this is certainly true of the osmium–carbyne complex. I reacts with HCl, forming the osmium(II)–carbene complex $OsCl_2(CHR)(CO)(PPh_3)_2$ (II) (see Scheme I for a summary of this and other transformations described in this paper). The ^1H NMR spectrum of II ($CDCl_3$) shows a low-field resonance at τ −8.05 [J(P–H) = 2.5 Hz], a position typical of other alkylidene complexes.[13] However, unusual features of this compound are air stability, a mp of 255 °C, and a lack of further reactivity with HCl. Reaction of I with Cl_2 leads to a 1:1 addition product which we formulate as the osmium(II)–chlorocarbene complex $OsCl_2(CClR)(CO)(PPh_3)_2$ (III). Further reactions of III support this formulation. As detailed in Scheme I, 1 equiv of $Li(Et_3BH)$ converts III to II; reaction with water leads to the osmium p-tolyl *di*carbonyl $OsRCl(CO)_2(PPh_3)_2$, easily understood as resulting from an intermediate acyl complex,[14] and reaction with SH^- produces the known η^2-thioacyl IV.[15] Similarly, reaction with SeH^- and TeH^- leads to examples of previously unknown η^2-selenoacyl and η^2-telluroacyl ligands, respectively. If the osmium–carbon triple bond is thought of as having "acetylene-like" character, then the thioacyl derivative can be thought of as an unsaturated episulfide derived from the carbyne complex. We therefore attempted the synthesis of the thioacyl directly from I and elemental sulfur and found that this reaction proceeds virtually quantitatively in benzene solution at room temperature over several minutes. Similar reactions with elemental selenium and tellurium are much slower but nevertheless proceed in good yield. Other reactions of I are suggested by the acetylene analogy and will be described subsequently.

---

(13) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(14) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46.

(15) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *157*, C23.

George R. Clark, Karen Marsden, Warren R. Roper*
L. James Wright

Department of Chemistry, University of Auckland
Auckland, New Zealand

Received April 25, 1980

1:14 Heteropolyvanadate of Phosphorus: Preparation and Structure

Sir:

A variety of heteropolyanions of vanadium have been reported but with few confirmed examples of structure determination.[1] In the case of phosphorus as the heteroatom, the knowledge about compositions and structures of heteropolyvanadates is still limited. There have been several reports of the preparation of $PV_{12}O_{36}^{7-}$,[2] but the existence of this anion was doubted by Preuss and Schug. Instead, they claimed to have characterized 1:13 and 1:14 vanadophosphates by chemical analyses and the ultracentrifuge technique.[3] We report here the isolation of 1:14 vanadophosphate as a guanidinium salt crystal suitable for X-ray characterization which revealed a new structural type, a bicapped Keggin structure.

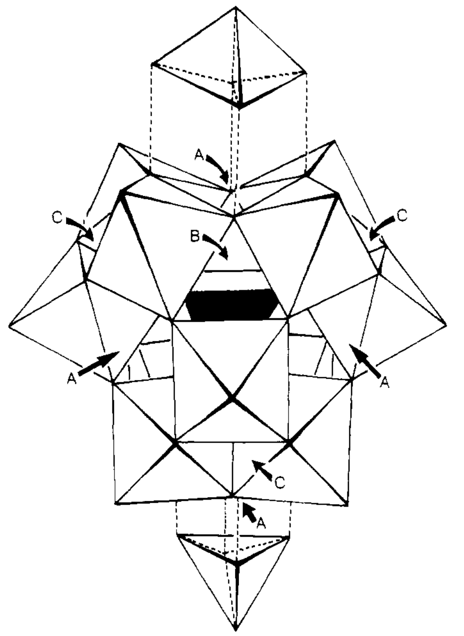

Figure 1. The polyhedral model of the $PV_{14}O_{42}^{9-}$ anion.

