm^{-1} are assigned to the ν_2 and ν_3 bands for tetrahedral Co(II) complexes.[10] The trend in the magnetic moment values (Table I) is consistent with an increasing orbital contribution to the "spin-only" value as the ligand field strength of the halides decreases.[9,10] By comparing the spectral and magnetic data (Table I) of the $[Co(P{-}P^+)X_3]$ complexes with those reported by Cotton, *et al.*,[9,10] for the tetrahedral $[CoX_4]^{2-}$ and $[Co(PPh_3)X_3]^-$ series, it is apparent that the $[Co(P{-}P^+)X_3]$ complexes are pseudo-tetrahedral and that the coordination tendency of the diphenylphosphino group is not affected adversely by the presence of the quaternary phosphorus atom.

Table I. Electronic Spectral[a] and Magnetic Data for the Cobalt(II) Complexes

Complex	E_{max}, cm^{-1} (ϵ)[b]	μ_{eff}, BM
$Co(P{-}P^+)Cl_3$[c]	7,940 (45)	4.60
	14,570 (421)	
	15,160 (423)	
	16,820 (418)	
$Co(P{-}P^+)Br_2Cl \cdot CH_3NO_2$[d]	6,170 (42)	4.61
	7,460 (36)	
	14,500 (574)	
	14,800 sh[e] (555)	
	15,800 (399)	
	16,100 sh[e] (365)	
$Co(P{-}P^+)I_3$	6,850 (28)	4.75
	13,500 (698)	
	13,950 (802)	
	14,400 (674)	

[a] Electronic spectra were obtained on nitromethane solutions. [b] ϵ, molar extinction coefficient at the band maximum. [c] $P{-}P^+$, ligand abbreviation for $C_{29}H_{29}P_2^+$. [d] A nitromethane solvate was obtained when the bromide complex was recrystallized from nitromethane. [e] sh, definite shoulder on a more intense absorption; ϵ is estimated from the observed absorbance value.

Donna Berglund, Devon W. Meek
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received October 25, 1967

---

[7] The naming of the phosphorus cation is based on the *Chemical Abstracts* system in which the compound is classified as a phosphorus heterocycle.

[8] A more detailed comparison of the different complexes will be reported elsewhere.

[9] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

[10] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *ibid.*, **83**, 4690 (1961).

Five-Coordinate Zinc(II) in [Zn(tren)(NCS)](SCN)

Sir:

We have recently[1] reported the crystal structure of [Cu(tren)(NCS)](SCN),[2] in which the copper(II) ion was found to be five-coordinate, and we have suggested[3,4] that the corresponding zinc compound is probably also five-coordinate. We now wish to report that the zinc compound is indeed five-coordinate.

[Zn(tren)(NCS)](SCN) was prepared from aqueous solution by the method of Barclay and Barnard[5] and recrystallized from water. *Anal.* Calcd for Zn(tren)$(NCS)_2$: Zn, 19.95; NCS, 35.4. Found: Zn, 19.92; NCS, 35.6.

A solution of [Zn(tren)(NCS)](SCN) in methanol gave a molar conductivity of 96 cm^2 ohm^{-1} mole^{-1} at 22°, while $[(n\text{-}C_4H_9)_4N]Br$ under the same conditions gave 88 cm^2 ohm^{-1} mole^{-1}. Therefore, the Zn(tren)$(NCS)_2$ behaves in methanol as a uni-univalent electrolyte. The infrared spectrum shows bands at 2080 and 2048 cm^{-1} and at 800 and 743 cm^{-1}, which suggest the presence of one N-bonded NCS ion and one nonbonded (or S-bonded) NCS ion, as in the copper[6] and cobalt[4] compounds.

---

[1] P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, **89**, 724 (1967).

[2] tren = $N(CH_2CH_2NH_2)_3$.

[3] P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

[4] M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).

[5] G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 2540 (1958).

[6] K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).