Synthesis, Isolation, and Spectroscopic Characterization of Trivanadium Polyoxoanion-Supported (C₅H₅)₃Ti³⁺: (Bu₄N)₄[CpTi₃Si₃W₁₅V₃O₆₀] and (Bu₄N)₆[CpTi₂P₂W₁₅V₅O₆₂]

Brian M. Rapko,* Matthias Pohl, and Richard G. Finke†,‡
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received March 16, 1994

Reaction of the trivanadium-substituted polyoxometalates (Bu₄N)₄Si₃W₁₅V₅O₆₀ and (Bu₄N)₆P₂W₁₅V₅O₆₂ with an equimolar amount of CpTi³⁺ leads to the formation of the polyoxometalate-supported organometallic complexes [CpTi₃Si₃W₇V₃O₆₁]⁺, 1, and [CpTi₂P₂W₁₅V₅O₆₂]⁴⁺, 2, respectively. These complexes were isolated as their Bu₄N⁺ salts and subsequently characterized by a complete elemental analysis and ³¹P, ¹³⁵W, ⁵¹V, and ¹³C NMR spectroscopy as well as FAB-MS, IR, and sedimentation-equilibrium molecular-weight measurements. For compound 1 additional data in the form of 2-D INADEQUATE ¹³⁵W[⁵¹V] NMR spectra were collected. Both 1 and 2 are homogeneous, regiospecifically supported CpTi³⁺ complexes of overall C₅ symmetry. Solution structures, derived from and in accord with the observed spectroscopic data, are proposed. The synthesis and initial solution spectroscopic characterization of the non-cyclopentadienyl, CITi³⁺ complex, CITi₃Si₃W₇V₃O₆₁⁺, is also reported, a nominally highly coordinatively unsaturated Ti(IV) complex on route to more reactive catalyst precursors.

Introduction

Recent work involving the synthesis of tribimetal-incorporated heteropolytungstates is motivated by the hypothesis that these compounds might serve as analogs of heterogeneous metal oxides, Figure 1. Following the first report of polyanion surface-supported metals by Flynn and Stucky and development (CsH5)Ti3+: [3]

(1) (a) Battelle, Pacific Northwest Laboratories, Box 999, Richland, WA 99352. (b) University of Oregon. (c) Present address: Colorado State University, Ft. Collins, CO 80523.

Klemperer and Day's Nb₂W₄O₁₉ isopolyoxoanion³ and our P₂W₁₅NbO₆₂⁻ and SiW₉V₃O₆⁻ heteropolyoxoanion systems. Our preliminary report⁶ of CpTi/Si₃W₇V₃O₆₁⁺ constituted the first example of a vanadium-substituted polyoxoanion-supported organometallic, and only three other examples of vanadium-supported organometallics, [(C₅Me₅)Rh](V₁₇O₅₄)⁶⁺ [(1,5-COD)-Ir(V₁₂O₃₂)]⁺, and [(1,5-COD)Ir(V₁₂O₃₂)]⁺, have since appeared.

The key goals for the present investigation are as follows: (a) preparation of the first organonitrogen-metallated derivatives supported on Keggin² and Dawson² trivanadium-substituted polyoxoanions, Si₃W₇V₃O₆₁⁻ and P₂W₁₅V₅O₆₂⁻, respectively; (b) verification that the organometallic complex is bonded directly and covalently to the surface of the heteropolytungstate in solution (there, because of our interest in polyoxoanion-supported homogeneous catalysts); and (c) determination of at least the symmetry of the complex and any other structure information that can be obtained, again in solution as well as in the solid state, if possible.

(7) (a) Recently we have shown that (Bu₄N)₄[N₅(1,5-COD)-Ir[P₂W₁₅NbO₆₂]-] is a good precatalyst leading to quite active catalysts for both hydrogenation⁷ and oxygenation reactions. This complex was characterized by a complete elemental analysis plus ³¹P, ¹³⁵W, ⁵¹V, and ¹³C NMR, IR, and sedimentation-equilibrium molecular-weight measurement.¹⁰¹³⁵W NMR studies demonstrate that (1,5-COD)Ir binds to NbO₂ bridging oxygens of the Nb₂O₃ oxygen surface in the soluble, metal oxide support system, P₂W₁₅NbO₆₂⁻. The resultant atom-level characterization in solution of [(1,5-COD)Ir(P₂W₁₅NbO₆₂)]⁺ makes it the only monomeric, regiospecifically-supported polyoxoanion-transition-metal complex that also serves as a demonstrated precatalyst (and for which extensive mechanistic studies of the true catalyst have been completed).¹¹ (b) Mizuno, N.; Lyon, D. K.; Finke, R. G. J. Catal. 1991, 128, 84. (c) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. Inorg. Chem. 1990, 29, 1784. (d) Pohl, M.; Finke, R. G. Organometallics 1993, 12, 1453. (e) Lin, Y.; Finke, R. G. J. Am. Chem. Soc., in press. (f) Trovarelli, A.; Weber, H.; Lin, Y.; Finke, R. G. Manuscript in preparation.


0020-1669/94/1333-3625$04.50/0 © 1994 American Chemical Society
CpTi(CH(CN))3(NO3)3 + (Bu4N)2SiW9V3O47 → (Bu4N)[CpTi2SiW9V3O47 + xCH3CN + 3Bu4N+NO3-]

The good but not excellent yield is actually a 3-fold improvement over that observed initially.\(^{6a}\) It represents a fairly optimized, checked Inorganic Syntheses preparation and yield.\(^{6b}\) Yield-liming side reactions appear to stem (a) from any use of CpTiCl3 that has not been vacuum sublimed (in fact, one cannot use commercial (Alfa) CpTiCl3, which shows several residues in the IH NMR over and above the one resonance for the Cp ligand), (b) from residual H2O, resulting from failure to dry the glassware or CH3CN sufficiently, which is known to react with\(^{10b}\) CpTiCl3, (c) from the fact that removal of the A+ from HSiW9V3O47- using OH- occurs with up to 25% decomposition\(^{10b}\) of the SiW9V3O472- and (d) from any residual OH-, present from the deprotonation/decomposition of HSiW9V3O472-, which reacts rapidly with CpTi+ leading to side products.

The (Bu4N)4[CpTi2SiW9V3O47 product is obtained as an analytically pure, homogenous, dark-orange solid (i.e., free of the contaminating by-product of 3 equiv of Bu4N+NO3−) by either repeated precipitation using chloroform or crystallization employing vapor-diffusion techniques. Elemental analysis of the recrystallized reaction product (all elements, and adding up to 100.07%) is in accord with an empirical formula of [(Bu4N)4[CpTi2SiW9V3O47], 6. Solution molecular weight measurements using the sedimentation equilibrium method \((M_C\text{calc for (Bu4N)4[CpTi2SiW9V3O47] = 3558, } M_C\text{found) 3500 (supplementary material, Figure A), where } M_C = \text{the weight-average molecular weight} \text{ are in accord with a monomeric formulation, } n = 1.\) A positive ion FAB mass spectrum (supplementary material, Figure B) verifies the solution MW results by showing the expected parent ion, \((\text{Bu4N})_4\text{[CpTi2SiW9V3O47]}, \text{ at } m/e = 3559.\) Well-established cationization processes, that is the exchange of Bu4N+ for H+, and fragmentation processes such as loss of oxygen, \(m/e = 16,\) were also seen as is typical for these heteropolytungstates.\(^{11,12}\) Interestingly, loss of the organometallic fragment CpTi2+ \((m/e \text{ for CpTi2+ = 113) is not observed,}^{11a}\) at least not in the positive ion FAB-MS spectrum (however, positive ion polyoxoanion FABMS typically exhibit less fragmentation than negative ion spectra).\(^{11}\)

