as they do in the unsubstituted $C_5H_5Mn(CO)_3$. The ABC pattern of the olefinic protons in the complex lies between 1.8 and 2.8 p.p.m. downfield (shifted 3.7 p.p.m. upfield from the free ligand). Precisely the same shift was observed in complexes of the type $Fe(CO)_4L$ involving olefinic ligands.[11]

An unequivocal proof of the existence of the monosubstituted complex $C_5H_5Mn(CO)_2C_4H_6$ (II) is difficult because of its instability. The evidence rests almost entirely on the infrared spectrum. Two infrared bands are clearly observed in the CO stretching region (see Table I). This is precisely what is expected assuming C_s symmetry. Even more to the point is the very close agreement between infrared CO stretching frequencies of the butadiene derivative and the previously established mono derivative of ethylene, $C_5H_5Mn(CO)_2C_2H_4$. This comparison, 1976 and 1916 cm.$^{-1}$ for the butadiene derivative and 1976 and 1917 cm.$^{-1}$ for the ethylene derivative, shown in Table I, is strong evidence that compound II is indeed the monosubstituted $C_5H_5(CO)_2C_4H_6$.

Analytical data for compound III are in excellent agreement with the assumption that there is one butadiene molecule for each two $C_5H_5Mn(CO)_2$ groups. No other simple empirical formula fits nearly as well. This strongly suggests that butadiene serves as a bridge between two $C_5H_5Mn(CO)_2$ groups in compound III. Utilizing the method of local symmetry, group theoretic considerations suggest that two infrared bands should be observed for this compound. This is precisely what is observed. Detailed considerations of the structure of this molecule must await a more thorough structural investigation. X-Ray analysis is in process in another laboratory.

Acknowledgment.—We are pleased to acknowledge the assistance, in the form of both important suggestions and help in the experiments, of Mr. Heinz Haas. Discussions of the various problems with Dr. Ronald Clark have also been helpful.

[11] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

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Stabilization of High Oxidation States of Representative Elements by Complexation[1]

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The use of complexing agents for the express purpose of stabilizing high oxidation states of representative elements has received little attention despite the conspicuous success of stabilizing uncommon oxidation states of transition metals by the appropriate choice of ligands. It has been established experimentally that the fluoride ion and oxygen-containing ligands are particularly effective in stabilizing the highest oxidation state of a metal. This stabilizing effect has been accounted for in a satisfactory manner by proposing that in addition to σ-bond formation between the metal ion and the ligand there is an appreciable overlap of p orbitals, and occasionally d orbitals, on the ligand with the metal d orbitals.[2] Ligands which contain lone pairs of electrons in p orbitals and which transfer electron density *onto the metal* through π bonds are effective in stabilizing high oxidation states. At the same time the ligand must be sufficiently electronegative so as not to give up an electron to the metal. This in effect would result in oxidation of the ligand. The fluoride ion and oxygen-containing ligands, such as phosphine oxides, sulfoxides, and phosphate esters, are particularly effective in stabilizing high oxidation states because of their apparent ability to increase the electron density on the metal and their resistance to oxidation. The chloride ion is less desirable as a stabilizing ligand because of its tendency to be oxidized when bound to a strong oxidizing agent.

Stabilization of arsenic pentachloride by complexation was chosen to demonstrate the usefulness of this concept. The nonexistence of free arsenic pentachloride is a well-known fact. Careful vapor pressure measurements of the $AsCl_3$–Cl_2 system have given no evidence for arsenic pentachloride.[3] The negligible chlorine exchange between radioactive chlorine and arsenic trichloride has been interpreted as evidence for the nonexistence of an activated complex equivalent to arsenic pentachloride.[4] The instability of arsenic pentachloride relative to arsenic trichloride and chlorine has been accounted for in terms of unfavorable thermodynamics.[5] The purpose of complexation is, therefore, simply to lower the potential energy of the arsenic(V) species below that of its decomposition products.

Three general methods for the stabilization of arsenic(V) bonded to three or more chloride ions are summarized in eq. 1–3.

$$AsCl_3 + Cl_2 + MCl_n = [AsCl_4^+][MCl_{n+1}^-] \qquad (1)$$

where MCl_n[6] = $AlCl_3$,[7] $GaCl_3$,[7] PCl_5,[8,9] and $SbCl_5$.[9]

$$AsCl_3 + Cl_2 + [Q^+][Cl^-] = [Q^+][AsCl_6^-] \qquad (2)$$

where $[Q^+]$ is any bulky cation such as $[(C_2H_5)_4N^+]$.

$$AsCl_3{\cdot}xD + Cl_2 = AsCl_5{\cdot}yD + (x-y)D \qquad (3)$$

where D is a neutral ligand.

