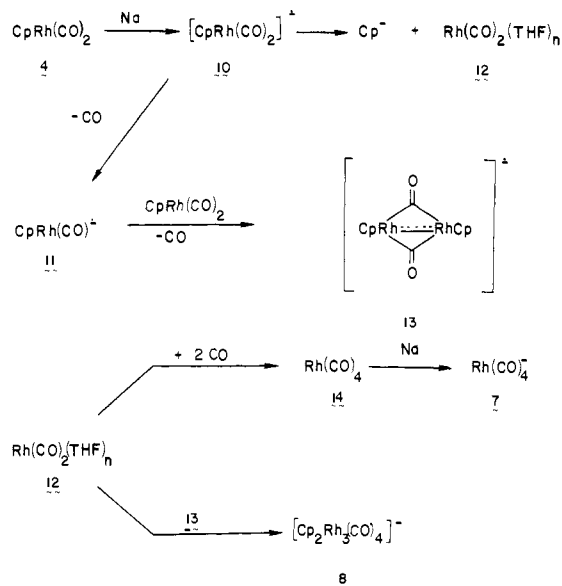(a)　　　　　　　　　　　　(b)

**Figure 3.** Schematic drawings of (a) a semi-bridging CO group; (b) a "semi-triple-bridging" CO group.

Scheme I



In complex **8,** three things reinforce this type of interaction: (a) the pseudo-square-planar configuration about the unique rhodium atom, (b) its coordinative unsaturation, and (c) the fact that Rh-1 formally carries the molecule's negative charge.

We offer the route outlined in Scheme I as a working hypothesis for the mechanism of formation of **7** and **8.** As in the cobalt case, we assume that initial reduction to radical anion **10** is followed by competing CO loss (giving **11**) and loss of the cyclopentadienyl ring (leading to a (probably highly solvated) $Rh(CO)_2$ fragment (**12**)). Complex **11** reacts with a second molecule of starting material, again followed by CO loss, to give radical anion **13.** Complex **13** is apparently more reactive than **3** and, instead of terminating the reaction at this stage, undergoes "radical coupling" with **12;** this leads to the isolated trinuclear cluster **8.** The alternative fate of **12** again parallels the cobalt reduction, giving **7** via coordination of CO and further reduction.

Carbonylation of **8** occurs unusually rapidly, leading cleanly to $Rh(CO)_4^-$ and $CpRh(CO)_2$ (no reaction between CO and **3** occurs in 24 h). It seems likely that this process involves initial dissociation, giving $Rh(CO)_4^-$ and **9.** By analogy to the corresponding doubly bonded cobalt dimer,[7.8] **9** should react immediately with CO, leading to **4,** as is observed.

**Supplementary Material Available.** Three tables, listing interatomic distances and angles, fractional coordinates, and intensity data (26 pages). Ordering information is given on any current masthead page.

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**Polyoxoanion Supported Organometallics: Synthesis and Characterization of** $\alpha$-$[(\eta^5$-$C_5H_5)Ti(PW_{11}O_{39})]^{4-}$

*Sir:*

Solid oxide supported organometallic compounds of the early transition elements have been studied extensively during the past 20 years as catalysts for a variety of hydrocarbon transformations.[1-3] These catalysts not only provide the practical advantages of heterogeneous catalysts relative to homogeneous systems with regard to product isolation and catalyst stability, but in many cases also provide activity which far exceeds that of their homogeneous analogues. The factors responsible for this enhanced activity remain obscure owing to the difficulty of characterizing surface-bound species. We have therefore sought the isolation of organometallic compounds bound to the surfaces of soluble oxide clusters with the hope that these species might provide insights into the factors responsible for the reactivity of solid oxide supported analogues. We report here the synthesis and characterization of $\alpha$-$[(\eta^5$-$C_5H_5)Ti(PW_{11}O_{39})]^{4-}$, the first polyoxoanion supported organometallic complex.

