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Synthesis, Isolation, and Spectroscopic Characterization of Trivanadium Polyoxoanion-Supported $(C_5H_5)Ti^{3+}$: $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ and $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$

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Reaction of the trivanadium-substituted polyoxometalates $(Bu_4N)_7SiW_9V_3O_{40}$ and $(Bu_4N)_9P_2W_{15}V_3O_{62}$ with an equimolar amount of $CpTi^{3+}$ leads to the formation of the polyoxometalate-supported organometallic complexes $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$, **1**, and $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$, **2**, respectively. These complexes were isolated as their Bu_4N^+ salts and subsequently characterized by a complete elemental analysis and ^{31}P, ^{183}W, ^{51}V, and ^1H 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 $^{183}W\{^{51}V\}$ NMR spectra were collected. Both **1** and **2** are homogeneous, regiospecifically supported $CpTi^{3+}$ complexes of overall C_s 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, $ClTi^{3+}$ complex, $ClTi{\cdot}SiW_9V_3O_{40}^{4-}$, 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 triheterometal-incorporated heteropolytungstates[2] is motivated by the hypothesis that these compounds might serve as analogs of heterogeneous metal oxides, Figure 1.[3] Following the first report of polyanion surface-supported metals by Flynn and Stucky,[4] and development of the area by Klemperer and Day,[5] numerous additional examples of heteropoly- and isopolyanion-supported organometallics have been described.[5,6,7] Most of these studies have employed niobium-incorporated heteropolytungstates as the support system, namely Klemperer and Day's $Nb_2W_4O_{19}^{4-}$ isopolyoxoanion[5] and our $P_2W_{15}Nb_3O_{62}^{9-}$ and $SiW_9Nb_3O_{40}^{7-}$ heteropolyoxoanion systems.[6] Our preliminary report[8a] of $CpTi{\cdot}SiW_9V_3O_{40}^{4-}$ constituted the first example of a vanadium-substituted polyoxoanion-supported organometallic, and only three other examples of vanadium-supported organometallics, $[(C_5Me_5)Rh]_4(V_6O_{19})$,[9a] $[(1,5\text{-COD})Ir(V_4O_{12})]^{3-}$,[9b] and $\{[(1,5\text{-COD})Ir]_2(V_4O_{12})\}^{2-}$,[9b] have since appeared.

The key goals for the present investigation are as follows: (a) preparation of the first organotransition-metal derivatives supported on Keggin[2] and Dawson[2] trivanadium-substituted polyoxoanions, $SiW_9V_3O_{40}^{7-}$ and $P_2W_{15}V_3O_{62}^{9-}$, respectively;[8b,c] (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[7]); 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.

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(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.

(2) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (d) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Proceedings of the July 15–17, 1992, Meeting at the Center for Interdisciplinary Research in Bielefeld, Germany; Müller, A., Pope, M. T., Eds.; Kluwer Publishers: Dordrecht, The Netherlands, 1992.

(3) This resemblance was first noted in: Baker, L. C. W. *Advances in the Chemistry of Coordination Compounds*; Kirschnerr, S., Ed.; MacMillan: New York, 1961; p 604.

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(5) Studies by Klemperer, Day, and co-workers on the synthesis and structural characterization of polyoxoanion–organometallic complexes: (a) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564. (b) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (d) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (e) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158. (f) Klemperer, W. G.; Yagasaki, A. *Bull. Chem. Soc. Jpn.* **1989**, 2041. (g) Main, D. J. Dissertation, University of Illinois, Urbana-Champaign, 1987. (h) Klemperer, D. J.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2990. (i) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (j) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Planalp, R. P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629. (k) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031.

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(7) (a) Recently we have shown that $(Bu_4N)_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ is a good precatalyst leading to quite active catalysts for both hydrogenation[7b] and oxygenation[7c] reactions. This complex was characterized by a complete elemental analysis plus ^{31}P, ^{183}W, ^1H, and ^{13}C NMR, IR, and sedimentation-equilibrium molecular-weight measurement.[7c] ^{17}O NMR studies demonstrate that $(1,5\text{-COD})Ir^I$ binds to Nb_2O bridging oxygens of the Nb_3O_6 oxygen surface in the soluble, metal oxide support system, $P_2W_{15}Nb_3O_{62}^{9-}$.[7d] The resultant atomic-level characterization in solution of $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ 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[7e,f]). (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.; Weiner, H.; Lin, Y.; Finke, R. G. Manuscript in preparation.

(8) This contribution is part 4 in a trivanadium polyoxoanion subseries of our polyxoxoanion work: (a) Part 1: see elsewhere.[6c] (b) Part 2: Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *107*, 2947. (c) Part 3: see elsewhere.[6f]

(9) (a) Chae, H. K.; Klemperer, W. G.; Day, V. W. *Inorg. Chem.* **1989**, *28*, 1423. (b) Day, V. W.; Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1990**, 1267. (c) See also the related work by Bottomley and co-workers: Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 7226. Bottomley, F.; Magill, C. P.; White, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3070. (d) Note that polyoaxanion *framework-incorporated* $CpTi^{3+}$ complexes have been reported by Klemperer and, separately, by Knoth. However, these are *quite distinct* from the polyoxoanion *surface-oxygen-supported* complexes reported herein (see elsewhere,[6c] footnotes 1f and 3f, for a discussion and lead references).

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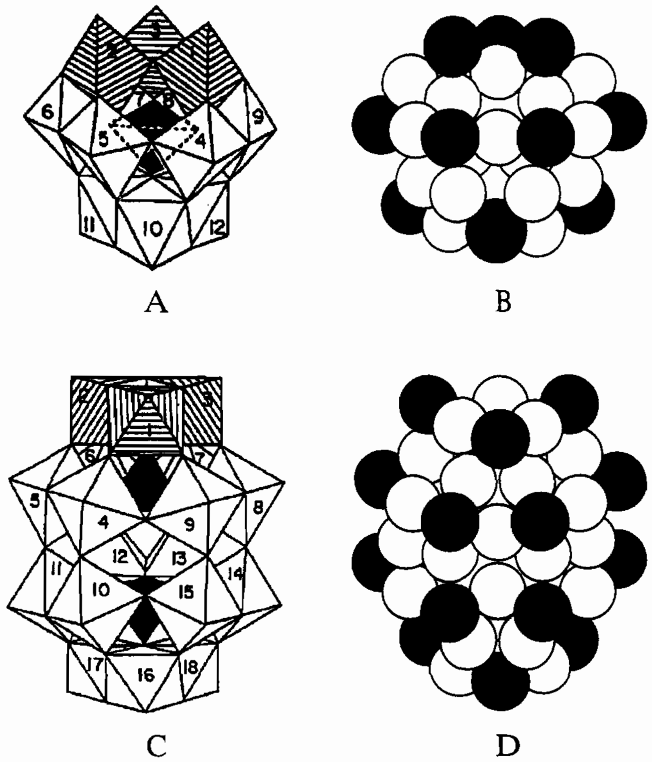

Figure 1. Polyhedral and space-filling representations of A-β $SiW_9V_3O_{40}^{7-}$ (A, B) and of B-α $P_2W_{15}V_3O_{62}^{9-}$ (C, D). In the polyhedral representation (A, C) the silicate (for A-β $SiW_9V_3O_{40}^{7-}$, A) and the phosphate cores (for B-α $P_2W_{15}V_3O_{62}^{9-}$, C) are represented by black tetrahedra, while the white octahedra represent the WO_6 groups. Hatched octahedra represent VO_6 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 $CpTi^{3+}$ complexes[9d] $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ and $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$. A preliminary communication[8a] and an *Inorganic Syntheses* preparation[8b] of $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ have appeared, but a full report of our characterization work has not been previously published. In addition, nothing about the synthesis and characterization of $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ has been previously published (i.e., beyond the initial work reported in a Ph.D. thesis[6e]). This latter complex is especially important in that its symmetry is unequivocally established to be C_s rather than the initially anticipated C_{3v} for reasons also discussed herein.