The IH NMR provides an easy and sensitive means to judge the isomeric purity of the complex. Specifically, upon support the CpTi2+ fragment shows a significant shift in the Cp resonance from δ 7.15 in the starting solvate CpTi(CD3CN)(NO3) to δ 6.90 in the (Bu4N)4[CpTi2SiW9V3O47 product. In addition, further evidence for the purity and homogeneity of the isolated product is provided by a single-line 29Si NMR, as well as clean \(^{115}V \text{(Figure 2, inset) and }^{183}W \text{ NMR (Figure 2) spectra.}\)

Chemical Evidence for Inner-Sphere TiIV-to-Polyoxoanion Binding. A crucial question is whether the organometallic fragment is chemically bonded to the surface of the heteropolytungstate or behaving as a simple counterion. Several pieces of chemical evidence require that the CpTi2+ fragment be tightly and covalently attached to the polyoxoanion surface. First and foremost is the stability of (Bu4N)4[CpTi2SiW9V3O47 to the humid Oregon atmosphere, especially since CpTi3+ compounds tend to be quite moisture sensitive\(^{10b}\) (as confirmed in a control experiment showing that the yellow starting material CpTi(CH3CN)(NO3)2 decomposes in solution within \(1/2\) h upon exposure to the atmosphere). In dramatic contrast to this, and with no precautions taken to exclude oxygen or moisture, (Bu4N)4[CpTi2SiW9V3O47 remains unchanged after several days in solution or after up to 1 year as a solid (by \(^{1}H \text{ and }^{115}V \text{ NMR and IR). This enhanced stability toward moist air is readily}}

Figure 1. Polyhedral and space-filling representations of A-β-SiW9V3O47-(A, B) and of B-α-P2W15V3O62-(C, D). In the polyhedral representation (A, C) the silicate (for A-β SiW9V3O47,- A) and the phosphate cores (for B-α P2W15V3O62,- C) are represented by black tetrahedra, while the white octahedra represent WO6 groups. Chalk octahedra represent VO4 units. The space-filling representations (B, D) show only the surface oxygens with the terminal oxygens represented in black and bridging oxygens in white. From the space-filling representation it becomes clear that heteropolyoxoanions are composed of close-packed oxygens, hence, their potential as soluble metal oxide analogs.

Herein we report the full details of the synthesis and characterization of the polyoxoanion-supported CpTi2+ complexes\(^{6a}\) [CpTi2SiW9V3O47]+ and [CpTi2P2W15V3O62]. A preliminary communication\(^{6a}\) and an Inorganic Syntheses preparation\(^{6b}\) of [CpTi2SiW9V3O47]+ have appeared, but a full report of our characterization work has not been previously published. In addition, nothing about the synthesis and characterization of [CpTi2P2W15V3O62]\(^{6c}\) has been previously published (i.e., beyond the initial work reported in a Ph.D. thesis).\(^{6d}\) This latter complex is especially important in that its symmetry is unequivocally established to be C3v rather than the previously anticipated C3, for reasons also discussed herein.

Results and Discussion

Synthesis and Initial Characterization of (Bu4N)4[CpTi2SiW9V3O47]. The deep orange title complex I is obtained from the reaction of freshly vacuum sublimed CpTiCl3 with 3 equiv of AgNO3 in CaHz/molecular sieve in situ generated, yellow solution of 100% CpTi(CH3CN)3-(NO3)2 to a cherry red solution of (Bu4N)4SiW9V3O47 also in dried CH3CN. Extractive workup and crystallization (see the Experimental Section) yields dark-orange (Bu4N)4[CpTi2SiW9V3O47] in 59% overall yield (eq 1).

Equation 1

\[
\text{CpTi(CH(CN))3(NO3)3 + (Bu4N)2SiW9V3O47} \rightarrow \text{(Bu4N)[CpTi2SiW9V3O47 + xCH3CN + 3Bu4N+NO3-]}
\]

(a) Evidence for TiIV-NO3 bonding exists, hence the CpTi(CH3CN)3-(NO3)2 formulation: Wailes, P. C.; Coutts, R. S. P.; Weingold, H. Organometallic Compounds of Titanium, Zirconium and Hafnium; Academic Press: New York, 1974. (b) The sensitivity of CpTi2+ compounds to hydrolysis is well established as detailed elsewhere.\(^{10c}\) Note that the hypothetical, 7-coordinate analog CpTi(OR)2- is apparently unknown as a stable entity (see Table III, pp 40-43 elsewhere), although 7 and higher coordination for CpZr2+ complexes are well established;\(^{10d}\) points verified in another tabulation: Cardin, D. J.; Lappert, M. F.; Raston, C. L. Chemistry of Organometallic Compounds; Ellis Horwood Ltd.: Chichester, U.K., 1986; Chapter 2.
surface oxygens. (In fact, the enhanced CpTi\(^{3+}\) stability is hard to rationalize in any other way.)

To confirm the nonexchangeability of the polyoxoanion surface-attached CpTi\(^{3+}\), experiments employing ion-exchange resins were performed. The prediction for a tightly bound [CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] complex is that both the cationic CpTi\(^{3+}\) organometallic fragment and the polyanionic SiW\(_9\)V\(_{30}\)O\(_m\)\(^{-}\) component—that is, the intact complex—should be retained on an anion-exchange resin, P-NR\(_3\)\(^{+}\)Cl\(^{-}\) (P = macroreticular polymer), but that both should pass together and unaltered through a cation-exchange resin, P-SO\(_3\)-Bu\(_4\)N\(^{+}\). On the other hand, if the CpTi\(^{3+}\) fragment is dissociable or behaving as a simple countercation, attached CpTi\(^{3+}\), experiments employing ion-exchange resins were only CpTiCl\(_3\) should be recovered following exposure to an anion-exchange resin, P-NR\(_3\)\(^{+}\)Cl\(^{-}\). Experimentally both the CpTi\(^{3+}\) fragment (as indicated by IR) in [CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] pass together and unaltered through a P-SO\(_3\)-Bu\(_4\)N\(^{+}\) cation-exchange resin, while both components are retained together on a P-NR\(_3\)\(^{+}\)Cl\(^{-}\) anion-exchange resin. Clearly, the CpTP fragment attaches close to (and probably onto) these edge-shared bridging oxygens (a full normal coordinate analysis plus Raman studies\(^{26}\) would, however, be required to unequivocally support or refute this interpretation).

