Greater paramagnetism for K_2TcH_8 would require uncoupling of the spins in the technetium compound.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA

The Preparation of $MoCl_4 \cdot 4(C_6H_5)_3AsO$

BY SALLY M. HORNER AND S. Y. TYREE

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In an extension of the study of reactions between molybdenum pentachloride and oxygen donors,[1] the reaction of molybdenum tetrachloride with the same donor molecules has been investigated. The triphenylarsine oxide adduct was the only Mo(IV) complex isolable.

Experimental

Reagents.—Reagent grade carbon tetrachloride was used as solvent. The oxygen donors were prepared as described by us previously.[1]

Molybdenum tetrachloride was prepared by two methods. The first method, described in an earlier report from this Laboratory,[2] was found to be not as reliable as we had supposed. About as often as not the product is a mixture of $MoCl_4$ and $MoCl_5$. Nonetheless, on occasion, excellent samples of the tetrachloride were obtained by this method. *Anal.* Calcd. for $MoCl_4$: Cl, 59.65; Mo, 40.35. Found for a good preparation: Cl, 59.78; Mo, 39.24. Perhaps a better test of the purity of the preparation was its ability (or failure) to give a pure white precipitate upon reaction with $(C_6H_5)_3AsO$ as described below.

The alternate method was reported by Epperson[3] and depends upon the reaction of MoO_2 with CCl_4 in a sealed tube. The principal impurity in the products of this method proved to be unreacted MoO_2. In cases of incomplete conversion the product is easily separated from unreacted starting material by virtue of the solubility of the former in CCl_4. *Anal.* Found for a good preparation: Cl, 58.31, 58.73; Mo, 39.67, 40.17.

Analyses.—Molybdenum and chlorine analyses were performed as described previously.[1] Carbon and hydrogen analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

Preparation of the Complex.—All operations were performed in a nitrogen atmosphere. A small amount (0.2–0.3 g.) of $MoCl_4$ was dissolved in 100 ml. of CCl_4. Sufficient $(C_6H_5)_3AsO$ to give a six- or eightfold excess (2–3 g.) was dissolved in 300 ml. of CCl_4, cooled to room temperature, and filtered. The red $MoCl_4$ solution was decanted slowly into the $(C_6H_5)_3AsO$ solution. It is decolorized instantaneously and a flocculent white precipitate forms. Care must be taken not to add too much $MoCl_4$, or the precipitate takes on a green color. The precipitate was filtered, washed with CCl_4, and dried. The resulting white powder is soluble in CH_2Cl_2, $CHCl_3$, and acetone. It is very slightly soluble in CCl_4. It is insoluble in water and apparently unaffected by contact with the same substance for several hours; m.p. 161–163°. *Anal.* Calcd. for $MoCl_4 \cdot 4(C_6H_5)_3AsO$: Cl, 9.30; Mo, 6.29; C, 56.67; H, 3.96. Found (on several preparations): Cl, 9.42, 9.93, 9.45, 9.18; Mo, 6.24, 6.81, 6.68; C, 53.50; H, 3.81.

Attempted Preparations of Other $MoCl_4$ Complexes.—A CCl_4 solution of $(CH_3)_2SO$ instantly decolorized CCl_4 solutions of $MoCl_4$, but evaporation produced no identifiable product. When the procedure for preparing the complex was used with $(C_6H_5)_3PO$ substituted for $(C_6H_5)_3AsO$, the red color of $MoCl_4$ did not disappear instantly. After 5–10 sec. the color did fade, and a white flocculent precipitate appeared. We feel that the precipitate was the phosphine oxide analog of the arsine oxide complex; but it changed rapidly to a yellow color, and all that could be isolated from the solution was yellow-orange $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$.[1]

Physical Measurements.—Magnetic susceptibility determinations and infrared spectra were obtained as described previously.[1] Conductance measurements were made in purified nitrobenzene.

Results

Magnetic susceptibility determinations on three different preparations showed the complex to be diamagnetic. For one determination $\chi_m' = -276 \times 10^{-6}$ c.g.s. units, after all diamagnetic corrections were made.

Infrared spectra showed three peaks in the region of the uncomplexed As–O stretching frequency, taken as 878 cm.$^{-1}$.[4] The observed peaks were 900, 878, and 848 cm.$^{-1}$. The maximum shift in the As–O frequency is -30 cm.$^{-1}$. The splitting of the As–O peak has been noted before.[1,4]

Conductance measurements were made on one preparation only. The molar conductance of a 10^{-3} *M* solution was 5.2×10^{-3} cm.^{2} ohm^{-1} mole^{-1}, indicating that it is essentially a nonelectrolyte in nitrobenzene.

