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.

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Received October 25, 1967

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(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.

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(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).

Three-dimensional X-ray diffraction data were collected using a Picker automated diffractometer with Mo Kα radiation. The cell has dimensions $a = 12.886$, $b = 16.462$, $c = 13.643$ Å and contains eight molecules. The systematic absence of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd indicates the space group Pbca. The positions of the zinc atoms were determined from a sharpened Patterson synthesis, and the other atoms were found in a series of Fourier syntheses. The structure has been refined by full-matrix least squares to a value of $R = 0.09$. The refinement is being continued and the final results will be published later.

Although the crystals are not isomorphous with the copper compound ($a = 9.158$, $b = 14.000$, $c = 11.285$ Å, $z = 4$, space group $P2_12_12_1$), the compounds are chemically isostructural. The zinc ion is surrounded by five nitrogen atoms from the tren molecule and one thiocyanate ion, in a slightly distorted trigonal bipyramid, with the tertiary nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), at the apices, and the three primary nitrogen atoms, N(2), N(3), N(4), in the equatorial positions. Bond lengths and angles in the coordination polyhedron are given in Table I.

Table I. Bond Lengths (Å) and Angles (Degrees)

Zn-N(1)	2.27	N(1)-Zn-N(2)	81
Zn-N(2)	2.07	N(1)-Zn-N(3)	81
Zn-N(3)	2.06	N(1)-Zn-N(4)	81
Zn-N(4)	2.07	N(5)-Zn-N(2)	96
Zn-N(5)	2.03	N(5)-Zn-N(3)	99
		N(5)-Zn-N(4)	102
		N(1)-Zn-N(5)	176
		N(2)-Zn-N(3)	119
		N(2)-Zn-N(4)	118
		N(3)-Zn-N(4)	117

The closest approaches of the second thiocyanate ions to the zinc ion give Zn–N(6) of 3.77 Å and Zn–S(2) of 3.95 Å. Thus the second thiocyanate ion is clearly not coordinated to the zinc ion.

Acknowledgments. This work was supported in part by a grant from the U. S. National Science Foundation. The pure sample of tren hydrochloride was supplied by Mr. J. L. Wilson.

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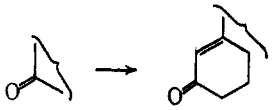
Received October 23, 1967

Bis Annelation with 6-Vinyl-2-picoline

Sir:

Several methods have been applied to the problem of elaborating a cyclohexenone ring around a carbonyl group and its adjacent carbon atom, as generalized by the transformation I → II. The most commonly used approach involves a four-carbon unit possessing electrophilic character at C_1, an actual or latent ketonic function at C_3, and, thus, nucleophilic capability at C_4. These requirements are, in principle, met by the well-known compound methyl vinyl ketone (MVK). In addition, a series of MVK equivalents,[1] III–VII, has been used to meet various structural challenges.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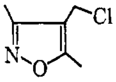
II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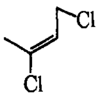
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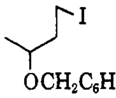
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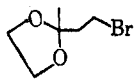
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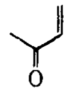
III

The problem which stimulated this research is the construction of a 3-ketohexalin ring system about a carbonyl group and its adjacent carbon atom, as illustrated by the transformation I → VIII. If such a transformation could be achieved, with provision for the stereospecific introduction of an angular methyl group and stereospecific saturation of the double bonds, the implements for the total synthesis of naturally occurring nonaromatic steroids would be in hand.[2,3] In the absence of these additional controls, the transformation is of immediate relevance to the synthesis of the physiologically important unsaturated 19-norsteroids.[4]

In principle, the projected transformation I → VIII can be achieved through successive annelations, *i.e.*, I → II followed by II → VIII[5] *via* some combination of the reagents III–VII. We were, however, tempted to explore the feasibility of utilizing the readily available[6] compound, 6-vinyl-2-picoline (IX), as an eight-carbon fragment which would achieve the desired transformation with an economy of synthetic operations. We report here some preliminary findings which augur well for the use of this compound as a bis annelating agent. The process is demonstrated by the conversion of cyclohexanone to the tricyclic dienone XVI.

Reaction of the pyrrolidine enamine of cyclohexanone with IX gave the picolylethylated ketone[7] X (54% yield) which was smoothly converted[8] to the ketal XI. Compound XI was subjected to the following sequence of reactions: (a) $Na-NH_3-EtOH-Et_2O$, (b) $NaOH-H_2O-MeOH$, (c) H^+-H_2O, (d) TsOH–HoAc. At the end of this sequence, the tricyclic dienone XVI was obtained in 40% yield (after molecular distillation). The structure assignment follows from its infrared

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(1) For a critical review on the use of MVK equivalents see G. Stork, *Pure Appl. Chem.*, **9**, 131 (1964). For subsequent publications on some of these reagents see G. Stork, S. Danishefsky, and M. Ohashi, *J. Am. Chem. Soc.*, **89**, 5459 (1967); J. A. Marshall and D. J. Schoeffer, *J. Org. Chem.*, **30**, 3642 (1965).

(2) Recently Stork and McMurry published an extraordinarily elegant bis annelation procedure which did indeed provide for the stereospecific introduction of a 19β-methyl group and 9β-, 10α-, and 14α-hydrogen atoms in converting the Wieland Miescher ketone to *dl*-D-homotestosterone. See G. Stork and J. E. McMurry, *J. Am. Chem. Soc.*, **89**, 5465 (1967).

(3) For comprehensive reviews of steroid total synthesis see I. V. Torgov, *Pure Appl. Chem.*, **6**, 525 (1963); L. Velluz, J. Valls, and G. Nomine, *Angew. Chem. Intern. Ed. Engl.*, **4**, 181 (1965).

(4) For a review of the synthetic approaches to this class of compounds see T. Windholz and M. Windholz, *ibid.*, **3**, 353 (1964).

(5) The transformation II → VIII presumes the presence of at least one γ-hydrogen atom to direct a new alkylation at the α position. In principle our method does not involve this structural condition.

(6) K. S. N. Prasad and R. Raper, *J. Chem. Soc.*, 257 (1957). We wish to thank Dr. Frank Cislak of the Reilly Tar and Chemical Corp. for providing us with generous supplies of this compound.

(7) *Cf.* G. Singerman and S. Danishefsky, *Tetrahedron Letters*, 2249 (1964).

(8) *Cf.* S. Danishefsky and M. Feldman, *ibid.*, 1131 (1965).