The 51\(^{V}\) NMR spectrum (Figure 2, inset) for [CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)]\(^{4-}\) shows two resonances of 1:2 intensity at -561 and -604 ppm and thus reveals that the symmetry of the complex is Cs, a change from the C\(_2\) symmetry seen for (and expected in) the starting material, SiW\(_9\)V\(_{30}\)O\(_{40}\)^{-} as deduced from its single 51\(^{V}\) NMR resonance at \(\delta = -531\). The 183\(^{W}\) NMR spectrum (Figure 2) confirms this Cs symmetry by exhibiting the expected five-line spectrum with relative intensities of 2:2:1:2:2 at -75.1, -83.2, -112.3, -129.3, and -132.2 ppm, respectively. Decoupling of the -561 ppm resonance in the 51\(^{V}\) NMR results in a corresponding sharpening of the -71.5 and -112.3 ppm resonances, analogous to the behavior observed\(^{26}\) with HSiW\(_9\)V\(_{30}\)O\(_{40}\)\(^{-}\) (and likewise indicating that the broadened resonances observed in the coupled spectrum result from scalar relaxation of the tungsten atoms coupled to the unique vanadium atom\(^{28}\)).

Tungsten to tungsten connectivities for the \(C_2\) symmetry (Bu\(_4\)N\(_2\))[CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] were unambiguously established by the 51\(^{V}\)-decoupled 2-D INADEQUATE 183\(^{W}\)(51\(^{V}\)) NMR spectrum previously reported\(^{26}\). The assignments for this 2-D INADEQUATE 183\(^{W}\)(51\(^{V}\)) NMR spectrum are consistent only with an A-\(\beta\) SiW\(_9\)V\(_{30}\)O\(_{40}\)\(^{-}\) heteropolyanion framework and, therefore, require that the attachment of the CpTP fragment occurs without isomerization of the A-\(\beta\)-structure\(^2\) of the parent SiW\(_9\)V\(_{30}\)O\(_{40}\)\(^{-}\) heteropolytungstate. The two most likely Cs symmetry solution structures for [CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)]\(^{4-}\) are presented in Figure 7 and will be discussed along with the (related) structure for

---

**Figure 2.** Five-line 183\(^{W}\) NMR (15 MHz) of 2:2:1:2:2 relative intensity of 0.23 M \(\beta\)(Bu\(_4\)N)\(_2\)[CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] in 2:1 DMF/CD\(_3\)CN following 100,000 pulses collected over 23 h. The sharpening of the -83 and -112 ppm resonances following decoupling of the -561 ppm resonance in the 51\(^{V}\) NMR (boxed inset) is shown as insets adjacent to the appropriate resonances.

**Figure 3.** IR of (Bu\(_4\)N)\(_2\)[CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] (A) (top) obtained with matched NaCl cells in CH\(_3\)CN vs a CH\(_3\)CN reference, showing the 35-cm\(^{-1}\) splitting of the 800-cm\(^{-1}\) band assignable\(^{12,13}\) to a \(v_{\text{M-O-M}}\) vibration between edge-sharing metal octahedra. The IR of (Bu\(_4\)N)-SiW\(_9\)V\(_{30}\)O\(_m\) (B) (bottom) is shown for comparison. The 800-cm\(^{-1}\) band splitting is good, albeit not unequivocal, evidence for attachment of the CpTP\(^{3+}\) to oxygens of edge-shared, rather than corner-shared, octahedra in SiW\(_9\)V\(_{30}\)O\(_{40}\)\(^{-}\).

---

(12) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *Specrrosc. Lett.* 1979, 12, 127. (b) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, *Inorg. Chem.* 1984, 23, 598. (c) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* 1983, 22, 207. (d) The 5\(^{1}V\) NMR spectrum (Figure 2, inset) for [CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)]\(^{4-}\) was obtained by IR and multinuclear \(5^{1}\)\(^{V}\) and 183\(^{W}\) NMR spectroscopy. Careful examination of the IR spectrum of (Bu\(_4\)N)\(_2\)[CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)] shows two especially informative features in comparison to the starting material, (Bu\(_4\)N)\(_2\)[SiW\(_9\)V\(_{30}\)O\(_m\)] (Figure 3). First, the band in the region assignable to a terminal M=O vibration\(^{12,13}\) increases from 940 cm\(^{-1}\) for (Bu\(_4\)N)\(_2\)[SiW\(_9\)V\(_{30}\)O\(_m\)] to 965 cm\(^{-1}\) for (Bu\(_4\)N)\(_2\)[CpTi-SiW\(_9\)V\(_{30}\)O\(_m\)]; triprotonation as in (Bu\(_4\)N)\(_2\)[SiW\(_9\)V\(_{30}\)O\(_m\)].

charged polyoxoanions as their Bu4N+ salts and from of crystallization (the primary method of purification available and adding up to 99.79%) in conjunction with solution molecular sphere, a complex set of reactions takes place leading to unidentified V-containing products. However, for Bu4N+OH-, only a single resonance at ca. -562 ppm was observed. (The nature of these products was not investigated further, in large part because of our decision to focus on the catalytic reactivity of polyoxoanion-supported [{(1,5-COD)Ir}]+, i.e., and not the stoichiometric reactions of supported CpTi3+).

The first, quasi-reversible quasi-reversible quasi-reversible reduction wave in the cyclic voltamogram of (Bu4N)6[CpTi-P2W15V3O62]6- (supplementary material, Figure D) occurs at a 0.7 V more positive potential (Ep = \( \approx 0.3 \) V vs SCE) in comparison to the deprotonated starting material, SiW9V3O401- (Ep = \(-1.0 \) V vs SCE; see Table 1 and Figure 25 on pp 76-78 elsewhere). This behavior is similar to the one observed for the tripotated heteropolytungstate (Bu4N)9P2W15V3O62 which also exhibits a positive quasi-reversible quasi-reversible quasi-reversible reduction wave (Ep = \( \approx 0.1 \) V vs SCE, consistent with the significantly reduced (four minus) negative charge in the CpTi3+ or H33+- attached heteropolytungstates, [CpTi-SiW9V3O401-] and H3Si-W9V3O401- relative to the (seven-minus) SiW9V3O401- starting material.

Synthesis and Establishment of the Molecular Formula of (Bu4N)6[CpTi-P2W15V3O62]6-. The reaction of CpTi3+ with the B-type deprotonated heteropolytungstate (Bu4N)9P2W15V3O62 (eq 2) proceeds in a fashion analogous to that previously reported for (Bu4N)6SiW9V3O401- to yield red-brown solid product. Again, it is important to use vacuum sublimed CpTiCl3, dry CH3CN, and dry glassware and to be sure that (Bu4N)9P2W15V3O62 has been prepared with the proper number of equivalents of Bu4N+-OH (i.e., that the (Bu4N)9P2W15V3O62 is free of excess OH; see the Experimental Section for further details).

Analytically pure 2 was obtained as a homogeneous, dark powder in 62% yield following the removal of the contaminating 3 equiv of Bu4N+NO3- by repeated reprecipitation, using ethyl acetate (i.e., instead of chloroform as was used for (Bu4N)x-[CpTi-SiW9V3O401-]). Unlike (Bu4N)9P2W15V3O62, the use of crystallization (the primary method of purification available in heteropolytungstate chemistry), was not successful despite repeated attempts. Unfortunately, the crystallization of highly charged polyoxoanions as their Bu4N+ salts and from organic solvents has, perhaps not unexpectedly, proved quite difficult in our experience.

The purity and molecular composition of (Bu4N)9P2W15V3O62 were established by elemental analysis (all elements, and adding up to 99.79%) in conjunction with solution molecular weight measurements (supplementary material, Figure E) (\( M_r^{cal} \) (calc for (Bu4N)9[CpTi-P2W15V3O62]) 5532, \( M_r^{found} \) (found) 5700).