Results and Discussion

Synthesis and Initial Characterization of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, 1. The deep orange title complex **1** is prepared from the reaction of *freshly vacuum sublimed* $CpTiCl_3$ with 3 equiv of $AgNO_3$ in CaH_2/molecular sieve *dried* CH_3CN and addition of this *in situ* generated, yellow solution of[10a] $CpTi(CH_3CN)_x(NO_3)_3$ to a cherry red solution of $(Bu_4N)_7SiW_9V_3O_{40}$, also in dried CH_3CN. Extractive workup and crystallization (see the Experimental Section) yields dark-orange $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ in 59% overall yield (eq 1).

$$CpTi(CH_3CN)_x(NO_3)_3 + (Bu_4N)_7SiW_9V_3O_{40} \rightarrow (Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}] + xCH_3CN + 3Bu_4N^+NO_3^- \quad (1)$$

The good but not excellent yield is actually a 3-fold improvement over that observed initially[6c,8a] and represents a fairly optimized, checked *Inorganic Syntheses* preparation and yield.[8c] Yield-limiting side reactions appear to stem (a) from any use of $CpTiCl_3$ that has not been vacuum sublimed (in fact, one cannot use[8c] commercial (Alfa) $CpTiCl_3$, which shows several resonances in the ^1H NMR over and above the one resonance for the Cp ligand), (b) from residual H_2O, resulting from failure to dry the glassware or CH_3CN sufficiently, which is known to react with[10b] $CpTiCl_3$, (c) from the fact that removal of the H^+ from $HSiW_9V_3O_{40}^{6-}$ using OH^- occurs with up to 25% decomposition[8b] of the $SiW_9V_3O_{40}^{7-}$, and (d) from any residual OH^-, present from the deprotonation/decomposition of $HSiW_9V_3O_{40}^{6-}$, which reacts rapidly with $CpTi^{3+}$ leading to side products.

The $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ product is obtained as an analytically pure, homogeneous, dark-orange solid (i.e., free of the contaminating by-product of 3 equiv of $Bu_4N^+NO_3^-$) by either repeated reprecipitation 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 $\{(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]\}_n$. Solution molecular weight measurements using the sedimentation equilibrium method ($\bar{M}_r$(calc for $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$) 3558, $\bar{M}_r$(found) 3500 (supplementary material, Figure A), where $\bar{M}_r$ = the weight-average molecular weight) 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, $(Bu_4N)_4H[CpTi{\cdot}SiW_9V_3O_{40}]^+$, at $m/e = 3559$. Well-established cationization processes, that is the exchange of Bu_4N^+ for H^+, and fragmentation processes such as loss of oxygen, $m/e = 16$, were also seen as is typical for these heteropolytungstates.[8a,11] Interestingly, loss of the organometallic fragment $CpTi^{3+}$ (m/e for $CpTi^{3+}$ = 113) is *not* observed,[11a] at least not in the positive ion FAB-MS spectrum (however, positive ion polyoxoanion FAB-MS typically exhibit less fragmentation than negative ion spectra[11c]).

The ^1H NMR provides an easy and sensitive means to judge the isomeric purity of the complex. Specifically, upon support the $CpTi^{3+}$ fragment shows a significant shift in the Cp resonance from δ 7.15 in the starting solvate $CpTi(CD_3CN)_x(NO_3)_3$ to δ 6.90 in the $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ product. In addition, further evidence for the purity and homogeneity of the isolated product is provided by a single-line ^{29}Si NMR, as well as clean ^{51}V (Figure 2, inset) and ^{183}W NMR (Figure 2) spectra.

Chemical Evidence for Inner-Sphere Ti^{IV}-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 countercation. Several pieces of chemical evidence require that the $CpTi^{3+}$ fragment be tightly and covalently attached to the polyoxoanion surface. First and most striking is the stability of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ to the humid Oregon atmosphere, especially since $CpTiL_3$ compounds tend to be quite moisture sensitive[10b] (as confirmed in a control experiment showing that the yellow starting material $CpTi(CH_3CN)_x(NO_3)_3$ 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, $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ remains unchanged after several days in solution or after up to 1 year as a solid (by ^1H and ^{51}V NMR and IR). This enhanced stability toward moist air is readily

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(10) (a) Evidence for Ti^{4+}/NO_3^- bonding exists, hence the $CpTi(CH_3CN)_x(NO_3)_3$ 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 $CpTi^{3+}$ compounds to hydrolysis is well established as detailed elsewhere.[10a] (c) Note that the hypothetical, 7-coordinate analog "$CpTi(OR)_4$" is apparently unknown as a stable entity (see Table III-3, pp 40–43 elsewhere[10a]), although 7 and higher coordination for $CpZr^{IV}$ complexes are well established,[10a] points verified in another tabulation: Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zriconium and -Hafnium Compounds*; Ellis Horwood Ltd.: Chichester, U.K., 1986; Chapter 2.

(11) (a) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750. (b) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241. (c) Trovarelli, A.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6034.

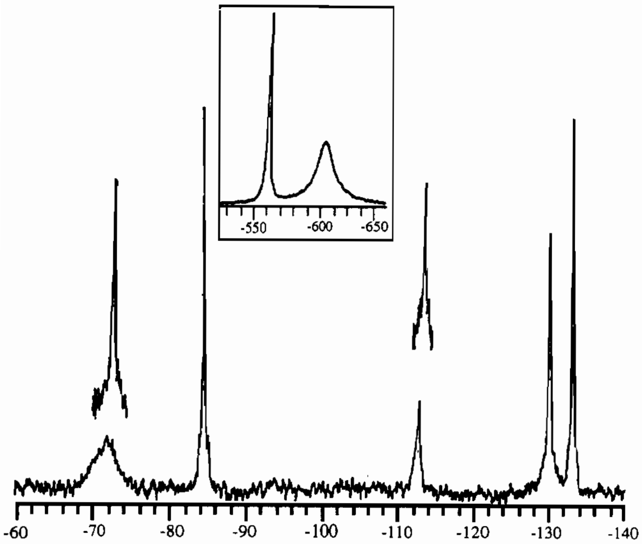

Figure 2. Five-line ^{183}W NMR (15 MHz) of 2:2:1:2:2 relative intensity of 0.28 M A-β $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ in 2:1 DMF/CD_3CN following 100 000 pulses collected over 23 h. The sharpening of the −83 and −112 ppm resonances following decoupling of the −561 ppm resonance in the ^{51}V NMR (boxed inset) is shown as insets adjacent to the appropriate resonances.

rationalized by having the rest of titanium's coordination sphere in $CpTi^{3+}$ fully and irreversibly occupied by three polyoxoanion 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 $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ complex is that both the cationic $CpTi^{3+}$ organometallic fragment and the polyanionic $SiW_9V_3O_{40}{}^{7-}$ component—that is, the intact complex—should be retained on an anion-exchange resin, $P\text{–}NR_3{}^+Cl^-$ (P = macroreticular polymer), but that both should pass together and unaltered through a cation-exchange resin, $P\text{–}SO_3{}^-Bu_4N^+$. On the other hand, if the $CpTi^{3+}$ fragment is dissociable or behaving as a simple countercation, the $CpTi^{3+}$ fragment should be removed following exposure to the anionic sites of a $P\text{–}SO_3{}^-Bu_4N^+$ cation-exchange resin, and only $CpTiCl_3$ should be recovered following exposure to a anion-exchange resin, $P\text{–}NR_3{}^+Cl^-$. Experimentally both the $CpTi^{3+}$ fragment (as indicated by ^1H NMR) and the heteropolytungstate fragment (as indicated by IR) in $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ pass together and unaltered through a $P\text{–}SO_3{}^-Bu_4N^+$ cation-exchange resin, while both components are retained together on a $P\text{–}NR_3{}^+Cl^-$ anion-exchange resin. Clearly, the $CpTi^{3+}$ fragment is tightly bound to the $SiW_9V_3O_{40}{}^{7-}$ polyoxoanion's surface. (The IR and multinuclear NMR spectroscopic data provided below further reinforce this conclusion.)

