American Chemical Society, Anaheim, Calif., March 1978; American Chemical Society: Washington, D.C., 1978; INOR 228. (b) Harris, W. R.; Weitl, F. L.; Raymond, K. N. *J. Chem. Soc., Chem. Commun.*, in press. (c) We have subsequently learned of the independent synthesis of **15** by M. C. Venuti and W. H. Rastetter (Massachusetts Institute of Technology). We thank Dr. Rastetter for communicating this information prior to publication.
(2) Harris, W. R.; Carrano, C. J.; Raymond, K. N., submitted for publication in *J. Am. Chem. Soc.*
(3) Cooper, S. R.; McArdle, J. V., Raymond, K. N. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3551–3554.
(4) Raymond, K. N., Ed. "Bioinorganic Chemistry—II", *Adv. Chem. Ser.* **1977**, *No. 162.*
(5) Isied, S. S.; Kuo, G.; Raymond, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 1763–1767.
(6) Raymond, K. N.; Isied, S. S.; Brown, L. D.; Fronczek, F. R.; Nibert, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 1767–1774.
(7) Neilands, J. B., Ed. "Microbial Iron Metabolism", Academic Press: New York, 1974.
(8) Tait, G. H. *Biochem. J.* **1975**, *146*, 191–204.
(9) Jacobs, A.; White, G. P.; Tait, G. H. *Biochem. Biophys. Res. Commun.* **1977**, *74*, 1626–1630.
(10) For a review see Neilands, J. B. "Inorganic Biochemistry", Eichorn, G., Ed.; American Elsevier: New York, 1973; p 167.
(11) Neilands, J. B. "Iron Metabolism", Ciba Foundation Symposium, No. 51; Elsevier: Amsterdam, 1977; p 117.
(12) Anderson, W. F.; Hiller, M. C., Eds. "Development of Iron Chelators for Clinical Use", Department of Health, Education and Welfare, Publication No. (NIH) 77-994, 1975.
(13) Weitl, F. L.; Raymond, K. N.; Smith, W. L.; Howard, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 1170–1172.
(14) Corey, E. J.; Hurt, S. D. *Tetrahedron Lett.* **1977**, 3923–3924.
(15) (a) Ito, T.; Neilands, J. B. *J. Am. Chem. Soc.* **1958**, *80*, 4645–4647. (b) Corbin, J. L.; Bulen, W. A. *Biochemistry* **1969**, *8*, 757–762. (c) Korth, H. *Arch. Mikrobiol.* **1970**, *70*, 297–302.
(16) Corey, E. J.; Bhattacharyya, S. *Tetrahedron Lett.* **1977**, 3919–3922.
(17) Green, A. *J. Chem. Soc.* **1927**, 500–504.
(18) Corey-Pauling molecular models; Ealing Corp., Cambridge, Mass. 02140.
(19) Perkin, W. H., Jr.; Trikojus, V. M. *J. Chem. Soc.* **1926**, 2925–2932.
(20) Koyama, H.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481–484.
(21) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268–2270.
(22) Nelson, E. R.; Maienthal, M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467.
(23) The overall formation constant for the complex of **15** with ferric ion is $10^{45.8}$. A preliminary report of the thermodynamic properties of this ligand appears in ref 1b.
(24) Carrano, C. J.; Raymond, K. N. Submitted for publication.

Communications to the Editor

Attachment of Organic Groups to Heteropoly Oxometalate Anions

Sir:

The large polyoxoanions of vanadium, molybdenum, and tungsten[1] have for many years attracted attention as catalysts, electron microscope "stains", analytical reagents, etc. Recently we have sought to develop the chemistry of possible organic derivatives of such polyanions[2] with a view to their potential use as selective labeling and imaging agents for biological systems. We report here a direct derivatization of heteropoly anions under mild aqueous conditions that leads to the first examples of organoheteropoly complexes that are stable at biological pH and are reducible to intensely colored heteropoly blues. Independent work by Knoth has lead to similar complexes.[3]