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[1] This work was supported by the National Science Foundation.

[2] For a discussion of $d\pi$–$p\pi$ bonding and its effects on the stability of oxidation states of transition metals in coordination compounds see J. Chatt, *J. Inorg. Nucl. Chem.*, **8**, 515 (1958), and R. S. Nyholm and M. L. Tobe, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963).

[3] R. R. Holmes, *J. Inorg. Nucl. Chem.*, **19**, 363 (1961).

[4] J. H. Owen and R. E. Johnson, *ibid.*, **2**, 260 (1956).

[5] See R. S. Drago, *J. Phys. Chem.*, **62**, 353 (1958), for a discussion of the thermodynamics of the "inert pair effect."

[6] Other salts which probably contain the $AsCl_4^+$ ion have been reported where MCl_n is $TaCl_5$, $AuCl_3$, and $FeCl_3$.

[7] L. Kolditz and W. Schmidt, *Z. anorg. allgem. Chem.*, **296**, 189 (1958).

[8] A. W. Cronander, *Bull. soc. chim. France*, [2] **19**, 499 (1873).

[9] V. Gutmann, *Monatsh.*, **82**, 473 (1951).

In the first type reaction, Lewis acid halides were added in order to promote ionic bonding in the arsenic(V) species and thereby introduce appreciable lattice energy stabilization. In this case stabilization from complexation is expected to be minor compared to lattice energy effects.

Stabilization of the higher oxidation state by the addition of an ionic chloride containing a bulky cation relies primarily upon a large lattice energy contribution to the stability of the arsenic(V) salt. The contribution from complexation to stability of the $AsCl_6^-$ anion, while less significant, is not unimportant. The usefulness of reaction type 2 was demonstrated in the preparation of tetraethylammonium hexachloroarsenate(V), the first hexachloroarsenate ever to be reported. It is an orange solid that melts at 146.5–149.0° with decomposition. It is readily soluble in acetonitrile and gives an intense absorption band at 329 ± 1 mμ, attributed to a charge-transfer transition. Because of the relatively rapid decomposition of this compound in acetonitrile, the extinction coefficient could not be measured accurately. The value for the extinction coefficient is in excess of 3×10^3. An infrared absorption band at 352 $cm.^{-1}$ is tentatively ascribed to an As–Cl asymmetric stretching frequency.

This compound loses chlorine very slowly at room temperature and will readily oxidize iodide to iodine in acidic water–acetonitrile solutions.

The third method of stabilization relies on the use of neutral ligands that are capable of π-bonding and of increasing the electron density on the metal. The effect is to reduce the oxidizing strength of arsenic in the arsenic(V) state. Similarly, the transfer of electrons from the stabilizing ligand to d orbitals on the metal may be viewed as an impairment of electron transfer by the chlorine to the metal d orbitals. Additional stability would be provided from lattice energy should ionic species of the type $[AsCl_{5-z}\cdot yD^{+z}][Cl^-]$ be formed. The preparation of a compound $AsCl_5\cdot 2OP(C_6H_5)_3$ was used to illustrate this method. The only other coordination compound of arsenic pentachloride that has been reported is $AsCl_5\cdot OP(CH_3)_3$.[10] The latter compound is an unstable orange solid which melts with decomposition near 50°.

Examination of the physical and chemical properties of $AsCl_5\cdot 2OP(C_6H_5)_3$ reveals a behavior which is consistent with the concepts just described. The compound is an orange solid which is insoluble in nonpolar organic solvents but soluble in acetonitrile, a solvent of moderate dielectric constant (37.5). This behavior suggests ionic character and may be due to a structure of the type $[AsCl_4(OP(C_6H_5)_3)_2^+]Cl^-$.

The ultraviolet absorption spectrum of an acetonitrile solution of the adduct has an intense charge-transfer band at λ_{max} 324 ± 1 mμ ($\epsilon \sim 2 \times 10^4$). Decomposition of the absorbing species is evident from the rather rapid decrease in intensity of this band with the passage of time.