Discussion

Three anionic, octacoördinate Mo(IV) complexes have been reported previously,[5-7] Mo-

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[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 122 (1962).

[2] T. E. Austin and S. Y. Tyree, *J. Inorg. Nucl. Chem.*, **14**, 141 (1960).

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$(CN)_8^{4-}$, $Mo(C_2O_4)_4^{4-}$, and $Mo(CO_3)_4^{4-}$. Each has been shown to be diamagnetic, indicative of d^4sp^3 bonding.[7-9]

The physical properties of $MoCl_4 \cdot 4(C_6H_5)_3AsO$ suggest that it is the first example of a neutral octacoördinate Mo(IV) complex. Uncomplexed $MoCl_4$ is extremely sensitive to oxidation and hydrolysis, but the present complex is unaffected by boiling in water for 15 min., and by subsequent prolonged standing in water at room temperature. $MoCl_4$ is highly colored; the complex is white. The presence of eight ligands, coupled with the conductance data, can only be accounted for by octacoördination.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Phosphorus Nuclear Magnetic Resonance Spectra of Polycyclic Phosphorus Compounds

BY J. G. VERKADE AND R. W. KING

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The chemical shifts of phosphorus in the polycyclic compounds I–III[1] and IV–VI[2] have been investigated.

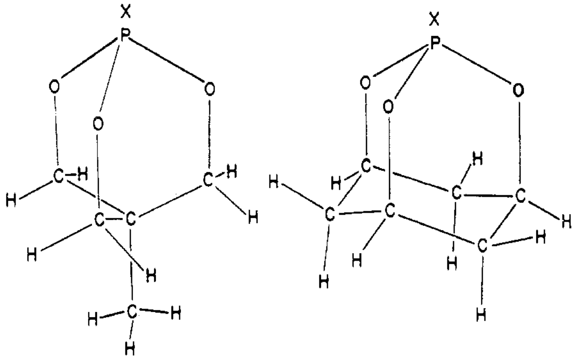
To ensure adequate signal strength, phosphorus spectra were obtained at 24.3 Mc./sec. on at least 1 *M* solutions. Where different solvents were used for the same compound, no significant difference in shift was observed.[3,4] Phosphorus chemical shifts are recorded in Table I in p.p.m. from external 85% phosphoric acid. The positive and negative signs refer to upfield and downfield values, respectively. Proton shifts were measured at 60 Mc./sec. and are recorded in p.p.m. downfield from tetramethylsilane in deuteriochloroform solutions at least 5% by weight in polycyclic compound.

TABLE I

PHOSPHORUS AND PROTON N.M.R. ABSORPTIONS

Compound	$\delta(P^{31})$	$J_{P-O-C-H}$ (c.p.s.)	$\delta(H^1)^d$ $C\beta$		
			$C\beta$	$C\gamma^e$	$C\delta$
I	$-91.5^{a,b}$	2	3.93		0.72
II	-57.4^c	6	4.48		.87
III	$+7.97^c$	7	4.48		.90
IV	$-137^{a,c}$	6	4.32	3.03, 1.87	
V	-64.0^c	19	4.97	2.73, 1.85	
VI	$+10.4^c$	20	5.05	2.82, 1.83	

[a] In chloroform. [b] In acetonitrile. [c] In dimethyl sulfoxide. [d] Greek subscripts refer to the position of the proton-bearing carbon atom with respect to phosphorus. [e] The difference in the chemical shifts of these protons is due to the chemically different axial and equatorial positions they occupy.



(I) (X = none) (IV) (X = none)
(II) (X = sulfur) (V) (X = sulfur)
(III) (X = oxygen) (VI) (X = oxygen)

Figure 1.

Theoretically, the threefold axial symmetry of these molecules requires that phosphorus coupling with the nearest hydrogen atoms in the molecule yield a P^{31} septet in compounds I–III and a quartet in compounds IV–VI. The theoretical number of peaks was observed in the spectra of compounds IV–VI but spectra of compounds I–III revealed only five peaks; the outer two of theoretical intensity 5% of that of the center peak being lost in the noise. Phosphorus–proton coupling constants, $J_{P-O-C-H}$, obtained from H^1 resonance spectra, were substantiated by values obtained from P^{31} resonance spectra. The only H^1 spectrum which did not afford a value for this coupling was that of compound IV where the more complicated proton–proton coupling caused broadening of the absorptions so that the relatively small phosphorus–proton coupling was unobservable. The value for this constant was ob-

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(2) H. Stetter and K. Steinacker, *Ber.*, **85**, 451 (1952). Compound names: 2,8,9-trioxa-1-phospha-adamantane (IV), its 1-sulfide (V), and 1-oxide (VI).

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