Certain polyanion structures undergo partial hydrolysis to yield so-called "defect" or "lacunary" structures in which one or more MO_6 octahedral units have been lost. Such defect structures act as penta- or tetradentate ligands to a broad variety of transition metal cations.[1] Defect structure polyanions derived from the α isomers[4] of 1:12 and 2:18 polytungstates, i.e., $XW_{11}O_{39}{}^{n-}$ (X = P, Si, Ge, B) and $X_2W_{17}O_{61}{}^{10-}$ (X = P, As), were treated with $RMCl_3$, RMO(OH) (RM = MeSn, *n*-BuSn, PhGe) or $PhPb(OAc)_3$ in buffered aqueous or mixed aqueous-organic solvents to yield $XW_{11}(MR)O_{39}{}^{(n-3)-}$ and $X_2W_{17}(MR)O_{61}{}^{7-}$. The conditions of pH and solvent used depended upon the charge and structure of the polyanion and the nature of R. The resulting complexes were isolated as potassium and guanidinium salts and characterized by chemical analysis,[5] vibrational, electronic, and ^1H NMR spectroscopy, polarography, and X-ray diffraction. The complexes are presumed to have structures in which octahedral $M(O_5R)$ occupies the "defect" caused by the loss of a WO_6 octahedron. Ultraviolet and infrared spectra of the products resemble the corresponding spectra of the "complete" anions $XW_{12}O_{40}{}^{n-}$ and $X_2W_{18}O_{62}{}^{6-}$, and are almost identical with those of the corresponding $XM^{II,III}W_{11}O_{39}(OH_2)^{p-}$ and $X_2M^{II,III}W_{17}O_{61}(OH_2)^{q-}$ anions[6] ($M^{II,III}$ = most bi- or trivalent transition or group 3b metal ions). They differ, however, clearly from those of the "defect" structures.[6] The potassium salts of $BW_{11}(Sn\text{-}n\text{-}Bu)O_{39}{}^{6-}$, $BW_{11}(GePh)O_{39}{}^{6-}$, $BW_{11}(PbPh)O_{39}{}^{6-}$, and $SiW_{11}(SnMe)O_{39}{}^{5-}$ are isomorphous with several other 12-tungstates, such as $K_5CoW_{12}O_{40}\cdot 20H_2O$ and $K_4SiW_{12}O_{40}\cdot{\sim}17H_2O$ (space group $P6_222$).[7] They are also isomorphous with the potassium salts of some $XM^{III}W_{11}O_{39}(OH_2)^{r-}$ anions (X = P, As, B).[14] As is frequently observed with hydrated salts of substituted Keggin anions, crystallographic disorder equalizes the twelve heavy metal atoms.[8] The $X_2W_{18}O_{62}{}^{6-}$ structure has six equivalent WO_6 octahedra in "polar" positions and twelve equivalent "equatorial" octahedra.[9] Two isomers (α_1,α_2-$P_2W_{17}O_{61}{}^{10-}$), corresponding to the loss of each type of WO_6 octahedron, have been prepared by Contant and Ciabrini,[10] who tentatively suggest that the α_1 isomer results from the loss of a "polar" tungsten and α_2 from loss of an equatorial tungsten. A single crystal structure analysis of the potassium salt of $P_2W_{17}(Sn\text{-}n\text{-}Bu)O_{61}{}^{7-}$ prepared from the α_2 isomer is nearing completion, and it shows clearly that the tin occupies a "polar" position in the $P_2W_{18}O_{62}{}^{10-}$ framework.[15]

The new complexes exhibit an extensive redox chemistry, as is to be expected from their structures.[11] Polarograms show a series of reversible one-, two-, and/or four-electron waves corresponding to the sequential reduction of W(VI) to form mixed-valence heteropoly blues.[12] The half-wave potentials and their dependence on pH are characteristic of each complex, and the polarograms are similar to those of the corresponding $XM^{III}W_{11}O_{39}(OH_2)^{p-}$ complexes;[14] they are readily distinguishable from those of the corresponding "complete" and "defect" structure anions.[10,13,14] The polarograms also demonstrate the hydrolytic stability of the complexes at millimolar concentrations; the common stability range of the $XW_{11}(Sn\text{-}n\text{-}Bu)O_{39}{}^{n-}$, $XW_{11}(GePh)O_{39}{}^{n-}$, and $X_2W_{17}(Sn\text{-}n\text{-}Bu)O_{61}{}^{7-}$ anions is, respectively, pH ~4 to ~6, ~4 to ~7, and ~2 to ~8. The first two series of complexes decompose to $XW_{12}{}^{m-}$ at pH 1 to ~4, the latter to $X_2W_{18}{}^{10-}$ at pH 1 to 2. Alkaline decomposition starts at pH ~6, ~7, and ~8, respectively. Extension of the chemistry of these complexes via reduction, introduction of functionalized organic groups, and the use of other polyanion structures is in progress.