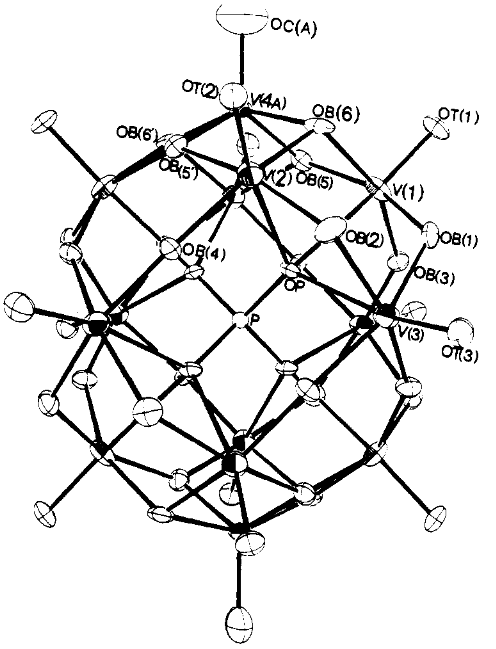

Figure 2. The geometry of the $PV_{14}O_{42}^{9-}$ anion. Bond lengths: P–OP, 1.529 (5); V(1)–OT(1), 1.608 (6); V(1)–OB(1), 1.831 (6); V(1)–OB(3), 1.891 (5); V(1)–OB(5), 1.981 (5); V(1)–OB(6), 1.922 (6); V(1)–OP, 2.350 (5); V(4A)–OC(A), 1.681 (10); V(4A)–OB(5), 1.829 (6); V-(4A)–OB(6), 1.999 (6) Å. Bond angles: OC(A)–V(4A)–OB(5), 116.4 (4); OC(A)–V(4A)–OB(6), 103.3 (4)°.

An insoluble dark red solid was obtained by treating an aqueous solution of H_3PO_4 and $NaVO_3$ (ref 4, 1:4 ratio, pH 2.7 with HNO_3)[4] with excess guanidine hydrochloride in water at room temperature. An octahedral single crystal for X-ray investigation was prepared by a diffusion method. Anal. Calcd for $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$: C, 4.75; H, 3.14; N, 16.61; V, 35.2; P, 1.53. Found: C, 4.86; H, 3.28; N, 16.64; V, 35.3; P, 1.44. The IR spectrum was similar to those of $PM_{12}O_{40}^{3-}$ (M = Mo, W) having the Keggin structure.

Crystal data for $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$ (M_w 2024.08): tetragonal, space group $I\bar{4}$; a = 13.058 (2), c = 18.431 (6) Å; U = 3143 (1) Å^3; Z = 2; d_{calcd} = 2.14 g·cm^{-3}; μ(Mo Kα) = 22.5 cm^{-1}. The structure was solved by the heavy-atom method and

---

(1) The structures of $Ni^{(IV)}V_{13}O_{38}^{7-}$, $Mn^{(IV)}V_{13}O_{38}^{7-}$, and $AlV^{(V)}{}_{12}V^{(IV)}{}_2O_{40}^{9-}$ which have octahedrally coordinated heteroatoms were established. C. M. Flynn, Jr., and M. T. Pope, *J. Am. Chem. Soc.*, **92**, 85 (1970); A. Kobayashi and Y. Sasaki, *Chem. Lett.*, 1123 (1975); H. T. Evans, Jr., and J. A. Konnert, *Am. Mineral.*, **63**, 863 (1978). The only known example of heteropolyvanadates containing tetrahedrally coordinated heteroatoms was $H_6As_6V_4O_{30}^{4-}$: A. Durif and M. T. Averbuch-Pouchot, *Acta Crystallogr., Sect. B*, **B35**, 1441 (1979).

(2) P. Souchay and S. Dubois, *Ann. Chim.* (*Paris*), **3**, 88 (1948); A. B. Bekturov and A. K. Il'yasova, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **10**, 130 (1964); R. Ripan, A. Duca, and V. Cordis, *Rev. Roum. Chim.*, **12**, 375 (1967); R. Ripan and V. Cordis, *ibid.*, **14**, 197 (1969); *ibid.*, **15**, 559 (1970); R. Hagenbruch and H. Hahn, *Z. Anorg. Allg. Chem.*, **438**, 273 (1978).

(3) F. Preuss and H. Schug, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **31B**, 1585 (1976).

(4) Ca. 0.2 M in H_3PO_4.

0002-7863/80/1502-6571$01.00/0

refined by the block-diagonal least-squares method, using anisotropic temperature factors for all the nonhydrogen atoms. The weighting scheme $w = [\sigma^2(F) + 0.000625F^2]^{-1}$ was employed, and the final R value was 0.062 for 2257 independent reflections [$\sin \theta/\lambda \leq 0.76$, $|F| \geq 3\sigma$, without absorption correction].