The infrared spectra of triphenylphosphine oxide and of the adduct are identical in the 4000–625 $cm.^{-1}$ region except for the region of the P=O stretching mode. Triphenylphosphine oxide has a single band at 1190 $cm.^{-1}$ (in KBr pellet) and 1197 $cm.^{-1}$ (in acetonitrile solution) which vanishes in the pelletized sample of the adduct. (Values for the P=O stretching frequency have been reported as 1190,[11] 1195,[12] and 1206 $cm.^{-1}$.[13]) Generally, bonding of phosphine oxides to a metal results in a shift of the P=O stretching vibration to lower frequencies.[14] The position of the shifted band is obscured in the envelope of the intense absorption band centering at 1100 $cm.^{-1}$, which is present in the spectrum of both the adduct and the triphenylphosphine oxide. Three shoulders at around 1175, 1155, and 1135 $cm.^{-1}$ on the band centering at 1110 $cm.^{-1}$ were observed. The spectrum of the acetonitrile solution of the adduct showed two bands of equal intensity at 1175 and 1230 $cm.^{-1}$. Coupling of the P=O stretching vibrations of the two ligands through metal–oxygen bonds may be responsible for this splitting. The arsenic adduct like the hexachloroarsenate salt has an absorption band at 352 $cm.^{-1}$ of medium intensity which is tentatively assigned to an As–Cl asymmetric stretching frequency. Two other unassigned bands at 480 (medium) and 448 $cm.^{-1}$ (weak) were observed.

The coordination compound slowly releases chlorine at room temperature and readily oxidizes iodide to iodine. The equivalent weight of $AsCl_5\cdot 2OP(C_6H_5)_3$, determined iodometrically, is 433 (404 theoretical). The large value for the equivalent weight is due to loss of chlorine prior to and during analysis.

Magnetic susceptibility studies by the Faraday method show that a freshly prepared sample of the compound is very weakly paramagnetic. This phenomenon is being carefully investigated for the rather interesting possibility that the paramagnetism arises from a low concentration of an As(IV) species, an intermediate in the solid-state reduction of As(V) to As(III).

The use of pyridine, 2,2′-dipyridine, and 1,10-phenanthroline as neutral ligands for the stabilization of arsenic pentachloride was also examined. The greater basic character of these ligands relative to the phosphine oxides is offset by their tendency to *withdraw electrons* from the metal into antibonding π orbitals on the ligand.[15] This electron-transfer effect increases the electronegativity of the arsenic and enhances the oxidation of chlorine in the As–Cl bond. Passage of chlorine into carbon tetrachloride solutions of arsenic trichloride and the nitrogenous bases yielded yellow or orange solids. These compounds readily evolved chlorine and were too unstable for characterization. The crystalline reduction product $AsCl_3\cdot$dipy, m.p.

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[10] I. Lindqvist and G. Olofsson, *Acta Chem. Scand.*, **13**, 1753 (1959).

[11] M. Halman and S. Pinkas, *J. Chem. Soc.*, 3264 (1958).

[12] F. A. Cotton, R. D. Barnes, and E. Bannister, *ibid.*, 2199 (1960).

[13] R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).

[14] (a) M. J. Frazer, W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963); (b) J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).

[15] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955); C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

193–196°, was prepared. The pyridine analog, $\text{AsCl}_3 \cdot 2\text{py}$, m.p. 64°, has been reported previously.[16]

Recent work on the preparation of Tl(III) adducts of the type $\text{TlX}_3 \cdot 2\text{D}$ and $[\text{Q}^+][\text{TlX}_4^-]$[17] further illustrates the general applicability of the methods outlined in this paper. Particularly noteworthy is the stabilization of thallium(III) iodide by complexation with triphenylphosphine oxide to give $\text{TlI}_3 \cdot 3\text{OP(C}_6\text{H}_5)_3$. Whereas solid TlI_3 is most surely thallium(I) triiodide,[18] in the presence of certain neutral ligands the Tl(III) state is stabilized.

It should be borne in mind that solvent molecules may also serve as stabilizing ligands. By the appropriate selection of a solvent it should be possible to stabilize species of desired oxidation states. An example serves to illustrate this point. Thallium(I) triiodide, when placed in methanol or ethanol, behaves as though it were a solution of thallium(III) iodide.[19] The stabilization of the thallium(III) state may be viewed in terms of complexation stabilization by the solvent according to the idealized equations

$$x\text{ROH} + \text{TlI}_3(\text{s}) = \text{Tl(ROH)}_x^+ + \text{I}_3^- \qquad (4)$$

$$y\text{ROH} + \text{Tl(ROH)}_x^+ + \text{I}_3^- = [\text{Tl(ROH)}_{x+y-n}\text{I}_n^{+(3-n)}] + (3-n)\text{I}^- \qquad (5)$$

Other explanations are possible,[19] but the complexation model should not be ignored.