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References and Notes

(1) T. J. R. Weakley, *Struct. Bonding (Berlin)*, **18**, 131 (1974).
(2) M. T. Pope, C. O. Quicksall, W. Kwak, L. M. Rajkovic, J. K. Stalick, K. M.

0002-7863/79/1501-2731$01.00/0

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Barkigia, and T. F. Scully, *J. Less-Common Met.*, **54**, 129 (1977).
(3) W. H. Knoth, *J. Am. Chem. Soc.*, **101**, 2211 (1979).
(4) M. T. Pope, *Inorg. Chem.*, **15**, 2008 (1976).
(5) For example, see the following. Found (theory) for $K_5SiW_{11}(SnCH_3)O_{39}\cdot 14H_2O$: K, 5.78 (6.00); Si, 0.96 (0.86); W, 61.91 (62.12); Sn, 3.71 (3.65); C, 0.38 (0.37); H, 1.11 (0.96). Found (theory) for $K_5GeW_{11}(Sn\text{-}n\text{-}C_4H_9)O_{39}\cdot 14H_2O$: K, 5.85 (5.83); Ge, 1.95 (2.17); Sn, 3.52 (3.55); W, 61.00 (60.50); C, 1.40 (1.44); H, 1.04 (1.12). Found (theory) for $gua_7P_2W_{17}(Sn\text{-}n\text{-}C_4H_9)O_{61}\cdot 8H_2O$): P, 1.14 (1.26); Sn, 2.48 (2.41); W, 62.98 (63.58); C, 2.72 (2.69); H, 1.41 (1.37); N, 5.85 (5.98). Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.
(6) C. Rocchicioli-Deltcheff and R. Thouvenot, *J. Chem. Res.* (*S*), 46 (1977).
(7) K. Eriks, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallogr.*, **13**, 1139 (1960); P. M. Smith, Ph.D. Thesis, Georgetown University, 1971.
(8) See, for example, T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.*, 341 (1973).
(9) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953); H. d'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).
(10) R. Contant and J. P. Ciabrini, *J. Chem. Res.* (*S*), 222 (1977).
(11) M. T. Pope, *Inorg. Chem.* **11**, 1973 (1972).
(12) J. M. Fruchart, G. Herve, J. P. Launay, and R. Massart, *J. Inorg. Nucl. Chem.*, **38**, 1627 (1976).
(13) P. Souchay and A. Teze, *C.R. Acad. Sci., Ser. C*, **268**, 804 (1969).
(14) F. Zonnevijlle, Thèse d'Etat, Université des Sciences et Techniques du Languedoc, Montpellier, France, 1976.
(15) R. L. Firor, personal communication.

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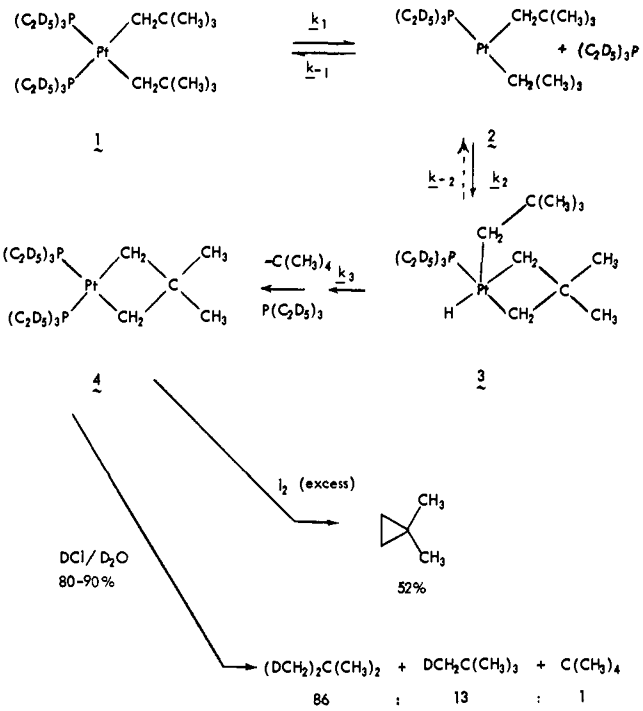
Thermal Generation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane from Dineopentylbis(triethylphosphine)platinum(II)[1]

Sir:

Reactions which cleave unactivated aliphatic carbon-hydrogen bonds are important in a range of heterogeneous platinum-catalyzed transformations of hydrocarbons, and a mechanistic understanding of these types of reactions is one objective of current research in catalysis.[2] The mechanisms of heterogeneous reactions are difficult to examine directly. Here we outline the mechanism of a tractable and well-defined solution reaction—the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**4**)—which involves cleavage of an unactivated C-H bond by intramolecular oxidative addition to a soluble platinum species. This mechanism establishes certain of the structural features which facilitate C-H bond activation in solution and suggests, by analogy, possible characteristics of the heterogeneous reactions.