The polyhedral model of the heteropolyanion $PV_{14}O_{42}^{9-}$ is shown in Figure 1. The central PO_4 tetrahedron shares its oxygen atoms with four V_3O_{13} groups, each of which is made up of three edge-sharing VO_6 octahedra, defining the well-known α-Keggin structure. There are 14 possible sites which are "pits" on a Keggin molecule for further coordination of vanadium atoms (six A sites, four B sites, and four C sites as shown in Figure 1). The last two VO units occupy trans-located A sites, forming trigonal bipyramidal caps. The geometry of the anion is shown in Figure 2, which includes some bond parameters.

In the region of pH 1.3–4.0, each of the 40.5-MHz ^{31}P NMR spectra of P/V 1:4 solutions showed only a singlet peak at −0.2 to +0.7 ppm (with respect to 85% H_3PO_4 as external standard) accompanied by a phosphate ion peak.

Such a Keggin structure with the capping 5-coordinated metal atoms has not been previously observed in the structures of polyanions. Compared with the polyanions of Mo(VI) and W(VI), a high negative charge will prevent the formation of Keggin-type anion $PV_{12}O_{40}^{15-}$ whereas bicapped Keggin anion $PV_{14}O_{42}^{9-}$ is stabilized by the two capping VO^{3+} units. The results of this work suggest the possibility of a capped Keggin ion series $PV_{12+n}O_{40+n}^{-(15-3n)}$ (n = 1–6).[5]

Acknowledgment. We are grateful to Dr. K. Sato for measuring ^{31}P NMR spectra.

Supplementary Material Available: Three tables listing atomic positions, thermal parameters, and structure factors (18 pages). Ordering information is given on any current masthead page.

---

(5) Very recently we have obtained a crystal of heteropolyvanadate containing arsenic as a heteroatom whose structure seems to be a capped Keggin type (n = 14 or 15?). A crystallographic analysis is in progress.

R. Kato, A. Kobayashi, Y. Sasaki*
Department of Chemistry and
Research Centre for Spectrometry
Faculty of Science, The University of Tokyo
Hongo, Tokyo 113, Japan

Received May 27, 1980

Olefin Metathesis Reaction: Characterization of an Active Catalyst Precursor, $CH_3WOCl_3{\cdot}O(C_2H_5)_2$, from the $WOCl_4$–$(CH_3)_2Mg$ Reaction

Sir:

Earlier[1] we had shown that $WOCl_4$ in combination with main group metal alkyls provided a consistent source of an exceedingly active catalyst precursor for the olefin metathesis reaction.[2] With the report of the synthesis, isolation, and characterization of CH_3WOCl_3,[4] we set out to identify the precursor and the intermediate(s) in the $WOCl_4$-based olefin metathesis reaction. We describe here the character of the $(CH_3)_2Mg$–$WOCl_4$ reaction, the spectroscopic and complex chemical properties of methyltungsten oxytrichloride–diethyl etherate complexes, and the catalytic properties of these methyltungsten complexes.

Riess and Santini[4] described the isolation of unsolvated CH_3WOCl_3 from the reaction of $(CH_3)_2Mg$ and $WOCl_4$ in a pentane–diethyl ether medium.[5,6] After an intensive examination of this reaction under the precise Riess and Santini conditions, and also widely varying conditions, we report the following. Reaction between $(CH_3)_2Mg$ and $WOCl_4$ did not proceed until temperatures of −30 to −20 °C were attained.[7] At minimal reaction temperatures, methane and methyl chloride were formed in addition to small amounts of ethane, ethylene, and propylene, with no detectable CH_3OH or H_2.[8] A major[10] coproduct was a green insoluble solid that had no hydrolyzable W–CH_3 or W–OCH_3 function, contained W, Cl, and Mg, and was catalytically inactive.[11a] The soluble fraction was isolated as red, apparently[11e] single crystals at low temperatures (<−30 °C).[12] These crystals contained tungsten and chlorine in the ratio of 1:2.93 and diethyl ether, but no magnesium; maximal yields of the isolated crystals were 45%. The extraordinary thermal reactivity precluded a normal high-precision analysis of all elements.[12] Nevertheless, the definition of the W/Cl ratio and the following spectroscopic studies establish these crystals to be an etherate of CH_3WOCl_3.[11f]

Red crystals of $CH_3WOCl_3{\cdot}O(C_2H_5)_2$ derived from a $WOCl_4$–$Mg(^{13}CH_3)_2$[11d] reaction were examined by ^{13}C and ^1H NMR as a function of temperature.[12] At low temperatures, there were

---

(1) M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 4689 (1976).