Experimental

Reagents.—All reagents were used without further purification except those for which purification procedures are given. Reagent grade carbon tetrachloride was fractionally distilled from potassium hydroxide and stored over anhydrous sodium sulfate until used. Reagent grade chloroform was shaken repeatedly with concentrated sulfuric acid, washed with water, dried over P_2O_5, and fractionally distilled.

Chlorine gas (Matheson) was dehydrated by passing through a sulfuric acid scrubbing tower.

Practical grade acetonitrile (Eastman Kodak) was fractionally distilled from phosphorus pentoxide. The constant-boiling center fraction was retained and shaken for several days with Linde Molecular Sieve, Type 3A, to remove the last traces of moisture.

Preparation of $\text{AsCl}_5 \cdot 2\text{OP(C}_6\text{H}_5)_3$.—In a typical reaction chlorine was added to 350 ml. of a carbon tetrachloride solution of 10.7 g. (0.0590 mole) of arsenic trichloride (Matheson Coleman and Bell) and 16.5 g. (0.0593 mole) of triphenylphosphine oxide (Metal and Thermit Corp.), m.p. 155.5–156.5°. The reaction temperature was held between −7 and 0° with a sodium chloride–ice bath. Within a short period after the introduction of the chlorine an orange solid separated from the solution. The solid was filtered, washed with chilled carbon tetrachloride, and dried under vacuum at room temperature for 3 hr. The yield was 17.4 g., 73.0%. The orange crystals evolve chloride slowly at room temperature. The compound melts partially at 42° with decomposition. At 70° the solid is completely melted to a yellow liquid that becomes colorless at 95°. The compound is slowly hydrolyzed by atmospheric moisture.

Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{P}_2\text{O}_2\text{AsCl}_5$: C, 53.46; H, 3.74; P, 7.66; O, 3.96; As, 9.26; Cl, 21.92. Found: C, 53.38; H, 4.04; P, 8.70; O (by difference), 4.20; As, 9.53; Cl, 20.15.

All melting points reported herein are for samples in open capillary tubes and are uncorrected.

Preparation of $[(\text{C}_2\text{H}_5)_4\text{N}^+][\text{AsCl}_6^-]$.—In a typical reaction a 10.7-g. (0.0590 mole) sample of arsenic trichloride was dissolved in 200 ml. of freshly distilled chloroform and the solution chilled to 0°. Chlorine gas was passed into the solution until the solution became saturated with the gas. A chloroform solution containing 5.33 g. (0.0321 mole) of tetraethylammonium chloride (Eastman Kodak White Label) in 100 ml. of solvent was added dropwise to the deep yellow AsCl_3–Cl_2 solution. Immediately an orange precipitate developed. The addition of the ammonium chloride solution required 30 min. An excess of chlorine was maintained at all times. The solid material was filtered and washed with chloroform under a nitrogen atmosphere. The yield of crude product was 12.5 g., 93.0% of theoretical.

The compound was recrystallized from acetonitrile to give orange platelets, m.p. 146.5–149.0° with decomposition. The dissolution of the crude material was carried out at room temperature and crystallization was immediately induced at 0° in order to reduce the amount of decomposition that spectral studies reveal takes place in acetonitrile.

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{NAsCl}_6$: C, 22.99; H, 4.82; N, 3.43; As, 17.92; Cl, 50.90. Found: C, 23.08; H, 4.78; N, 3.35; As, 17.99; Cl, 50.74.

Preparation of AsCl_3.—The yellow solid adduct, m.p. 193–196°, was obtained in essentially quantitative yields by the addition of arsenic trichloride to 2,2′-dipyridine (Eastman Kodak White Label) in carbon tetrachloride.

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{AsCl}_3$: C, 35.59; H, 2.39; N, 8.30; Cl, 31.52. Found: C, 35.46; H, 2.51; N, 8.27; Cl, 31.38.

Elemental Analyses and Spectral Analyses.—All elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Infrared spectra in the 4000–650 cm.$^{-1}$ region were taken on a Beckman spectrophotometer, Model IR8. All spectra were of samples in potassium bromide pellets except where stated otherwise.

The Perkin-Elmer Model 521 grating spectrophotometer was used for measuring spectra in the 650–200 cm.$^{-1}$ region.

Ultraviolet spectra were measured on a Cary Model 15 spectrophotometer.

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The Radical Decomposition of Peroxysulfuryl Difluoride, FSO_2OOF, and Related Compounds by Chemical and Electron Paramagnetic Resonance Methods

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The synthesis of peroxysulfuryl difluoride (FSO_2OOF) by the reaction of sulfur trioxide and oxygen di-