Heating a solution of **1** (0.08 M, 157 °C, 2.25 h, 0.02 M Et_3P)[3] in cyclohexane results in the disappearance of **1** and the appearance of 1 equiv of neopentane, 0.8 equiv of **4**, and 0.1 equiv of 2,2,5,5-tetramethylhexane. The solution remains homogeneous throughout the decomposition. Compound **4** was isolated as a light yellow oil by removing cyclohexane and titurating with acetonitrile to remove unreacted **1**. **4** showed the following: ^1H NMR (C_6D_6) δ 0.73 (t of t, 4 H, 1:4:1, J_{Pt-H} = 74, J = 12 Hz, Pt-CH_2), 1.57 (t, 6 H, J = 3 Hz, $C(CH_3)_3$; ^{31}P (C_6H_{12}, H_3PO_4 external reference) δ +9 ppm (t, 1:4:1, J_{Pt-P} = 1862 ± 8 Hz). Treatment of **4** with aqueous 38% DCl in D_2O yielded a mixture of deuterated neopentanes.[4] Examination of the cracking pattern of this neopentane indicated that the deuterium was present in CH_2D rather than CHD_2 groups and is consistent with activation of a γ C-H bond and not an α C-H bond.[5] Treatment of **4** with excess iodine generated 1,1-dimethylcyclopropane. The dimethylcyclopropane derived from thermolysis of $[(CH_3)_3CCD_2]_2Pt(PEt_3)_2$ followed by treatment with I_2 was d_2.



Scheme I. Mechanism of Conversion of **1** into **4**. No Stereochemistry Is Implied by **3**

The origin of the hydrogen atom consumed in conversion of a neopentyl group of **1** to neopentane was established as a methyl group of a second neopentyl group by deuterium labeling experiments:

$$[(CH_3)_3CCH_2]_2Pt[P(C_2D_5)_3]_2 \xrightarrow[157\ ^\circ C]{C_6D_{12}} (CH_3)_3CCH_2H\ (97\%\ d_0,\ 3\%\ d_1) \qquad (1a)$$

$$[(CH_3)_3CCD_2]_2Pt[P(C_2D_5)_3]_2 \xrightarrow[157\ ^\circ C]{C_6D_{12}} (CH_3)_2CCD_2H\ (93\%\ d_2,\ 7\%\ d_3) \qquad (1b)$$

The decomposition of $[(CH_3)_3CCH_2]_2Pt[P(C_2D_5)_3]_2$ in solutions of C_6D_{12} containing added $P(C_2D_5)_3$ (0.02-0.3 M) was followed by NMR spectroscopy. These decompositions obeyed the empirical rate equation

$$d[\mathbf{1}]/dt = k_{obsd}[\mathbf{1}][P(C_2D_5)_3]^{-1} \qquad (2)$$

The observed rate equation is compatible with the formal rate expression

$$d[\mathbf{1}]/dt = k_1k_2[\mathbf{1}]/(k_2 + k_{-1}[P(C_2D_5)_3]) \qquad (3)$$

derived for a preequilibrium dissociation of phosphine followed by rate-limiting C-H addition, and with an analogous expression for a scheme in which C-H reductive elimination (k_3) is rate limiting (Scheme I). Analysis of the temperature dependence for decomposition of **1** over the range 118-157 °C yielded these values for the Arrhenius activation parameters: E_a = 49 ± 4 kcal mol^{-1}, $A = 10^{20\pm 2}$ s^{-1}. The exchange of $(CH_3CH_2)_3P$ into $[(CD_3CD_2)_3P]_2Pt[CH_2C(CH_3)_3]_2$ was followed by ^{31}P NMR spectroscopy. This exchange was complete at 100 °C in 1.0 h with no detectable decomposition of **1**. The rate of this exchange was independent of added Et_3P concentration from 0.1 to 1.7 M and indicated that exchange occurred by an S_N1 process. This observation is consistent with the preequilibrium dissociation of Et_3P implied in Scheme I.[6]

The solubility of **1** in solutions of cyclohexane containing triethylphosphine established that the decrease in rate of decomposition of **1** observed on adding triethylphosphine could

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