The $\alpha$-$[(\eta^5$-$C_5H_5)Ti(PW_{11}O_{39})]^{4-}$ ion (see Figure 1) was selected as an initial synthetic objective since several of its structural features are precedented. This ion is related to the well-characterized $PW_{12}O_{40}^{3-}$ ion[4] by substitution of a $[W^{VI}O]^{4+}$ subunit with $[Ti^{IV}(\eta^5$-$C_5H_5)]^{3+}$. Similar substitution of a $[W^{VI}O]^{4+}$ unit in the $PW_{12}O_{40}^{3-}$ anion by inorganic cations has been demonstrated to yield stable complexes.[5-7] $[Ti^{IV}(\eta^5$-$C_5H_5)]^{3+}$ was chosen as an organometallic subunit for three reasons. First, $Ti^{IV}$ has a 0.745 Å crystal radius[8] which is almost identical with the 0.74 Å crystal radius[8] for $W^{VI}$, indicating that $Ti^{IV}$ is geometrically well suited for $W^{VI}$ substitution in the $PW_{12}O_{40}^{3-}$ structure. Second, $Ti^{IV}$ has a vast oxygen chemistry,[9] assuring the thermodynamic stability of $Ti^{IV}$–O bonds. Finally, the $[Ti^{IV}(\eta^5$-$C_5H_5)]^{3+}$ unit has been thoroughly characterized in a large number of organometallic compounds and can be easily identified using routine spectroscopic techniques.[10]

Synthesis of the desired complex is accomplished by allowing $\alpha$-$[(n$-$C_4H_9)_4N]_4H_3PW_{11}O_{39}$ to react with $(\eta^5$-$C_5H_5)TiCl_3$ in 1,2-$C_2H_4Cl_2$. Recrystallization of the crude reaction product from $(CH_3)_2CO/C_6H_5CH_3$ yields pure $\alpha$-$[(n$-$C_4H_9)_4N]_4$-
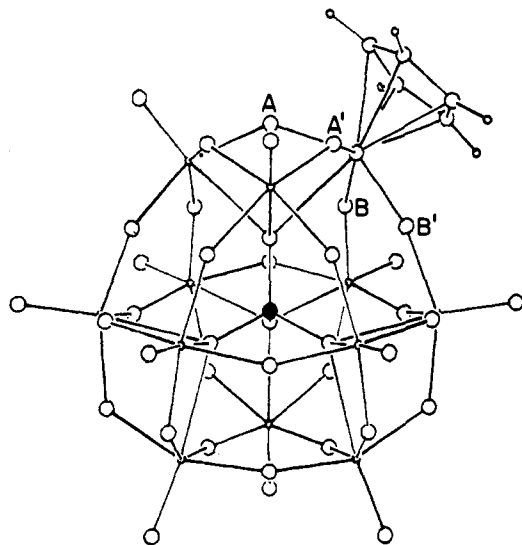
**Figure 1.** Proposed $C_s$ structure of the $\alpha$-[($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)]$^{4-}$ ion viewed approximately down the pseudo-$C_3$ axis of the central phosphate group. Within the $\alpha$-PW$_{11}$O$_{39}$$^{7-}$ ligand, small open circles represent tungsten atoms, large open circles represent oxygen atoms, and the large filled circle represents the phosphorus atom. The OWTi oxygens which are bonded to tungsten and titanium atoms are labeled; oxygens labeled with primes (') are related to those labeled without primes by reflection symmetry.

**Table I.** 13.5-MHz $^{17}$O NMR Chemical Shift Data

| anion[a] | chemical shifts[b,c] | | |
|---|---|---|---|
| | OW | OWTi | OW$_2$ |
| $\alpha$-PW$_{12}$O$_{40}$$^{3-}$ | 769 | | 431 |
| | | | 405 |
| $\alpha$-SiW$_{12}$O$_{40}$$^{4-}$ | 761 | | 427 |
| | | | 405 |
| $\alpha$-($\eta^5$-C$_5$H$_5$)Ti-(PW$_{11}$O$_{39}$)$^{4-}$ | 729 | 575 | 415 |
| | 720$^d$ | 558 | 396 |
| | | | 383$^d$ |

[a] Spectra were measured from 0.03–0.05 M CH$_3$CN solutions of $^{17}$O-enriched anions as ($n$-C$_4$H$_9$)$_4$N$^+$ salts at 80 °C. [b] Positive chemical shift in parts per million downfield from pure H$_2$O at 25 °C (±3 ppm). [c] Chemical shifts for the OXW$_3$ oxygens, X = P or Si, are not given here. [d] Shoulder.