A positive ion FAB mass spectrum (supplementary material, Figure F) confirms the solution MW with envelopes corresponding to the parent ion plus loss of oxygen being observed, ([Bu4N]H+[CpTi-P2W15V3O62] - 2(O))6+ and ([Bu4N]H+[CpTi-P2W15V3O62] - 6(O))6+. The expected cationization is also observed in the FAB-MS, but again, loss of the CpTi3+ organometallic fragment is not observed. In addition, the lack of any intensity corresponding to a [(Bu4N)9P2W15V3O62]6+ envelope in the positive ion FAB mass spectrum, where cationization is such a characteristic phenomenon, provides strong evidence in and of itself that CpTi3+ is a tightly attached moiety (i.e., it is not behaving as a simple counterion).

Chemical and Spectroscopic Evidence for Inner-Sphere TiN-to-Polyoxoanion Binding. Both chemical tests and spectroscopic evidence again suggest, as with (Bu4N)9[CpTi-SiW9V3O401-], that the CpTi3+ in [CpTi-P2W15V3O62]-6 is tightly attached to the surface of the heteropolyanion. Specifically, the (Bu4N)x-[CpTi-P2W15V3O62] product appears to be indefinitely stable as a solid or in solution, that is, is not moisture sensitive in contrast to CpTi(CH3CN)4(NO3)3. And, running (Bu4N)9[CpTi-P2W15V3O62] down a P2O5-Bu4N+cation-exchanger resin showed no retention of the dark orange solution, suggesting that CpTi-(solvate),16 does not readily dissociate from the polyoxoanion's surface.

The 31P NMR spectrum (Figure 4) shows a simple two-line spectrum with resonances at -8.9 and -13.6 ppm, substantially different from the -6.9 and -14.6 ppm resonances of (Bu4N)9P2W15V3O62 starting material. This two-line 31P NMR spectrum confirms the homogeneity of, and thus the support-site reactivity of [CpTi-P2W15V3O62]-6. Further fortification for the single product nature of the CpTi3+ support reaction is

\[ \text{[CpTi-P}_2\text{W}_{15}\text{V}_0\text{O}_{62}]^6- \]
the single Cp resonance seen in the 1H NMR, δ 6.85 (CD3CN). The shift in this Cp resonance from δ 7.05 for the starting material to a value very similar to that of δ 6.90 seen for (Bu4N)6[CpTi(SiW9V3O40).1, is consistent with a closely similar titanium coordination sphere in both the supported Cpti3+ complexes, 1 and 2.

Examination of the 51V NMR spectrum (Figure 5) proved both surprising and structurally informative. Rather than the single-line 51V NMR spectrum expected for a C3v symmetry product, a clean, two-line, 2:1 intensity spectrum is observed with resonances at -544 and -519 ppm, respectively. This result requires that [CpTi(P2W15V3O62)-] has overall C3v symmetry (a result confirmed by the eight-line 183W NMR; vide infra). Variable-temperature 51V NMR studies between 5 and 45 °C demonstrate that the two-line spectrum, and therefore the C3v symmetry, is unchanged in this temperature range (only reversible line width changes are seen).

The IR spectrum of (Bu4N)6[CpTi(P2W15V3O62)3 provides relatively little structural information. The major change relative to the (Bu4N)6[P2W15V3O62] starting material is in the ca. 800-cm⁻¹ band, assignable12 to edge-sharing M=O-M oxygens, which broadens and shifts to lower energy. Again, this is suggestive of (but, again, is not conclusive proof of) Cpti3+ attachment to a value very similar to that of 6 6.90 seen for (Bu4N)6[CpTi(P2W15V3O62)3.

Proposed [CpTi(P2W15V3O62)+] Structure in Solution. Since there is unequivocal demonstration of C3v symmetry for [CpTiP2W15V3O62]-, and if the highly probable (but rigorously unproven) "piano-stool" or pseudotetrahedral ligand arrangement usually found for CpTiL3 compounds16 is maintained, then a single structure for [CpTi(P2W15V3O62)-] becomes the most reasonable solution structure, Figure 6. [If, however, Cpti3+ prefers to attach to four ligands oxygen of P2W15V3O62]-, then C3v symmetry structures (supplementary material, Figure G) with Cpti3+ off the side of the polyoxoanion become possible, although this seems much less likely given that the edge-sharing V-O-V bridging oxygens are the most basic (more so than V=O), and the central dark tetrahedrons are PO4 groups. In the close-packed oxide representation (A) and as its more realistic, close-packed oxide representation (B).

![Figure 5](image_url)  
**Figure 5.** Clean, two-line 51V NMR spectrum of (Bu4N)6[CpTi(P2W15V3O62)] showing the 1:2 intensity of the two signals. The two-line spectrum requires that the Cpti3+ attach to the originally C3v symmetry P2W15V3O62- heteropolytungstate in a way that yields an overall C3v symmetry complex.

![Figure 6](image_url)  
**Figure 6.** Proposed C3v symmetry structure for [CpTi(P2W15V3O62)+] shown with the polyoxoanion represented as its idealized corner and edge-sharing polyhedra representation (A) and as its more realistic, close-packed oxide representation (B). In the polyhedra representation (A), the hatched octahedra represent VO6, the white octahedra represent WO6 and the central dark tetrahedrons are PO4 groups. In the close-packed oxide representation (B), the open circles represent bridging oxygens while the solid ones represent terminal, multiply bonded oxygens. The Cpti3+ group is shown attached to a C3v symmetry site formed by two 


... (continued)
Figure 7. Two most probable C₄ symmetry structures for [CpTi-SiW₉V₃O₆]⁺ shown with the polyoxoanion represented as its idealized corner and edge-sharing polyhedra representation (A, C) and as its more realistic, close-packed oxide representation (B, D). In the polyhedra representation (A, C), the VO₆ octahedra are numbered 1–3, the WO₆ octahedra are numbered 4–12, and the central dark tetrahedron is the SiO₄ group. In the close-packed oxide representation (B, D) the open circles represent bridging oxygens, while the solid ones represent terminal, multiply bonded oxygens. The most likely structure of the two possibilities, based primarily on analogy to the proposed structure of [CpTi₂P₂W₁₅V₃O₆]⁻ shown in Figure 6, is the one in A and B where the CpTi⁺ group is attached to the two bridging oxygens (V₁–O–W₄, V₁–O–W₈) plus one terminal oxygen (V₁–O) of a B-type triad array (V₁, W₄, W₈) of edge-sharing octahedra. Note that two additional symmetry-equivalent sites exist (V₂, W₅, W₆ and V₃, W₇, W₈). [Again, it is not possible to exclude unequivocally CpTi attachment at the 4 oxygen, C₄ symmetry sites (e.g., the 4 bridging oxygens between V₁, V₂, W₄, W₈) but the large perturbation of IR band assignable to the edge-sharing M–O–M, and the precedent of [CpTi₂P₂W₁₅V₃O₆]⁻ in Figure 6, make this a seemingly unlikely possibility.]