IR and Multinuclear NMR Characterization. Information about the nature and symmetry of the regiospecific site of attachment of $CpTi^{3+}$ in $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ was obtained by IR and multinuclear ^{51}V and ^{183}W NMR spectroscopy. Careful examination of the IR spectrum of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ shows two especially informative features in comparison to the starting material, $(Bu_4N)_7SiW_9V_3O_{40}$, Figure 3. First, the band in the region assignable to a terminal M═O vibration[12,13] increases from 940 cm^{-1} for $(Bu_4N)_7SiW_9V_3O_{40}$ to 965 cm^{-1} for $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$; triprotonation as in $(Bu_4N)_4H_3SiW_9V_3O_{40}$ similarly shifts this band to 960 cm^{-1}.[8b] Second, the ca. 800-cm^{-1} band of $SiW_9V_3O_{40}{}^{7-}$ exhibits a pronounced perturbation with a 35-cm^{-1} splitting in the case of $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$. The strong perturbation of this band, assignable[12,13] to a M–O–M edge-shared octahedra for this class of polyoxometalates,[12a,b] suggests that the $CpTi^{3+}$ attaches close to (and probably onto) these edge-shared bridging oxygens (a full normal coordinate analysis plus Raman studies[12e] would, however, be required to unequivocally support or refute this interpretation).

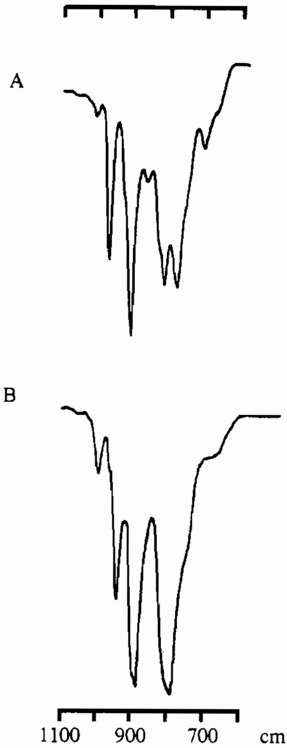

Figure 3. IR of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ (A) (top) obtained with matched NaCl cells in CH_3CN vs a CH_3CN reference, showing the 35-cm^{-1} splitting of the 800-cm^{-1} band assignable[12,13] to a ν_{asym}(M–O–M) vibration between edge-sharing metal octahedra. The IR of $(Bu_4N)_7SiW_9V_3O_{40}$ (B) (bottom) is shown for comparison. The 800-cm^{-1} band splitting is good, albeit not unequivocal, evidence for attachment of the $CpTi^{3+}$ to oxygens of edge-shared, rather than corner-shared, octahedra in $SiW_9V_3O_{40}{}^{7-}$.

The ^{51}V NMR spectrum (Figure 2, inset) for $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ shows two resonances of 1:2 intensity at −561 and −604 ppm and thus reveals that the symmetry of the complex is C_s, a change from the C_{3v} symmetry seen for (and expected in) the starting material, $SiW_9V_3O_{40}{}^{7-}$, as deduced from its single ^{51}V NMR resonance at δ −531.[8b] The ^{183}W NMR (Figure 2) confirms this C_s 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[8b] with $HSiW_9V_3O_{40}{}^{6-}$ (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[8b]).

Tungsten to tungsten connectivities for the C_s symmetry $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ were unambiguously established by the ^{51}V-decoupled 2-D INADEQUATE $^{183}W\{^{51}V\}$ NMR spectrum previously reported.[8a] The assignments for this 2-D INADEQUATE $^{183}W\{^{51}V\}$ NMR are consistent *only* with an A-β $SiW_9V_3O_{40}{}^{7-}$ heteropolyanion framework and, therefore, require that the attachment of the $CpTi^{3+}$ fragment occurs without isomerization of the A-β-structure[2] of the parent $SiW_9V_3O_{40}{}^{7-}$ heteropolytungstate. The two most likely C_s symmetry solution structures for $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ are presented in Figure 7 and will be discussed along with the (related) structure for

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(12) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *Spectrosc. Lett.* **1979**, *12*, 127. (b) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *25*, 598. (c) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207. (d) The γ_{sym} at ca. 530–560 cm^{-1} should also split if this assignment is correct. (e) See ref 12b, Table 2, for example.

(13) Some classic studies of M–O–M vibrations: (a) Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *8*, 871. (b) San Filippo, J.; Grayson, R. L.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 269.

$[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$, as the latter proved to suggest that one of the two C_s symmetry structures is most probable (*vide infra*).

Chemical and Electrochemical Behavior of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, 1. Since there are relatively few studies of the reactivity of organometallics supported on polyoxoanions,[5k,7] the reactivity of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ in the presence of nucleophiles and electrophiles was briefly investigated. In the presence of electrophiles such as Et_3O^+ or Br_2 or nucleophiles such as $Bu_4N^+OH^-$, loss of the Cp ligand occurs under fairly mild conditions (1 h at room temperature under N_2), as indicated by ^1H NMR. The ^{51}V NMR, however, shows that different products are formed in the reaction with the electrophiles vs the reaction with nucleophilic $Bu_4N^+OH^-/H_2O$ (supplementary material, Figure C). With the electrophiles Et_3O^+ or Br_2 for example, a complicated ^{51}V NMR spectrum results, suggesting that, following loss of the Cp ligand and opening of the titanium coordination sphere, a complex set of reactions takes place leading to unidentified V-containing products. However, for $Bu_4N^+OH^-$, 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 $[(1,5\text{-COD})Ir]^+$, i.e., and not the stoichiometric reactions of supported $CpTi^{3+}$).[7]

The first, quasi-reversible[14] reduction wave in the cyclic voltammogram of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ (supplementary material, Figure D) occurs at a 0.7 V more positive potential ($E_{pc} \approx 0.3$ V vs SCE) in comparison to the deprotonated starting material, $SiW_9V_3O_{40}^{7-}$ ($E_{pc} \approx -1.0$ V vs SCE; see Table 1 and Figure 25 on pp 76–78 elsewhere[6e]). This behavior is similar to the one observed for the triprotonated heteropolytungstate $(Bu_4N)_4H_3SiW_9V_3O_{40}$, which also exhibits a more positive quasi-reversible[8b] $E_{pc} \approx 0.1$ V vs SCE, consistent with the significantly reduced (four minus) negative charge in the $CpTi^{3+}$- or H_3^{3+}-attached heteropolytungstates, $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ and $H_3SiW_9V_3O_{40}^{4-}$, relative to the (seven-minus) $SiW_9V_3O_{40}^{7-}$ starting material.

Synthesis and Establishment of the Molecular Formula of $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$, 2. The reaction of $CpTi^{3+}$ with the B-type deprotonated heteropolytungstate $(Bu_4N)_9P_2W_{15}V_3O_{62}$ (eq 2) proceeds in a fashion analogous to that previously reported

$$CpTi(CH_3CN)_x(NO_3)_3 + (Bu_4N)_9P_2W_{15}V_3O_{62} \rightarrow (Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}] + xCH_3CN + 3Bu_4N^+NO_3^- \quad (2)$$

for $(Bu_4N)_4SiW_9V_3O_{40}$ to yield red-brown solid product. Again, it is important to use vacuum sublimed $CpTiCl_3$, dry CH_3CN, and dry glassware and to be sure that $(Bu_4N)_9P_2W_{15}V_3O_{62}$ has been prepared with the proper number of equivalents of $Bu_4N^+OH^-$ (i.e., that the $(Bu_4N)_9P_2W_{15}V_3O_{62}$ 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 $Bu_4N^+NO_3^-$ by repeated reprecipitation, using ethyl acetate (i.e., instead of chloroform as was used for $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$). Unlike $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, 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 Bu_4N^+ salts and from *organic* solvents has, perhaps not unexpectedly, proved quite difficult in our experience.[6]

The purity and molecular composition of $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$ were established by elemental analysis (all elements, and adding up to 99.79%) in conjunction with solution molecular weight measurements (supplementary material, Figure E) ($\bar{M}_r$(calc for $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$) 5532, $\bar{M}_r$(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, $\{(Bu_4N)_6H[CpTi{\cdot}P_2W_{15}V_3O_{62} - 2(O)]\}^+$ and $\{(Bu_4N)_6H[CpTi{\cdot}P_2W_{15}V_3O_{62} - 6(O)]\}^+$. The expected cationization[11] is also observed in the FAB-MS, but again, loss of the $CpTi^{3+}$ organometallic fragment is *not* observed. In addition, the lack of any intensity corresponding to a $[(Bu_4N)_8P_2W_{15}V_3O_{62}]^+$ envelope in the positive ion FAB mass spectrum, where cationization is such a characteristic phenomenon, provides strong evidence in and of itself that $CpTi^{3+}$ is a tightly attached moiety (i.e., it is not behaving as a simple countercation).