[($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)] (**1**). This formulation is consistent with elemental analysis,[11] conductivity measurements,[12] and $^1$H NMR data.[13] The $C_s$ structure shown in Figure 1 is proposed on the basis of $^{17}$O NMR and IR spectroscopic data. The $^{17}$O NMR spectrum of **1** in CH$_3$CN displays two resonances of approximately equal intensity at 575 and 558 ppm which are assigned to the two types of bridging oxygens, each bonded to W and Ti atoms (see Table I and Figure 1). Comparison of the IR spectra of $\alpha$-[($n$-C$_4$H$_9$)$_4$N]$_3$PW$_{12}$O$_{40}$ (**2**) and **1** (see Figure 2) reveals striking similarities in the 650–1050-cm$^{-1}$ metal–oxygen stretching region which provide support for the proposed structural similarity of **2** and **1**. Note, however, that the 1080-cm$^{-1}$ triply degenerate asymmetric phosphate stretch for **2** is split into two bands at 1088 and 1060 cm$^{-1}$ in the spectrum of **1**. This splitting, caused by lowering of the tetrahedral phosphate site symmetry in **2**, has been observed in related complexes derived from PW$_{12}$O$_{40}$$^{3-}$ by replacement of a [W$^V$O]$^{4+}$ subunit by inorganic cations.[14] Evidence for the mode of cyclopentadienyl bonding is provided by the IR spectrum of the potassium salt $\alpha$-K$_4$($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)·$n$H$_2$O[15] (**3**) which displays a single, sharp absorption at 1445 cm$^{-1}$ in the 1300–1500-cm$^{-1}$ region. This feature is characteristic of the C–C stretch for a $\eta^5$-C$_5$H$_5$ ligand bonded to Ti$^{IV}$.[16]
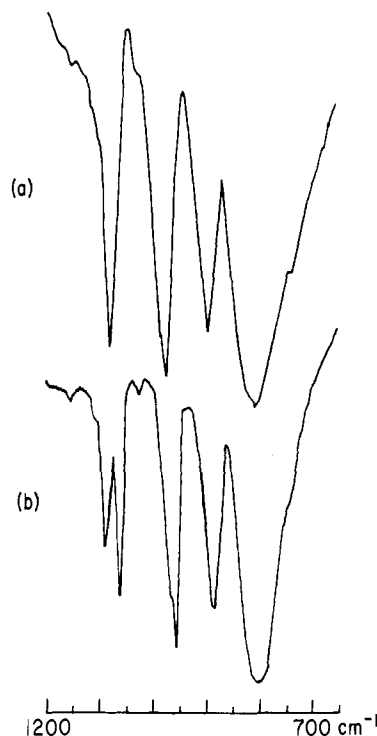


**Figure 2.** IR spectra of (a) $\alpha$-[($n$-C$_4$H$_9$)$_4$N]$_3$PW$_{12}$O$_{40}$ (**2**) in KBr pellet and (b) $\alpha$-[($n$-C$_4$H$_9$)$_4$N]$_4$[($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)] (**1**) in KBr pellet.