Table 1. 2Jw-w. Coupling Constants for the Organometallic Supported Heteropolytungstates A-β-(Bu₄N)₂(Cp*Rh*SiW₉V₃O₆), and A-β-(Bu₄N)₃(SiW₉V₃O₆)

<table>
<thead>
<tr>
<th>octahedra</th>
<th>A-β-(Bu₄N)₂(Cp<em>Rh</em>SiW₉V₃O₆)</th>
<th>A-β-(Bu₄N)₃(CpTi*SiW₉V₃O₆)</th>
<th>A-β-(Bu₄N)₃(SiW₉V₃O₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₁₀ to W₄,₈</td>
<td>13.4</td>
<td>16.8</td>
<td>15.3 ± 1.2</td>
</tr>
<tr>
<td>W₄,₈ to W₅,₈</td>
<td>30</td>
<td>28</td>
<td>(W₄,₈ to W₁₀,₁₂)²</td>
</tr>
<tr>
<td>W₁₁,₁₂ to W₆,₇</td>
<td>not obsd (&gt;13 Hz)</td>
<td>12.8</td>
<td>15</td>
</tr>
<tr>
<td>W₁₁,₁₂ to W₅,₈</td>
<td>16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* That is, only two types of W are present in this C₄₆ symmetry complex.

Figure 7 involving a terminal V–O oxygen. Unfortunately, extensive attempts to date to obtain highly diffracting single crystals have been unsuccessful (see the Experimental Section for details), although there may still be hope here using alkali metal cations in water.¹⁹

The analogous triinobium heteropolytungstate again provides an interesting comparison. Specifically in (Bu₄N)₂(Cp*Rh*SiW₉V₃O₆), an important piece of background information is that the heteropolyoxoanion's W–W connectivity was established by examining the 2Jw-w coupling constants in the ¹⁸¹W NMR,²² Table 1. Marked changes in the corner-sharing W–O–W coupling constants from their normal values were noted.²² On the basis of the M–O–M long/short bond-alternation model for charge delocalization investigated in detail in other systems by Klemperer and Day,²³ it was concluded that the observed pattern of coupling

(21) (a) This argument follows even though Pope's system is d₁, V⁴⁺=O, since the d₂ electron is added primarily to a d₄ orbital and thus the terminal V⁴⁺=O oxygen should still be relatively nonbasic. (b) See the MO diagram that is in Figure 4 on p 369 elsewhere: Pope, M. T. Mixed-Valence Compounds; Brown, P. B., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1980.

constants in [Cp*RhSiW9Nb3O40]5− could be accounted for by strong Rh(III)−O−polyyxanion bonding. This, in turn, results in a "lifting" of the triad of M−O−M-containing octahedra to which the Cp*Rh(III) is attached, that is, a lifting of the M−O−M triad of octahedra away from the rest of the heteropolytungstate and toward Cp*Rh(III). The key point here is that the C1 symmetry and same pattern of coupling constant deviations are observed for \([Bu4N]2[Cp*TiSiW9V4O40]\), Table 1. Consequently (and regardless of the detailed explanation of the 2\(J_{W-W}\) coupling constant changes), the bonding between Cp*Ti(III) and SiW9V4O40− must be very similar if not essentially identical to that in \([Cp*RhSiW9Nb3O40]\).

Overall, then, the simplest explanation of all the available data (and requirement for C1 symmetry structures) is that \([Cp*Ti2P2W15V4O68]6−\) and \([Cp*TiSiW9V4O40]5−\) both have structures analogous to that shown in Figure 6, in which a terminal V−O oxygen is involved (plus 2 V−O−V oxygens for \([Cp*Ti2P2W15V4O68]6−\) or plus 2 V−O−W oxygens for \([Cp*TiSiW9V4O40]5−\)).

Preliminary Investigation of the More Reactive Catalyst Precursor \((Bu4N)4[C1TiSiW9V4O40]\). Preliminary attempts to make a more reactive, polyyxanion "oxide-supported" titanium center proved very promising (see pp 261−263 and 267 elsewhere). Using either TiCl4 or the crystalline, sublimable \(TiCl4(CH2)2\) plus \((Bu4N)3SiW9V4O40)\) in an inert-atmosphere (N2) drybox and using dry dichloroethane with refluxing for 1 h resulted in a reasonable clean product according to eq 3.

\[
(Bu4N)3SiW9V4O40 + TiCl4 \rightarrow (Bu4N)4[C1TiSiW9V4O40] + 3Bu4N+Cl− \tag{3}
\]

The 183W NMR again shows a five-line spectrum, indicative of a C1 symmetry product, with peaks at −76.8, −94.3, −104.0, −114.0, and −115.4 of relative intensities 2:2:2:2:1, respectively (supplementary material, Figure H). IR further confirms that the supported C1TI3+ product is quite similar to \([Cp*Ti2P2W15V4O68]6−\) in that a 30-cm−1 shift to higher energy of the band assignable to a terminal M−O−M vibration is seen along with the characteristic ca. 35-cm−1 splitting of the 800-cm−1 band. The implication is that \([C1TiSiW9V4O40]5−\) has the same structure as \([Cp*TiSiW9V4O40]5−\). Some additional details for this interesting complex are available in the Experimental Section and on pp 261−263 and 267 elsewhere. This supported C1TI3+ complex is worthy of additional studies of its reactivity and possible catalysis, as is the preparation of the currently unknown analog, \([C1TiP2W15V4O68]5−\).

Summary

The synthesis and characterization in solution of surface-supported C1TI3+ complexes, using the trivanadium-substituted heteropolytungstates SiW9V4O40− and P2W15V4O68− as support systems, has been described. Both complexes \((Bu4N)4[Cp*TiSiW9V4O40]\), 1, and \((Bu4N)4[Cp*TiP2W15V4O68]\), 2, were obtained as analytically pure, homogenous solids, and both complexes were characterized compositionally by a complete elemental analysis, solution molecular-weight measurements, and FAB-MS. Multinuclear NMR spectroscopy was also employed, especially 51V and 183W NMR (and including 2-D INADEQUATE 183W 51V NMR for 1). The spectroscopic results unequivocally demonstrate the C1 symmetry of both complexes and allow deduction of the most probable C1 symmetry solution structures for 1 and 2. Preliminary evidence for a more reactive, also C1 symmetry complex \((Bu4N)4[C1TiSiW9V4O40]\) (and, by inference, its \("[C1TiP2W15V4O68]5−\) analog) was also reported.

There are, however, still a number of needed or interesting experiments in this area worthy of additional effort. Our own resources and efforts have taken a different turn and are focused on the [(1,5-COD)Ir2P2W15Nb3O62]6− system, its catalytic oxidation chemistry, and the novel, catalytically active, polyyxanion-stabilized Ir−300–900 metal nanoclusters it has given rise to under reductive conditions.7

Experimental Section

Materials. All compounds were of reagent grade and were used as received except as otherwise indicated: 3−Å Davison molecular sieves (Fluka); d6-DMSO, Br2 (Malinckrodt); KCl, DMF, DMSO, CH3CN, ethyl acetate, HCl, NaOH, THF, benzene (Baker); CD3CN, CD3C1 (Cambridge Isotope Laboratories); Amberlyst 15 ion-exchange resin; PrN3Br2, Cs2CO3, Ag2CF3SO3; CHCl3, EtOH, CCl4, Bu4N+PF6-, Et4NBF4 (Alrich); hexyltrimethylammonium bromide, butyltrimethylammonium bromide (Tokyo Kasei); AgNO3 (Alfa); Celite (Sigma). Et4NBF4 was stored under nitrogen at −30 °C until use. Cesium and potassium triflate were prepared by the action of silver triflate on either cesium or potassium chloride in aqueous solution, followed by filtration to remove AgCl and evaporation to dryness.