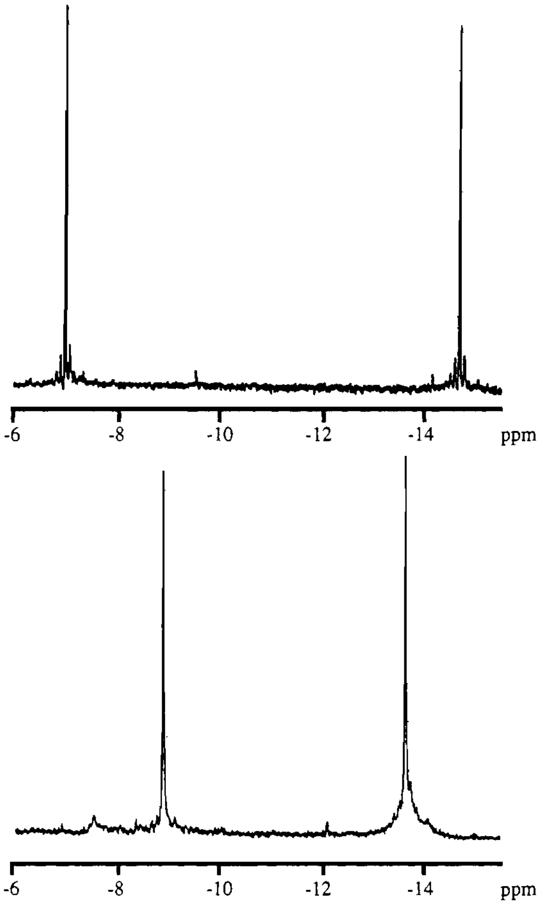

Figure 4. ^{31}P NMR of (top) $(Bu_4N)_9P_2W_{15}V_3O_{62}$ [(21 °C, 0.031 M, CD_3CN) δ: −7.1, −14.9], which serves as the starting material, and (bottom) the $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$ reaction product [(21 °C, 0.031 M, CD_3CN) δ: −8.9, −13.6]. Upon binding of the $CpTi^{3+}$ to $P_2W_{15}V_3O_{62}^{9-}$, the phosphorus resonance closest to the vanadium cap experiences a dramatic highfield shift whereas the phosphorus resonance closer to the tritungsten cap moves downfield.

Chemical and Spectroscopic Evidence for Inner-Sphere Ti^{IV}-to-Polyoxoanion Binding. Both chemical tests and spectroscopic evidence again suggest, as with $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, that the $CpTi^{3+}$ in $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ is tightly attached to the surface of the heteropolyanion. Specifically, the $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$ product appears to be indefinitely stable as a solid or in solution, that is, is not moisture sensitive in contrast to $CpTi(CH_3CN)_x(NO_3)_3$. And, running $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$ down a $P\text{–}SO_3^-Bu_4N^+$ cation-exchange resin showed no retention of the dark orange solution, suggesting that $CpTi(solvate)_x^{3+}$ does not readily dissociate from the polyoxoanion's surface.

The ^{31}P 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 the $(Bu_4N)_9P_2W_{15}V_3O_{62}$ starting material. This two-line ^{31}P NMR spectrum confirms the homogeneity of, and thus the support-site regiospecificity in, $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$, **2**. Further fortification for the single product nature of the $CpTi^{3+}$ support reaction is

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[14] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; J. Wiley & Sons, Inc: New York, 1980.

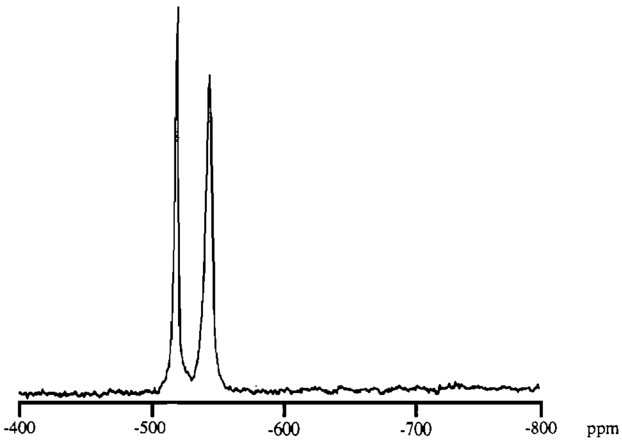

Figure 5. Clean, *two-line* ^{51}V NMR spectrum of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ showing the 1:2 intensity of the two signals. The two-line spectrum requires that the $CpTi^{3+}$ attach to the originally C_{3v} symmetry $P_2W_{15}V_3O_{62}^{9-}$ heteropolytungstate in a way that yields an overall C_s symmetry complex.

the single Cp resonance seen in the ^1H NMR, δ 6.85 (CD_3CN). 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 $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$, **1**, is consistent with a closely similar titanium coordination sphere in both the supported $CpTi^{3+}$ complexes, **1** and **2**.

Examination of the ^{51}V NMR spectrum (Figure 5) proved both surprising and structurally informative. Rather than the single-line ^{51}V NMR spectrum expected for a C_{3v} symmetry product, a clean, *two-line*, 2:1 intensity spectrum is observed with resonances at −544 and −519 ppm, respectively. This result requires that $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ has overall C_s symmetry (a result confirmed by the eight-line ^{183}W NMR; *vide infra*). Variable-temperature ^{51}V NMR studies between 5 and 45 °C demonstrate that the two-line spectrum, and therefore the C_s symmetry, is unchanged in this temperature range (only reversible line width changes are seen).

The IR spectrum of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ provides relatively little structural information. The major change relative to the $(Bu_4N)_9P_2W_{15}V_3O_{62}$ starting material is in the ca. 800-cm^{-1} band, assignable[12,13] 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) $CpTi^{3+}$ attachment to M–O–M of edge-sharing octahedra of the $P_2W_{15}V_3O_{62}^{9-}$ polyoxoanion.

Proposed $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ Structure in Solution. Since there is unequivocal demonstration of C_s symmetry for $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$, and *if* the highly probable (but rigorously unproven) "piano-stool" or pseudotetrahedral ligand arrangement usually found for $CpTiL_3$ compounds[10a] is maintained, then a single structure for $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ becomes the most reasonable solution structure, Figure 6. [If, however, $CpTi^{3+}$ prefers to attach to *four*[10c] surface oxygens of $P_2W_{15}V_3O_{62}^{6-}$, then C_s symmetry structures (supplementary material, Figure G) with $CpTi^{3+}$ off to 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 terminal oxygens and considerably more so than W–O–V oxygens).[15]]

It should be noted that the observation of C_s symmetry for $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ contrasts the C_{3v} symmetry proven by X-ray crystallography (i.e., in the solid state) and by ^{183}W NMR (in solution) for the related triniobium-substituted system[16] $[Cp^*Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$; in the triniobium polyoxometalate, Cp^*Rh^{2+} attaches with Rh on the C_3 axis of the "Nb_3O_6" cap (face) of $P_2W_{15}Nb_3O_{62}^{9-}$. (Similarly, $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ exhibits C_{3v} symmetry.[7d]) This in turn suggests (but does not prove[17]) that the C_s site is the sterically least congested site of kinetic attack[5,18] (i.e., leading, apparently, to a C_s symmetry kinetic product), while the C_{3v} product may be the more stable, thermodynamic product. However, additional experiments will be needed to support or refute this preliminary hypothesis since the above comparison involves changing more than one variable (V vs Nb, and $CpTi^{3+}$ vs Cp^*Rh^{2+}).[7b] Attempts to crystallize $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ for a single-crystal X-ray structural analysis are continuing,[7b] especially using the alkali metal cation/H_2O techniques that we have been exploiting and developing more recently.[19]