The $\alpha$-[($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)]$^{4-}$ ion differs markedly from all previously studied mononuclear oxygen-bonded complexes of mono(cyclopentadienyl)titanium(IV) with regard to hydrolytic stability. The alkoxides, phenoxides, carboxylates, and $\beta$-diketonates of [Ti$^{IV}$($\eta^5$-C$_5$H$_5$)]$^{3+}$ all decompose in the presence of water with loss of inorganic and/or organic ligands. The $\alpha$-[($\eta^5$-C$_5$H$_5$)Ti(PW$_{11}$O$_{39}$)]$^{4-}$ ion, however, is remarkably stable toward hydrolysis. A 0.05 M aqueous solution of its potassium salt, **3**, may be refluxed for 12 h without detectable decomposition.[17] Furthermore, a 0.05 M solution of **3** in 1 M aqueous HCl shows no decomposition after 12 at 25 °C.[17] Although this unprecedented stability is undoubtedly due in part to steric factors, we believe that electronic properties of the PW$_{11}$O$_{39}$$^{7-}$ ligand are also responsible. The ability of this ligand to serve as a "charge sink" which delocalizes negative charge away from the titanium coordination sphere is demonstrated by $^{17}$O NMR data given in Table I. Substitution of P$^V$ in $\alpha$-PW$_{12}$O$_{40}$$^{3-}$ by Si$^{IV}$ to yield $\alpha$-SiW$_{12}$O$_{40}$$^{4-}$ leads to an upfield shift of only 8 ppm for the terminal oxygen resonance, reflecting only a slight delocalization of the additional anionic charge to the terminal oxygens.[18] This result is consistent with the weakness (>2.2 Å[4,19]) of the bonds which connect the central (X$^{n+}$O$_4$)$^{(8-n)-}$ subunit with the surrounding W$_{12}$O$_{36}$ cage in the $\alpha$-X$^{n+}$W$_{12}$O$_{40}$$^{(8-n)-}$ structure. Substitution of a [W$^{VI}$O]$^{4+}$ subunit in $\alpha$-PW$_{12}$O$_{40}$$^{3-}$ by [Ti$^{IV}$($\eta^5$-C$_5$H$_5$)]$^{3+}$ to yield $\alpha$-[($\eta^5$-C$_5$H$_5$)-Ti(PW$_{11}$O$_{39}$)]$^{4-}$ leads to upfield shifts of at least 40 ppm for all terminal oxygen resonances. This pronounced displacement of chemical-shift values reflects extensive delocalization of the additional negative charge over the surface of the entire polyoxo anion. A comparison of the IR spectra of **1** and **2** (see Figure 2) similarly shows the effect of charge delocalization. The terminal oxygen vibrations for **1** at 995 cm$^{-1}$ are shifted to lower energy by 18 cm$^{-1}$ relative to the terminal oxygen vibrations for **2** at 973 cm$^{-1}$.

The stability of polyoxoanion supported [Ti$^{IV}$($\eta^5$-C$_5$H$_5$)]$^{3+}$ leads naturally to the question of whether more reactive organometallic species might be stabilized when incorporated into polyoxoanion structures. We are currently characterizing

compounds resulting from the reaction of a series of organo-metallic reagents with the $\alpha$-$H_3PW_{11}O_{39}^{4-}$ anion and other polyoxoanions. Preliminary results indicate that the compound reported here is only the first representative of a large family of polyoxoanion supported organometallic compounds.

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(12) The Onsager limiting slope for 1 in $CH_3CN$ is $2.6 \times 10^3$ $\Omega^{-1}$ $cm^2$ $equiv^{-3/2}$ $L^{1/2}$, a value which compares well with the slope of $2.5 \times 10^3$ $\Omega^{-1}$ $cm^2$ $equiv^{-3/2}$ $L^{1/2}$ for the 1:4 electrolyte $\alpha$-$[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ in $CH_3CN$.
(13) The $^1H$ NMR spectrum of 1 in $CD_3CN$ displays a $C_5H_5$ resonance at $\delta$ 6.5 ppm and an $NCH_2$ multiplet at $\delta$ 3.1–3.3 ppm with relative intensities 1: 6.6.
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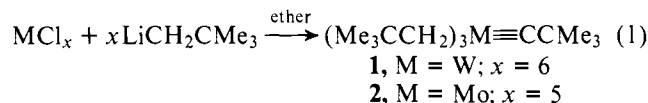
*Received May 26, 1978*

## Multiple Metal–Carbon Bonds. 12.[1] Tungsten and Molybdenum Neopentylidyne and Some Tungsten Neopentylidene Complexes
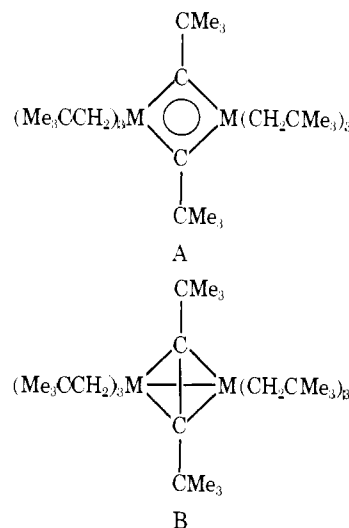
*Sir:*

The formation of alkylidene ($=CHR$) and alkylidyne ($\equiv CR$) complexes of Nb and Ta by $\alpha$-hydrogen abstraction, and acceleration of that process by adding small, basic tertiary phosphines, is now well established[1] ($R = CMe_3$ or $C_6H_5$). A significant question is whether any of these principles can be extended to group 4 or 6 metals. Establishing the latter is probably more important owing to the suspected role of W and Mo alkylidene complexes in the olefin metathesis reaction.[2] We present results here which demonstrate that this is possible. The rather extraordinary Mo and W complexes formed thereby are thermally stable, well-behaved, and easily characterized by standard techniques.