Dried acetonitrile was prepared by refluxing overnight over CaH2 under dry nitrogen before distillation followed by standing for at least 48 h over 3−Å molecular sieves (ca. 30% by volume) previously activated at 170 °C. Less well dried acetonitrile, or its use in glassware not carefully dried at 150 °C and cooled under vacuum, causes lower yields or impure product in the syntheses reported herein. Dried d6-DMSO was prepared by storing the commercially available compound over activated 3−Å molecular sieves until no water could be observed by H NMR. The Amberlyst resin was initially prepared by washing with neutral water followed by 2 N NaOH until the filtrate was colorless, rewashing with water until the filtrate tested neutral, packing into a column and passing 0.1 N HCl through the column until the eluant tested acidic with pH paper, and then rewashing with water until the eluant tested neutral. Colorless tetrabutylammonium hydroxide was standardized by titration with a standardized HCl solution; only solutions where identical end points using both methyl red and phenolphthalein as indicators were judged satisfactory (as these test for amine decomposition product vs total base content).

Standard literature procedures were followed for the syntheses of CpTiCl3.10a In a more recent synthesis of \((Bu4N)4[C1TiSiW9V4O40]\), CpTiCl3 was obtained from a commercial vendor (Strem; Alfa’s "CpTiCl3" causes the synthesis to fail as described elsewhere). Strem’s CpTiCl3 was found to be satisfactory by H NMR spectroscopy and partial elemental (C, H) analysis. \((Bu4N)4SiW9V4O40\) and \((Bu4N)4P2W15V4O68\) were prepared and their purity assayed as previously described.15

Oxygen- and Moisture-Sensitive Technique. Oxygen- and/or moisture-sensitive compounds were routinely manipulated under an inert-nitrogen atmosphere in a Vacuum Atmospheres "Dry" Box. O2 levels were maintained at less than 1.0 ppm and monitored by use of a Vacuum Atmospheres O2 level monitor (VAC Model AO 316-C). All glassware and Celite used for moisture- or air-sensitive preparations were dried in an oven at 150 °C overnight and cooled under vacuum in the drybox anochamber before use.

Instrumentation/Analytical Procedures. UV−visible spectra were recorded using a Cary 15 UV−visible spectrometer. IR spectra were recorded on a Sargent-Welch SP3-200 or a Beckman 4240 spectrometer. IR samples were prepared either as KBr disks or as CH3CN solutions using either 0.1 mm path length CaF2 or 0.1 mm path length NaCl cells with CH3CN in the reference cell. Spectra were calibrated by reference to the 1601 cm−1 band of polystyrene.

Early elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and, more recently, from E + R Microanalytical Laboratory, Inc., Corona, NY, and Mikroanalytisches Labor Pascher, Remagen, Germany. The source of the analytical data is indicated with such analysis.

183W, 51P, 51V, and 29Si NMR spectra were recorded on a Nicolet NT-360 NMR system with field/frequency lock on the appropriate


deuterated solvent at 21 °C unless otherwise noted. A 1-Hz exponential apodization of the FID (i.e., multiplication of the original FID by a decaying exponential function) was employed in the 13C, 31P, and 59Si (but not 29Si) NMR unless otherwise noted. Chemical shifts are reported in parts per million with negative values upfield of the standard. 13C NMR spectra (15.04 MHz) were obtained using 10-mm o.d. samples tubes and are referenced to saturated Na2SO4 in D2O using the substitution method. Spectral parameters include the following: pulse width = 70 μs (90° flip angle); acquisition time = 1914.9 ms (1.2 Hz/data point); repetition rate = 819.6 ms; sweep width = ±2500 Hz. The broad band power amplifier was attenuated by 6 dB to prevent any ringing. Acoustic rangi were the introduction of a 1000-μs delay before acquisition. 31P NMR spectra (71.74 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to TMS in δ-acetone using the substitution method. Spectral parameters include the following: pulse width = 20 μs (90° flip angle); acquisition time = 1.03 s (1.1 Hz/data point); repetition rate = 1.28 s; sweep width = ±4000 Hz; a 1-Hz exponential apodization of the FID. 59Si NMR spectra (141.8 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to 1% phosphoric acid in D2O using the substitution method. Spectral parameters include the following: pulse width = 20 μs (60° flip angle); acquisition time = 1.02 s (0.92 Hz/data point); repetition rate = 2.02 s; sweep width = ±2000 Hz; a 1-Hz exponential apodization of the FID. 31V NMR spectra (94.92 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to neat VOCl₃ using the substitution method. Typical spectral parameters included the following: pulse width = 20 μs (90° flip angle); acquisition time = 1.34 s (1.1 Hz/data point); repetition rate = 1.361 ms; sweep width = ±19 000 Hz. A 25-Hz exponential apodization of the FID was employed unless otherwise noted. A preamp attenuation of 10–30 dB was applied as necessary to prevent receiver saturation. For all the above nuclei, line widths were obtained by best fitting the data to Lorentzian line shapes using standard Nicolet software and are corrected for any added exponential line broadening. 1H NMR were recorded on a Varian XL-100 NMR spectrometer operating in the continuous-wave mode. Samples were reported using the δ scale and are referenced to the residual 1H impurity of the deuterated solvent. All 1H NMR spectra of Bu₄N⁺ salts of the polyoxometalates have the characteristic losses of 0 (m/e = 16) and cationization.25,26 UV/vis (CH₃CN) showed end absorbance from high-energy tailing into the visible region with a shoulder around 250–300 nm (λmax = 300 cm⁻¹ mol⁻¹ L) and ca. 455 nm (ε₄5 = 455 cm⁻¹ mol⁻¹ L⁻¹). IR (CH₃CN, cm⁻¹) (Figure 3): 1005 (w); 965 (m); 900 (s); 860 (m); 810 (m); 775 (m); 700 (w). 31P (21 °C, 0.09 M, CD₃CN, 26 000 transients, S/N = 30:3:1, δ (multiplicity, Δν1/2): –83.2 (s, 0.56 ± 0.06 Hz). 31P (21 °C, 0.09 M, CD₃CN, δ (multiplicity, no. of ν, Δν1/2) (Figure 2, inset): –604 (s, 2, 0.196 Hz), –561 (s, 1, 1.146 Hz). 1H CW (21 °C, 0.28 M, in 2.1 MF/CD₃CN, 100 000 transients), (multiplicity, no. of ν, Δν1/2) (Figure 2): –7.51 (s, 2, 60 Hz), –83.2 (s, 2, 2.1 Hz), –112.3 (s, 0.2 Hz), –561.2 ppm (s, 2, 2.2 ± 0.5 Hz). The –561 ppm resonance in the 1H NMR result in the sharpening of the –75.1 and –123.2 ppm resonances. 1H (100 MHz, CW mode, 21 °C, CD₃CN), 1H/NMR. The 1H NMR showed a single resonance at δ 7.15. (The reasons for formulation of the in situ generated product as “Bu₄N⁺[Cp₂Ti+Sc₂W₈O₃₀]O₄” are discussed in a footnote.)27 Stability of the [Cp₂Ti+Sc₂W₈O₃₀]⁺ anion. The stability of the [Cp₂Ti+Sc₂W₈O₃₀]⁺ anion was tested both in solution and in the solid state. Examining a solution of (Bu₄N)[Cp₂Ti+Sc₂W₈O₃₀] in CH₂CN after ca. 1 month at room temperature showed no discernible difference by 1H and 13C NMR. The solid was examined by IR and by 1H NMR (i.e., after redissolving it in CH₂CN) and showed no discernible differences in the spectrum; no discernible change in the chemical behavior of the benzene ring. Thus, no discernible change in the material is observed.