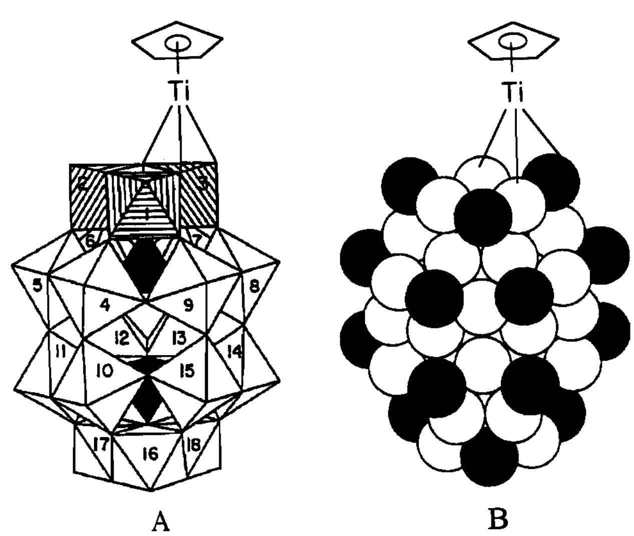

Figure 6. Proposed C_s symmetry structure for $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ shown with the polyoxoanion represented as its idealized corner and edge-sharing polyhedra representation (A) and as its more realistic, close-packed oxide representation (B). In the polyhedra representation (A), the hatched octahedra represent VO_6, the white octahedra represent WO_6, and the central dark tetrahedrons are PO_4 groups. In the close-packed oxide representation (B), the open circles represent bridging oxygens while the solid ones represent terminal, multiply bonded oxygens. The $CpTi^{3+}$ group is shown attached to a C_s symmetry site formed by two bridging (V–O–V) and one terminal oxygen (V=O). [Structures where the $CpTi^{3+}$ is off the side of the structure, for example at a 4 oxygen site defined by the 4 bridging oxygens between the $V_1V_3W_8W_9$ (and the symmetry-equivalent sites), cannot be unequivocally excluded but are believed to be much less likely (see supplementary material, Figure G).]

Independent support for kinetic vs thermodynamic control in the support chemistry of at least $SiW_9M_3O_{40}^{7-}$ ($M = V^V, Nb^V$) comes from Pope's study of the closely related, one-electron reduced $SiW_{11}V^{IV}(OH)O_{39}^{5-}$.[20] In this species, Pope found the first evidence for kinetic protonation of a (less basic[15,21]) terminal V=O site followed by its H^+ or $R_{3-x}H_xN$ amine base assisted

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(15) (a) Knoth, W. h.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265. (b) Knoth, W. H.; Farlee, R. D. *Inorg. Chem.* **1984**, *23*, 4765. (c) Fruchart, J. M.; Herve, G.; Launay, J. P.; Massart, R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1627. (d) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(16) Pohl, M.; Lin, Y.; Weakley, T. J. R.; Nomiya, K.; Kaneko, M.; Weiner, H.; Finke, R. G. Trisubstituted Heteropolytungstates as Soluble Metal–Oxide Analogs. The Isolation and Characterization of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ and $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, Including the First Crystal Structure of a Dawson-Type Polyoxoanion-Supported Organometallic Complex. *Inorg. Chem.*, submitted for publication.

(17) (a) The inherent problems in changing more than a single variable at a time, in this (hindsight) cross comparison of Nb- and V-containing $P_2W_{15}M_3O_{62}^{9-}$ polyoxoanions and their Cp^*Rh^{2+} and $CpTi^{3+}$ organometallics, means that more studies will be required to test this idea.[17b] (b) Some useful experiments might include the following: (i) crystal structures for compounds **1** and **2** prepared herein; (ii) the solution and solid-state structure of Cp^*Rh^{2+} plus $P_2W_{15}V_3O_{62}^{9-}$; (iii) additional experiments (i.e., besides the variable-temperature ^{51}V NMR and added $CpTi(solvate)^{3+}$ studies reported herein) to see if the C_s isomer is a kinetic or thermodynamic product; (iv) further characterization, reactivity, and catalysis studies of the potential precatalyst, $(Bu_4N)_4[ClTi\cdot SiW_9V_3O_{40}]$, reported herein.

(18) See Figure 61, p 242, in B.M.R's Ph.D. thesis.[6e]

(19) (a) Nomiya, K.; Kaneko, M.; Kasuga, N.; Finke, R. G.; Pohl, M. *Inorg. Chem.* **1994**, *33*, 1469. (b) Weiner, H.; Finke, R. G. Experiments in progress.

(20) Harmalker, S. P.; Pope, M. T. *J. Inorg. Biochem.* **1986**, *28*, 85.

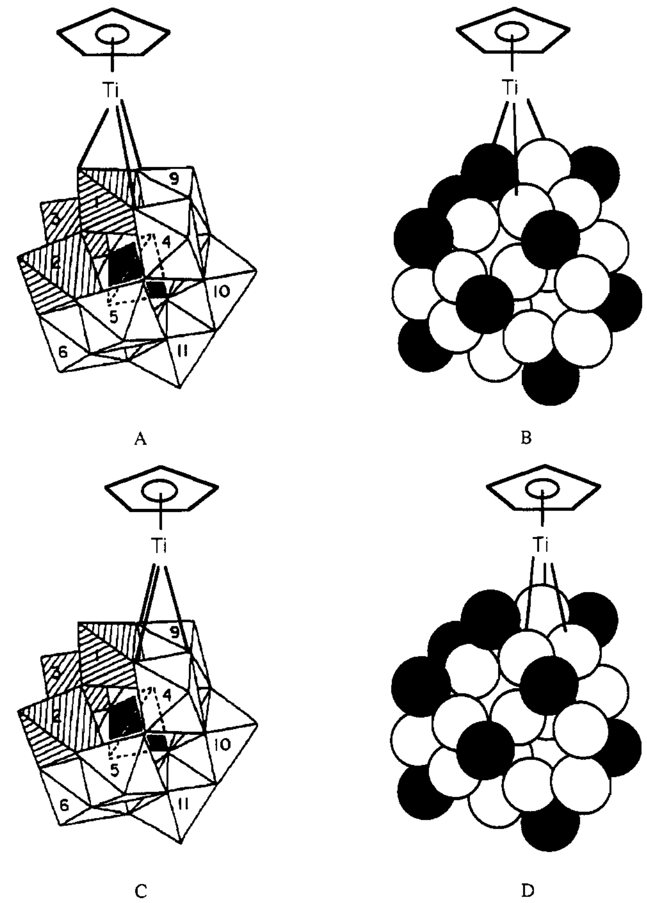

Figure 7. Two most probable C_s symmetry structures for $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ shown with the polyoxoanion represented as its idealized corner and edge-sharing polyhedra representation (A, C) and as its more realistic, close-packed oxide representation (B, D). In the polyhedra representation (A, C), the VO_6 octahedra are numbered 1–3, the WO_6 octahedra are numbered 4–12, and the central dark tetrahedron is the SiO_4 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 $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ shown in Figure 6, is the one in A and B where the $CpTi^{3+}$ group is attached to the two bridging oxygens (V_1–O–W_4, V_1–O–W_9) plus one terminal oxygen (V_1=O) of a B-type triad array (V_1, W_4, W_9) of edge-sharing octahedra. Note that two additional symmetry-equivalent sites exist (V_2, W_5, W_6 and V_3, W_7, W_8). [Again, it is not possible to exclude unequivocally $CpTi^{3+}$ attachment at the 4 oxygen, C_s symmetry sites (e.g., the 4 bridging oxygens between V_1, V_2, W_4, W_5) but the large perturbation of IR band assignable[12,13] to the edge-sharing M–O–M, and the precedent of $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ in Figure 6, make this a seemingly unlikely possibility.]