(2) Especially active was the product from alkylaluminum chlorides.[1] Products from WCl_6 and main group metal alkyls were shown to be inactive except under conditions wherein small amounts of air were admitted to the reaction system.[1] The reaction system of WCl_6, $[(C_2H_5)_xAlCl_{3-x}]_2$, and ethanol is an alternative source of an active olefin metathesis catalyst.[3]

(3) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).

(4) C. C. Santini-Scampucci and J. G. Reiss, *J. Organomet. Chem.*, **73**, C13 (1974); *J. Chem. Soc., Dalton Trans.*, 196 (1976).

(5) C. Santini, Ph.D. Thesis, Institut de Mathematiques and Sciences Physiques, Nice, France (1973).

(6) We are indebted to Professor Riess and to Dr. Santini for detailed information. Unfortunately, the original NMR spectral data for unsolvated CH_3WOCl_3 could not be obtained for precise comparison. They reported J_{H-W} = 3 Hz for CH_3WOCl_3.

(7) Variations of temperature, ratio of pentane to diethyl ether solvent, reactant ratios, and modes of addition were explored in a glass high-vacuum system wherein all operations of filtration, gas-phase analysis, and recrystallization could be performed quantitatively as a function of temperature.

(8) With $(CH_3)_2Mg$ to $WOCl_4$ reactant ratios of 0.5:1.0, the percentages of methyl equivalents in the hydrocarbons formed at reaction temperatures were CH_4 (3.2%), CH_3Cl (10.9%), C_2H_6 (2.7%), C_2H_4 (0.2%), and C_3H_6 (~0.1%). These hydrocarbons when generated from the $(CD_3)_2Mg$ reaction were fully deuterated with the exception of methane, which contained ~30% CD_3H. CD_3H formation may have been due to protons present on the surface on the Pyrex vessel.[9]

(9) Hydrogen incorporation was observed in the alkanes produced from the decomposition of tantalum perdeuterioalkyls when Pyrex vessels (flamed out under vacuum) were used but not when Vycor vessels (flamed out under vacuum) were employed: R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, **100**, 3359 (1978).

(10) 90% of the tungsten was present in this material with reactant ratios of $(CH_3)_2Mg$ to $WOCl_4$ of 1:1. This yield dropped to the 55–65% level at reactant ratios of $(CH_3)_2Mg$ to $WOCl_4$ of 0.5:1.0. The other product was crystalline CH_3WOCl_3 etherate.

(11) (a) This green solid contained W, Cl, and Mg in the ratios of 1:3.46:0.65 (typical analysis). (b) Qualitatively, some of our observations did not coincide with those of Santini and Riess. Their insoluble product was described as brown and CH_3WOCl_3 as yellow; the only yellow species we observed was $WOCl_4[O(C_2H_5)_2]$. Our soluble tungsten products invariably contained diethyl ether;[11c] Riess and Santini pointedly described their CH_3WOCl_3 as ether free. Their reported optimal conditions of stoichiometry diverged from our findings: Our optimal yields of methyltungsten complexes were realized at $WOCl_4/(CH_3)_2Mg$ ratios of 2:1. Extensive variations of these procedures were examined over a 3-year period, but we were unable to achieve the Riess–Santini accomplishments. Reaction of the methyl–tungsten complexes produced in our research with strong donor molecules led to formation of green, reduced tungsten species. (c) Quantitative gravimetric studies with $WOCl_4$ established that this oxychloride formed a 1:1 etherate isolable as a crystalline solid, but high-vacuum pumping converted the crystals to an ether-free form at 20 °C in about 2 h. At −30 °C, evacuation removed only about 2% of the ether from the solid etherate at −30 °C in ~1 h. Because of the thermal reactivity of $CH_3WOCl_3{\cdot}O(C_2H_5)_2$[12], ether removal by evacuation was not feasible. (d) The ^{13}C content was 18%. (e) The CH_3WOCl_3 etherate was purified by low-temperature crystallization to give large red needles. Visually, the crystals appeared to be single crystals. Attempts to obtain X-ray diffraction data at low temperatures failed in the processes of mounting the crystals in capillaries, where, because of the extreme thermal reactivity of the crystals, inadvertant temperature rises led to loss of crystallinity.[12] (f) The ratio of ether to tungsten in the complex was not established but was assumed to be 1:1 by analogy to $WOCl_4[O(C_2H_5)]$.

(12) These crystals decomposed rapidly at 0–20 °C (s), slowly at −30 °C (min), detectably at −78 °C (h), and undetectably at −197 °C. In solution, the decomposition was slow at 20 °C.

0002-7863/80/1502-6572$01.00/0