Cation-Exchange Resin (P-SO₂Bu⁺)[Bu₄N⁺] Test of (Bu₄N)[Cp₂Ti+Sc₂W₈O₃₀]A Test of (Bu₄N)[Cp₂Ti+Sc₂W₈O₃₀]A 10-g amount of macroreticular, strongly acidic resin Amberlyst 15 (H⁺ form; P-SO₂H₃) was placed in a beaker together with ca. 50 mL of water. The resin was swirled for ca. 1 min following the water. This was repeated until the aqueous phase was clear and colorless. The resin was then rinsed onto a 27 cm × 1 cm (length × diameter) column. A large excess, ca. 30 mL of 40% Bu₄NOH/H₂O was diluted by ca. 1 part in 10 with distilled water and then passed dropwise through the column. When the eluant tested basic with litmus paper, distilled water was passed through the column until the eluant tested neutral with litmus paper. The resin was next washed with water. 50 mL of 40% Bu₄NOH was added, and then the methanol was decanted and the process repeated with CH₂CN. The resulting P-SO₂Bu⁺ column was packed and flushed with ca. 250 mL of CH₂CN. A solution of ca. 0.5 g of (Bu₄N)[Cp₂Ti+Sc₂W₈O₃₀] in

---

10 mL of CH3CN was passed dropwise through the column. This colored solution passed through the column with no apparent retention (i.e., the CpTi** group was not removed from the polyoxoanion). The colored eluant was collected and the solvent removed by rotary evaporation under reduced pressure. The resulting purple Sb2O5-treated (Bu4N)3 [CpTi3(SiW10V2O40)2] was unchanged by 1H NMR and IR spectroscopy.

Anion-Exchange Resin (P-201, Cl) Test of (Bu4N)4[CpTiSiW5V3O19]
A 10-g amount of the macroreticular Amberlyst A-27 basic pH resin (Cl form; P-201, Cl) was washed with water, methanol, and CH3CN. A sample of (Bu4N)4[CpTiSiW5V3O19] was passed through a column containing this anion-exchange resin using CH3CN as described above for the cation-exchange resin. All of the colored sample was retained on the resin, indicating that the orange CpTi** group had not been cleaved from the cation.

Reaction of (Bu4N)4[CpTiSiW5V3O19] with Br2
In the drybox, 0.1 g (0.0281 mmol) of (Bu4N)4[CpTiSiW5V3O19] in 10 mL of dry CH3CN was prepared. A solution composed of 1.427 g of Br2 in CCl4 (25-mL total volume) was prepared. An aliquot of 0.237 mL of this Br2/CCl4 solution (3.00 equiv) was added to the heteropolytungstate solution and the resulting solution stirred for 1 h. The solution was then removed by rotary evaporation under reduced pressure, the residue was dissolved in CD3CN, and the solution was examined by NMR. 1H NMR showed no trace of the δ 6.9 resonance characteristic of the starting complex, indicating that it had reacted completely. 31P NMR (supplementary material, Figure C) showed a complex set of resonances.

Reaction of (Bu4N)4[CpTiSiW5V3O19] with Et2OBF4
In the drybox, 0.100 g (0.0281 mmol) of (Bu4N)4[CpTiSiW5V3O19] was dissolved in 10 mL of dry CH3CN. To this stirring solution, 16 mg (0.084 mmol) Et2OBF4 was added. This reaction solution was stirred for 1 h, and the solvent was removed by rotary evaporation under reduced pressure. The residue was dissolved in CD3CN, removed from the drybox, and examined by NMR. 1H NMR showed that the complex had completely reacted as judged by the complete lack of the δ 6.9 resonance characteristic of the starting material. 31P NMR (supplementary material, Figure C) showed a complex set of resonances.

Reaction of (Bu4N)4[CpTiSiW5V3O19] with Bu4NOH/H2O
In the drybox, 0.100 g (0.0281 mmol) of (Bu4N)4[CpTiSiW5V3O19] was dissolved in 10 mL of dry CH3CN. To this stirring solution, 1.165 mL (50 mmol, 3 equiv) of Bu4NOH/H2O was added to the stirring solution. The solution immediately turned green. Following stirring for 1 h, the solvent was removed by rotary evaporation under reduced pressure, the residue was dissolved in CD3CN, and the solution was examined by NMR. 1H NMR showed appreciable broadening of the Bu4N+ resonances but no trace of the δ 6.9 resonance characteristic of the starting material. However, 31P NMR (supplementary material, Figure C) showed a single resonance at 51.68 ppm that is δ 51.68 ppm downfield from the δ 53.1 resonance of SiW10V3O40−. As a ca. −562 ppm resonance also appears as one of the major lines resulting from the reaction of (Bu4N)4[H]SiW5V3O19 with excess Bu4NOH/H2O, it is unclear whether or not follow-up chemistry is also occurring in this reaction of (Bu4N)4[CpTiSiW5V3O19] with Bu4NOH/H2O. Specifically, follow-up chemistry due to hydrolysis of the Ti**-heteropolytungstate complex to yield SiW5V3O19− or one of its degradation products may be involved.

Electrochemistry of [CpTiSiW5V3O19]4−
The cyclic voltammogram (supplementary material, Figure D) (Pt flat working electrode, Pt wire auxiliary electrode, SCE reference electrode) in 0.1 M Bu4NPF6 showed features similar to those observed for (Bu4N)4[H]SiW5V3O19 with a scan 200 mV/s. The first peak occurs at +0.20 V vs SCE.

Metathesis of (Bu4N)4[CpTiSiW5V3O19] to Other Alkylammonium Salts
A solution of (Bu4N)4[CpTiSiW5V3O19] in CH3CN (concentration typically 1 g/5 mL solution) was added dropwise to a stirring solution containing Bu4N+OH− or Pr4N+OH− under dry solvent at 150 OC over 0.1 h while still in the drybox, followed by rotary evaporation to dryness and back into CH3CN. A red, sand-like precipitate (washed with CH3CN and dried before weighing) is formed. This suggests that the multiple equivalents of the alkali cation precipitate the (noncrystalline) solid until all of the alkali cation is consumed and that this is then followed by the "normal" precipitation of the Bu4N+ salt. In the case of the K+/Bu4N+ system, however, a crystalline product whose morphology appeared different than the Bu4N+ salt alone was observed, but all material of sufficient size to be used for X-ray crystallography was comprised of unassembled aggregates.

Preparation of (Bu4N)4[CpTiP2V2W2O20]4− [This preparation was carried out under the same conditions for dry solvent, 150 OC and vacuum as those described above and succeeded in producing a crystalline product whose morphology appeared different than the Bu4N+ salt alone, but all material of sufficient size to be used for X-ray crystallography was comprised of unassembled aggregates.]