Table 1. $^2J_{W-O-W}$ Coupling Constants for the Organometallic Supported Heteropolytungstates A-β-$(Bu_4N)_5(Cp^*Rh{\cdot}SiW_9Nb_3O_{40})$,[6b] A-β-$(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$), and A-β-$(Bu_4N)_7(SiW_9Nb_3O_{40})$[6b]

	$^2J_{W-O-W}$, Hz		
octahedra	A-β-$(Bu_4N)_5(Cp^*Rh{\cdot}SiW_9Nb_3O_{40})$	A-β-$(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$	A-β-$(Bu_4N)_7(SiW_9Nb_3O_{40})$
W_{10} to $W_{4,9}$	13.4	16.8	
$W_{4,9}$ to $W_{5,8}$	30	28	15.3 ± 1.2
$W_{11,12}$ to $W_{6,7}$	not obsd (>13 Hz)	12.8	(W_{4-9} to W_{10-12})[a]
$W_{11,12}$ to $W_{5,8}$	16	15	

[a] That is, only two types of W are present in this C_{3v} symmetry complex.

tautomerization to the (more stable) protonated bridging oxygen species, V–O(H)–V. This is, again, highly consistent with and supportive for $CpTi^{3+}$ attack kinetically at the less basic terminal V=O in $P_2W_{15}V_3O_{62}{}^{6-}$ (and $SiW_9V_3O_{40}{}^{7-}$; *vide infra*) leading to a C_s symmetry isomer involving a terminal V=O—TiCp bond as one of the presumably three Ti–O-polyoxoanion bonds.[21]

Proposed $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ Structure in Solution. Even with the assumption of a 3-coordinate, piano stool, $CpTiL_3$ type coordination geometry for $CpTi^{3+}$, there are still two plausible C_s symmetry structures for $CpTi{\cdot}SiW_9V_3O_{40}{}^{4-}$, Figure 7. However, by analogy with the favored structure for $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ above, one is led to favor the upper structures in 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 triniobium heteropolytungstate again provides an interesting comparison. Specifically in $(Bu_4N)_5[Cp^*Rh{\cdot}SiW_9Nb_3O_{40}]$, an important piece of background information is that the heteropolyoxoanion's W–W connectivity was established by examining the $^2J_{W-O-W}$ coupling constants in the ^{183}W 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 a 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

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(21) (a) This argument follows even though Pope's system is d^1, V^{IV}=O, since the d^1 electron is added primarily to a d_{xy} orbital[21b] and thus the terminal V^{IV}=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.

(22) (a) Droege, M. W. Ph.D. Dissertation, University of Oregon, 1984. (b) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274.

constants in $[Cp^*Rh{\cdot}SiW_9Nb_3O_{40}]^{5-}$ could be accounted for by strong Rh–(O)$_3$-polyoxoanion bonding. This, in turn, results in a "lifting" of the triad of M–O–M-containing octahedra to which the Cp^*Rh^{2+} 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^{2+}.[24] *The key point here is that the C_s symmetry and same pattern of coupling constant deviations are observed for $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, Table 1.* Consequently (and regardless of the detailed explanation of the $^2J_{W-O-W}$ coupling constant changes), the bonding between $CpTi^{3+}$ and $SiW_9V_3O_{40}{}^{7-}$ must be very similar if not essentially identical to that in $[Cp^*Rh{\cdot}SiW_9Nb_3O_{40}]^{5-}$.

Overall, then, the simplest explanation of all the available data (and requirement for C_s symmetry structures) is that $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ and $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ 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 $[CpTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$ or plus 2 V–O–W oxygens for $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$).

Preliminary Investigation of the More Reactive Catalyst Precursor $(Bu_4N)_4[ClTi{\cdot}SiW_9V_3O_{40}{}^{4-}$. Preliminary attempts to make a more reactive, polyoxoanion "oxide-supported" titanium center proved very promising (see pp 261–263 and 267 elsewhere[6e]). Using either $TiCl_4$ or the crystalline, sublimable[25] $TiCl_4(CH_3CN)_2$ plus $(Bu_4N)_7SiW_9V_3O_{40}$ in an inert-atmosphere (N_2) drybox and using dry dichloroethane with refluxing for 1 h resulted in a reasonable clean product according to eq 3.

$$(Bu_4N)_7SiW_9V_3O_{40} + TiCl_4 \rightarrow (Bu_4N)_4[ClTi{\cdot}SiW_9V_3O_{40}] + 3Bu_4N^+Cl^- \quad (3)$$

The ^{183}W NMR again shows a five-line spectrum, indicative of a C_s 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 $ClTi^{3+}$ product is quite similar to $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ in that a 30-cm^{-1} shift to higher energy of the band assignable[12,13] to a terminal M=O vibration is seen along with the characteristic ca. 35-cm^{-1} splitting of the 800-cm^{-1} band. The implication is that $[ClTi{\cdot}SiW_9V_3O_{40}]^{4-}$ has the same structure as $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$. (Some additional details for this interesting complex are available in the Experimental Section and on pp 261–263 and 267 elsewhere.[6e]) This supported $ClTi^{3+}$ complex is worthy of additional studies of its reactivity and possible catalysis, as is the preparation of the currently unknown analog, "$[ClTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$".[16]

Summary

The synthesis and characterization in solution of surface-supported $CpTi^{3+}$ complexes, using the trivanadium-substituted heteropolytungstates $SiW_9V_3O_{40}{}^{7-}$ and $P_2W_{15}V_3O_{62}{}^{9-}$ as support systems, has been described. Both complexes $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, **1**, and $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$, **2**, were obtained as analytically pure, homogeneous 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 ^{51}V and ^{183}W NMR (and including 2-D INADEQUATE 183W{^{51}V} NMR for **1**). The spectroscopic results unequivocally demonstrate the C_s symmetry of both complexes and allow deduction of the most probable C_s symmetry solution structures for **1** and **2**. Preliminary evidence for a more reactive, also C_s symmetry complex $(Bu_4N)_4[ClTi{\cdot}SiW_9V_3O_{40}]$ (and, by inference, its "$[ClTi{\cdot}P_2W_{15}V_3O_{62}]^{6-}$" analog) was also reported.

There are, however, still a number of needed or interesting experiments in this area worthy of additional effort.[16] Our own resources and efforts have taken a different turn and are focused on the $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ system, its catalytic oxidation chemistry, and the novel, catalytically active, polyoxoanion-stabilized $Ir_{\sim300-900}$ 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 Davidson molecular sieves (Fluka); d_6-DMSO, Br_2 (Mallinckrodt); KCl, DMF, DMSO, CH_3CN, ethyl acetate, HCl, NaOH, THF, benzene (Baker); CD_3CN, $CDCl_3$ (Cambridge Isotope Laboratories); Amberlyst 15 ion-exchange resin, $Pr_4N^+Br^-$, CaH_2, $Bu_4N^+OH^-$ (40% in water), $ZnBr_2$, CsCl, $Ag^+CF_3SO_3^-$, $CHCl_3$, EtOH, CCl_4, $Bu_4N^+PF_6^-$, $Et_3O^+BF_4^-$ (Aldrich); hexyltrimethylammonium bromide, butyltrimethylammonium bromide (Tokyo Kasei); $AgNO_3$ (Alfa); Celite (Sigma). $Et_3O^+BF_4$[26] 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 CaH_2 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 d_6-DMSO was prepared by storing the commercially available compound over activated 3-Å molecular sieves until no water could be observed by ^{1}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 $CpTiCl_3$.[10a] In a more recent synthesis of $(Bu_4N)_6[CpTi{\cdot}P_2W_{15}V_3O_{62}]$, $CpTiCl_3$ was obtained from a commercial vendor (Strem; Alfa's "$CpTiCl_3$" causes the synthesis to fail as detailed elsewhere[8c]). Strem's $CpTiCl_3$ was found to be satisfactory by ^{1}H NMR spectroscopy and partial elemental (C, H) analysis. $(Bu_4N)_7SiW_9V_3O_{40}$ and $(Bu_4N)_9P_2W_{15}V_3O_{62}$ were prepared and their purity assayed as previously described.[8b]

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. O_2 levels were maintained at less than 1.0 ppm and monitored by use of a Vacuum Atmospheres O_2 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 antechamber 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 CH_3CN solutions using either 0.1 mm path length CaF_2 or 0.1 mm path length NaCl cells with CH_3CN 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 each analysis.