A clear, brilliant yellow solution is obtained when 6 mol of $LiCH_2CMe_3$ is added to $WCl_6$ in ether at $-78$ °C. When this is warmed to 25 °C, the color darkens to red-brown. Removing the solvent in vacuo and subliming the residue at 70 °C (1 $\mu$) gives yellow crystals of air-sensitive $(Me_3CCH_2)_3W\equiv CCMe_3$ (**1**) in 25% yield (eq 1) (Calcd for $WC_{20}H_{42}$: C, 51.51; H, 9.07. Found: C, 51.32; H, 8.90.). A similar reaction at 25 °C also gives **1** in 25% yield. The analogous $-78$ °C reaction between $MoCl_5$ and 5 mol of $LiCH_2CMe_3$ gives pale yellow, air- and light-sensitive $(Me_3CCH_2)_3Mo\equiv CCMe_3$ (**2**, 15% yield). Since the first mole of $LiCH_2CMe_3$ at 25 °C reduces W(VI) to W(V),[3] each reaction is not a straightforward double $\alpha$ abstraction (neopentyl $\rightarrow$ neopentylidene $\rightarrow$ neopentylidyne[1,4]) in a M(VI) alkyl complex. The tacky residue which remains after subliming out **1** or **2** gives broad, uninterpretable $^1H$ and $^{13}C$ NMR spectra. The residue is extremely soluble in pentane and no crystalline product could be obtained, even at $-78$ °C.

$$MCl_x + x LiCH_2CMe_3 \xrightarrow{\text{ether}} (Me_3CCH_2)_3M\equiv CCMe_3 \quad (1)$$

$$\textbf{1}, M = W; x = 6$$
$$\textbf{2}, M = Mo; x = 5$$

The molecular weight of **2** in cyclohexane is that expected for a dimer, while that of **1** is $\sim$75% of that expected for the dimer.[5] The mass spectra of **1** and **2** show only the monomeric ion.[6] These data suggest that **1** and **2** are dimers which dissociate readily. (Further evidence for this behavior is the reaction of **1** with $PMe_3$ to give monomeric products.) The two most reasonable formulations, A and B, are based on known ex-



amples containing each type of $MC_2M$ core. We favor A (or a distorted version thereof[7]) since two related molecules, $[Nb(CH_2SiMe_3)_2(CSiMe_3)]_2^{7b}$ and $[W(CH_2SiMe_3)_2(CSiMe_3)]_2^{7c,8}$ are planar, since we have not been able to add acetylenes to $(Me_3CCH_2)_3Mo\equiv Mo (CH_2CMe_3)_3^9$ to give B-type molecules,[10,11] and since the $^{13}C$ signal for the bridging carbon in $Mo_2Cp_2(CO)_4(MeC\equiv CMe)$ (a B-type molecule) is far upfield of where those in **1**, **2**, $[W(CH_2SiMe_3)_2(CSiMe_3)]_2$, and $[Ta(CH_2SiMe_3)_2(CSiMe_3)]_2$ are found (see below).[12] The metal in known B-type molecules is also in a lower than maximum oxidation state, while that in known A-type molecules is in the maximum formal oxidation state.

The gated decoupled $^{13}C$ NMR spectrum of **1** in $C_6D_6$ shows only one set of six resonances.[13] Therefore, either monomer–dimer interconversion is fast on the $^{13}C$ NMR time scale or $>\sim$95% of one is present. The neopentylidyne $C_\alpha$ resonance is found at 317 ppm, at the high end of the range for $C_\alpha$ in terminal alkylidyne complexes of several types[4,14] and bridging alkylidyne $\alpha$-carbon atoms in $[W(CH_2SiMe_3)_2(CSiMe_3)]_2$ (353 ppm)[8b] and $[Ta(CH_2SiMe_3)_2(CSiMe_3)]_2$ (404 ppm).[8b] Its coupling to $^{183}W$ ($J_{CW} = 230 \pm 5$ Hz) is