Approaches towards Growing X-ray-Quality Crystals for [CpTi-SiW3V3O9]4−
Multiple attempts by two of us over several years were aimed at growing X-ray-quality crystals of [CpTi-SiW3V3O9]4−. The following sets of conditions were tried with multiple attempts for each set of conditions cited performed. Using vapor diffusion methods, initial attempts involved hydrolysis of either THF, benzene, or CHCl3 into either DMF or CH3CN solutions of the Bu4N+ or Pr4N+ salts or DMF solutions of the Hex4N+ or Bu4N+ salts. Attempts were made to use a commercially available oil-absorbing membrane in the Marvapor, a commercially available oil-absorbing membrane in the Marvapor, but this did not produce crystals. Attempts involved heterogeneous polyanions oils under these conditions. Crystals of the Bu4N+ salts could be obtained from the DMF or CH3CN/CHCl3 or benzene vapor diffusion systems, but single crystals did not result, as "snowflake" or "dendritic" patterns always resulted. Cut subsections of the above-mentioned systems showed either no tendency to diffuse in an X-ray beam or, in a couple of cases for the Bu4N+ salt (Professor V. Day, private communication), a weakly diffracting crystal in a large ca. ~3500 A unit cell and cubic crystal system was produced.

Multiple Cation Experiments
Vapor diffusion of the Bu4N+ salt of [CpTi-SiW3V3O9]4− in the presence of 1 equiv of cesium triflate/DMF or potassium triflate/CH3CN or ZnBr2/CH3CN was examined as a possible route to grow X-ray-quality crystals of these heteropolyanions. Although the initial mixed-cation systems were homogeneous, orange noncrystalline solids formed. This suggests that the multiple equivalents of the alkali cation precipitate the (noncrystalline) solid until all of the alkali cation is consumed and that this is then followed by the "normal" precipitation of the Bu4N+ salt. In the case of the K+/Bu4N+ system, however, a crystalline product whose morphology appeared different than the Bu4N+ salt alone was observed, but all material of sufficient size to be used for X-ray crystallography was comprised of unassembled aggregates.
\[
\text{(Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \quad \text{(Figure 1)}
\]

**Experiments Probing Whether or Not the C\text{\textgreek{g}} Symmetry Isomer of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) is the Kinetic or Thermodynamic Product (Isomer).** Variable-Temperature \(\text{\textgreek{i}V}\) NMR. Variable-temperature \(\text{\textgreek{i}V}\) NMR of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) shows an increase in line-broadening at lower temperatures \(\theta\) (sample temperature, \(\text{\textgreek{i}V}\), \(25^\circ\text{C}\), \(372\pm 31\text{ Hz}\) \(5^\circ\text{C}\), \(473\pm 52\text{ Hz}\); \(550\text{ (25 }^\circ\text{C, 842 }\pm 29\text{ Hz) (5 }^\circ\text{C, 1053 }\pm 56\text{ Hz)\. Unsurprisingly, upon subjection of the sample to elevated temperature, a sharpening of the resonances (a decrease in the line-broadening) was observed (\(\theta\) (sample temperature, \(\text{\textgreek{i}V}\), \(25^\circ\text{C}\), \(372\pm 31\text{ Hz}\) \(45^\circ\text{C}\), \(292\pm 23\text{ Hz); \(-550\text{ (25 }^\circ\text{C, 842 }\pm 29\text{ Hz) (45 }^\circ\text{C, 692 }\pm 12\text{ Hz).\ Resolving the sample to 25 \text{ and } 45^\circ\text{C, the two broadening vs. intensity envelopes at } 25^\circ\text{C and } 45^\circ\text{C are completely reversible.

Note that in all cases that two \(\text{\textgreek{i}V}\) NMR lines are seen requiring that the C\text{\textgreek{g}} symmetry of the complex be maintained (at least up to the \(45^\circ\text{C measured).}

**Experiments with Added CpTi(CH\text{\textgreek{e}}\text{CN})_3^+ as a Possible Isomerization Catalyst.** In the drybox, 200 mg (0.036 mmol) of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) was dissolved in 0.6 mL of CD\text{\textgreek{e}}CN. To this solution was added a solution containing 1.0 mmol (1 equiv) of CpTiCl\text{\textgreek{e}} in 0.1 M Bu\text{\textgreek{e}}N+PF\text{\textgreek{e}}-/CH\text{\textgreek{e}}CN (Figure D), plot of In absorbance (A) vs time (Figure E), ultracentrifugation molecular weight measurement for \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) (Figure F), possible diastereomeric form of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) (Figure G), l\text{\textgreek{s}}3W NMR of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) (Figure H), and \(\text{\textgreek{i}V}\) NMR spectrum of \((\text{Bu}_4\text{N})_6[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) (Figure I).

**Preparation of \((\text{Bu}_4\text{N})_4\text{CITiSiW}_6\text{V}_2\text{O}_{16}\) as a Possible Isomerization Catalyst.** In the drybox, a solution containing 5.0 g (1.2 mmol) of \((\text{Bu}_4\text{N})_4\text{CITiSiW}_6\text{V}_2\text{O}_{16}\) in 30 mL of 1.2-dichloroethane was prepared. A 132-mL volume (1.0 equiv) of TiCl\text{\textgreek{e}} was added by syringe. The resulting solution was refluxed for 1 h, and then all solvent was removed by rotary evaporation under reduced pressure.

**Acknowledgment.** FAB-MS spectra are courtesy of Professors K. S. Suslick and, for the early spectra, J. C. Cook, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, IL. Early financial support of our polynucleoxyan chemistry was provided by NSF Grant CHE-831345 and, more recently, by the Department of Energy, Chemical Sciences Division, Office of Basic Energy, Grant DOE FG06-089ER13998.

**Supplementary Material Available:** Plot of In absorbance (A) vs time (Figure A) from the ultracentrifugation molecular weight measurement for \((\text{Bu}_4\text{N})_4[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) in thioglycerol (Figure B), \(\text{\textgreek{i}V}\) NMR spectra of \((\text{Bu}_4\text{N})_4[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) following treatment with ca. 3 equiv of \((\text{Bu}_4\text{N})_4[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) in thioglycerol (Figure C), cyclic voltammogram for 1 mM \((\text{Bu}_4\text{N})_4[\text{CpTi.P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\) in d3-acetonitrile, filtering off the AgCl precipitate, and adjusting to a final volume of 4.0 mL with \(d_7\)-acetonitrile. The \(\text{\textgreek{i}V}\) NMR spectrum, collected immediately after the addition of 1 equiv of \((\text{Bu}_4\text{N})_4[\text{CpTi(CH\text{\textgreek{e}}CN)})_3^+\) remains unchanged, showing the familiar two-line spectrum (side supra) with \(\theta\) 524, -554. Similarly, addition of a total of 2 and 3 equiv of \((\text{Bu}_4\text{N})_4[\text{CpTi(CH\text{\textgreek{e}}CN)})_3^+\) to the above heteropolyanion solution did not change the number of observed line-broadening vs. intensity envelopes at \(25^\circ\text{C} and \(45^\circ\text{C}.\)

**Inorganic Chemistry, Vol. 33, No. 17, 1994**

Rapko et al.