^{183}W, ^{31}P, ^{51}V, and ^{29}Si NMR spectra were recorded on a Nicolet NT-360 NMR system with field/frequency lock on the appropriate

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[23] Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533.

[24] An interesting side point here is the ability of the (partially ionically bonded) polyoxoanion oxide surface to move "on demand", a movement reminiscent of similar flexibility seen on the surfaces of (ionic) solid metal oxides: Mackrodt, W. C.; Tasker, P. W. *Chem. Brit.* **1985**, 366.

[25] (a) Hessett, B.; Perkins, P. G. *J. Chem. Soc. A* **1970**, 3229. (b) Cooney, R. P.; Fraser, D. B. *Aust. J. Chem.* **1974**, *27*, 1855. (c) Kawano, A.; Hase, Y.; Sala, O. *J. Mol. Struct.* **1976**, *30*, 45. (d) Habeeb, J. J.; Said, F. F.; Tuck, D. G. *Can. J. Chem.* **1977**, *55*, 3882.

[26] (a) King, R. B. *Organometallic Syntheses, Vol. I: Transition Metal Compounds*; Academic Press: New York, 1965; p 78. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654. (c) Meerwein, H. In *Organic Synthesis*; Corey, E. J., Ed.; John Wiley & Sons: New York, 1966; Vol. 46, pp 113 ff.

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 ^{183}W, ^{31}P, and ^{29}Si (but not ^{51}V) NMR unless otherwise noted. Chemical shifts are reported in parts per million with negative values upfield of the standard. ^{183}W NMR spectra (15.04 MHz) were obtained using 10-mm o.d. samples tubes and are referenced to saturated Na_2WO_4 in D_2O using the substitution method. Spectral parameters include the following: pulse width = 70 μs (90° flip angle); acquisition time = 819.4 ms (1.22 Hz/data point); repetition rate = 819.6 ms; sweep width = ±2500 Hz. The broad band power amplifier was attenuated by 6 dB to prevent probe arcing. Acoustic probe ringing required the introduction of a 1000-μs delay before acquisition. ^{29}Si NMR spectra (71.74 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to TMS in d_6-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. ^{31}P NMR spectra (146.18 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to 1% phosphoric acid in D_2O 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. ^{51}V NMR spectra (94.92 MHz) were obtained using 12-mm o.d. sample tubes and are referenced to neat $VOCl_3$ using the substitution method. Typical spectral parameters includethe following: pulse width = 20 μs (90° flip angle); acquisition time = 13.34 ms (75 Hz/data point); repetition rate = 13.61 ms; sweep width = ±19 000 Hz. A 5–25-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. ^{1}H 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 ^{1}H impurity of the deuterated solvent. All ^{1}H NMR spectra of Bu_4N^+ salts of the polyoxometalates have the characteristic resonances (^{1}H NMR: δ 1.04, 1.56, 1.72, 3.35) associated with the cation; hence, these resonances are not reported for individual compounds.

Potentiometric titrations were performed using a Corning calomel combination electrode attached to a Corning Model 125 pH meter operating in the mV scale. The system was calibrated using commercially available solutions of pH 3, 7, and 10 prior to use. Cyclic voltammetry was performed in a H-cell designed for cyclic voltammetry with the PAR Model 175 universal programmer and Model 174 potentiostat/galvanostat. Glassy carbon or platinum bead, as indicated, was used as the working electrode, platinum wire as the auxiliary electrode, and saturated calomel for the reference electrode. The electrolyte was 0.1 M $Bu_4N^+PF_6^-$ in dried acetonitrile for the tetrabutylammonium polyoxoanions. The reference electrode was connected to the cell via a salt bridge containing the electrolyte solution. Solutions were degassed prior to each scan with purified nitrogen, or the entire operation was performed under a dry nitrogen atmosphere, either in a glovebag or in a Vacuum Atmosphere glovebox. Voltammograms were recorded at room temperature.

Solution molecular weights were determined using a Beckman Instruments Spinco Model E ultracentrifuge equipped with a scanning photoelectric system using the sedimentation equilibrium method.[27] Heteropolytungstate solutions were prepared by dissolving the sample in acetonitrile containing 0.1 M of $Bu_4N^+Br^-$, until an absorbance of 0.2–0.4 was observed at 250 or 260 nm, as was convenient.

Fast atom bombardment mass spectra were obtained on a VG Analytical ZAB-HF ultrahigh resolution 8-kV mass spectrometer with accompanying 11/250 data system. Milligram samples were dissolved in CH_3CN, for Bu_4N^+ salts, and a few microliters added to 100 μL of thioglycerol or other low-volatility matrices. For water-soluble salts the samples were either dissolved directly in the desired matrix or dissolved in water in a fashion analogous to the Bu_4N^+ salts above. In some cases, sample preparation leads to the formation of "polyoxoanion blues",[2] which, however, does not appear to significantly affect the spectra. Spectral simulations were obtained using the ISO program of VG Analytical.

Preparation of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$, 1. This material was prepared by our checked *Inorg. Synth.* procedure. Keys to the procedure include carefully dried CH_3CN and glassware (150 °C; cooling under vacuum), the use of sublimed $CpTiCl_3$ (and noncommercial; see the note about this elsewhere),[8c] and strict adherence to the other hints in the detailed procedure.[8c] The resulting product is dried *in vacuo* overnight at 25 °C, yield 7.6 g (59%).[8c] Alternatively, the product may be crystallized by vapor diffusion (using $CHCl_3$ or benzene) following the first EtOH wash and $CHCl_3$ precipitation[8c] by dissolving the sample in a minimum amount of CH_3CN. Crystallization proceeded over the course of several days, yielding typically 3.2 grams (25% yield) of dark crystals after two such crystallizations.

Anal. Calcd (found) (from Pascher): C, 23.29 (23.10); H, 4.22 (4.25); N, 1.57 (1.65); Ti, 1.35 (1.09); Si, 0.79 (0.78); W, 46.5 (46.4); V, 4.26 (4.60); O, 18.0 (18.2); total, 100.0 (100.07).

Molecular weight (sedimentation equilibrium method, in 0.1 M $Bu_4N^+PF_6^-/CH_3CN$; $\bar{M}_r$ = weight-average molecular weight): $\bar{M}_r$(calc for $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$) 3558, $\bar{M}_r$(found) 3470 (supplementary material, Figure A). In the calculation of the weight-average molecular weight an apparent specific volume of 0.4073 was used, as measured in a 0.1 M $Bu_4N^+PF_6^-/CH_3CN$ solution via a pycnometer using the method of densities.[27] The CH_3CN solution alone exhibited an apparent specific volume of 0.4060.

The positive ion FAB mass spectrum (supplementary material, Figure B) was obtained as a thioglycerol solution and shows the expected most abundant mass ion at $(M + H)^+$ = m/e 3559 together with the characteristic losses of O (m/e = 16) and cationization.[8a,11a]

UV/vis (CH_3CN) showed end absorbance from high-energy tailing into the visible region with a shoulder around 250–300 nm ($\epsilon_{260} \approx$ 33 000 cm^{-1} mol^{-1} L) and ca. 455 nm ($\epsilon_{455} \approx$ 2400 cm^{-1} mol^{-1} L).

IR (CH_3CN, cm^{-1}) (Figure 3): 1005 (w); 965 (m); 900 (s); 860 (w); 810 (m); 775 (m); 700 (w).

^{29}Si (21 °C, 0.09 M, CD_3CN, 26000 transients, S/N = 30.3:1), δ (multiplicity, $\Delta\nu_{1/2}$): –83.2 (s, 0.56 ± 0.06 Hz).

^{51}V (21 °C, 0.09 M, CD_3CN), δ (multiplicity, no. of V, $\Delta\nu_{1/2}$) (Figure 2, inset): –604 (s, 2, 1096 Hz), –561 (s, 1, 146 Hz).

^{183}W (21 °C, 0.28 M, in 2:1 DMF/CD_3CN, 100 000 transients), δ (multiplicity, no. of W, $\Delta\nu_{1/2}$) (Figure 2): –75.1 (s, 2, 60 Hz), –83.2 (s, 2, 2.1 ± 0.1 Hz), –112.3 (s, 1, 11 Hz), –129.3 (s, 2, 5.3 ± 0.2 Hz), –132.2 ppm (s, 2, 2.2 ± 0.5 Hz). Decoupling of the –561 ppm resonance in the ^{51}V NMR resulted in the sharpening of the –75.1 and –12.3 ppm resonances.

^{1}H (100 MHz, CW mode, 21 °C, CD_3CN), δSPCLN 6.90 (in addition to the Bu_4N^+ resonances). The calculated, relative intensity of the δ 6.9 (Cp) resonance vs the methyl group in $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ is 32:5, found = 34:5. At 360 MHz (FT experiment) the relative intensities varied as a function of the repetition rate, varying from a ratio of 11.8:1 with a repetition rate of ca. 102.5 s to 18.7:1 with a repetition rate of ca. 3.5 s.

Control Reaction of $CpTiCl_3$ and $AgNO_3$ in CH_3CN. A control experiment was performed involving the reaction of $CpTiCl_3$ with 3 equiv of $AgNO_3$ in CD_3CN to exclude the presence of multiple species or decomposition. Collection of the AgCl showed, after rinsing it with CH_3CN, drying, and weighing, that ≥96% of the expected AgCl is produced in this reaction. A ^{1}H NMR showed a single resonance at δ 7.15. (The reasons for formulation of the *in situ* generated product as "$CpTi(CH_3CN)_x(NO_3)_3$" are discussed in a footnote.[10])

Stability of the $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$. The stability of the $[CpTi{\cdot}SiW_9V_3O_{40}]^{4-}$ anion was tested both in solution and in the solid state. Examining a solution of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ in CH_3CN after ca. 1 month at room temperature showed no discernible difference by ^{51}V or by ^{183}W NMR. The solid has been examined by IR and by ^{1}H NMR (i.e., after redissolving it in CH_3CN) after over 1 year on the benchtop; again, no discernible change in the material is observed.

Cation-Exchange Resin ($P\text{-}SO_3^-Bu_4N^+$) Test of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$. A 10-g amount of macroreticular, strongly acidic resin Amberlyst 15 (H^+ form; $P\text{-}SO_3^-H$) was placed in a beaker together with ca. 50 mL of water. The resin was swirled for ca. 1 min followed by decanting the water. This process was repeated until the aqueous phase was clear and colorless. The resin was then packed onto a 27 cm × 1 cm (length × diameter) column. A large excess, ca. 30 mL, of 40% $Bu_4N^+OH^-/H_2O$ 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 removed from the column and suspended in ca. 50 mL of anhydrous methanol. The methanol was decanted and the process repeated with CH_3CN. The resulting $P\text{-}SO_3^-Bu_4N^+$ column was repacked and flushed with ca. 250 mL of CH_3CN. A solution of ca. 0.5 g of $(Bu_4N)_4[CpTi{\cdot}SiW_9V_3O_{40}]$ in

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(27) (a) Chervenka, C. H. *A Manual of Methods for the Analytical Ultracentrifuge*; Spinco Division of Beckman Instruments: Palo Alto, CA, 1970. (b) Fujita, H. *Foundations of Ultracentrifugal Analysis*; John Wiley & Sons: New York, 1975; pp 308–313.

10 mL of CH_3CN was passed dropwise through the column. This colored solution passed through the column with no apparent retention (i.e., the $CpTi^{3+}$ group was not removed from the polyoxoanion). The colored eluant was collected and the solvent removed by rotary evaporation under reduced pressure. The resulting $P–SO_3^-Bu_4N^+$-treated $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ was unchanged (by ^1H NMR and IR spectroscopy).

Anion-Exchange Resin ($P–NR_3^+Cl$) Test of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$. A 10-g amount of the macroreticular Amberlyst A-27 basic pH resin (Cl^- form; $P–NR_3^+Cl$) was washed with water, methanol, and CH_3CN. A sample of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ was passed through a column containing this anion-exchange resin using CH_3CN as described above for the cation-exchange resin. All of the colored sample was retained on the resin, indicating that the orange $CpTi^{3+}$ group had not been cleaved from the complex.

Reaction of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ with Br_2. In the drybox, 0.1 g (0.0281 mmol) of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ in 10 mL of dry CH_3CN was prepared. A solution composed of 1.427 g of Br_2 in CCl_4 (25-mL total volume) was prepared. An aliquot of 0.237 mL of this Br_2/CCl_4 solution (3.00 equiv) was added to the heteropolytungstate solution and the resulting solution stirred for 1 h. The solvent was then removed by rotary evaporation under reduced pressure, the residue was dissolved in CD_3CN, 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. ^{51}V NMR (supplementary material, Figure C) showed a complex set of resonances.

Reaction of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ with $Et_3O^+BF_4^-$. In the drybox, 0.100 g (0.0281 mmol) (of $Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ was dissolved in 10 mL of dry CH_3CN. To this stirring solution, 16 mg (0.084 mmol) $Et_3O^+BF_4^-$ 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 CD_3CN, 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. ^{51}V NMR (supplementary material, Figure C) showed a complex set of resonances.

Reaction of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ with $Bu_4N^+OH^-/H_2O$. In the drybox, 0.100 g of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ was dissolved in 10 mL of CH_3CN. An aliquot of $Bu_4N^+OH^-/H_2O$ (0.165 mL of 0.511 M of 3 equiv) 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 CD_3CN, and the solution was examined by NMR. ^1H NMR showed appreciable broadening of the Bu_4N^+ resonances but no trace of the δ 6.9 resonance characteristic of the starting material. However, ^{51}V NMR (supplementary material, Figure C) showed a single resonance at δ −568 that was different than the δ −531 resonance characteristic of $SiW_9V_3O_{40}^{7-}$. As a ca. −562 ppm resonance also appears as one of the major lines resulting from the reaction of $(Bu_4N)_4H_3SiW_9V_3O_{40}$ with excess $Bu_4N^+OH^-/H_2O$, it is unclear whether or not follow-up chemistry is also occurring in this reaction of $(Bu_4N)_4(CpTi·SiW_9V_3O_{40})$ with $Bu_4N^+OH^-/H_2O$. Specifically, follow-up chemistry due to hydrolysis of the Ti^{4+}–heteropolytungstate complex to yield $SiW_9V_3O_{40},^{7-}$ or one of its decomposition products, may be occurring.

Electrochemistry of $[CpTi·SiW_9V_3O_{40}]^{4-}$. The cyclic voltammogram (supplementary material, Figure D) (Pt bead working electrode, Pt wire auxiliary electrode, SCE reference electrode in 0.1 M $Bu_4N^+PF_6^-$) showed features similar to those observed for $(Bu_4N)_4H_3SiW_9V_3O_{40}$.[8b] With a scan speed of 200 mV/s, the first E_{pc} occurs at +0.30 V vs SCE.

Metathesis of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ to Other Alkylammonium Salts. A solution of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$ in CH_3CN (concentration typically 1 g/5 mL of solvent) was added dropwise to a stirring solution containing about 10 equiv of the desired alkylammonium salt in a minimum of CH_3CN. The resulting solution was then added dropwise to a well-stirred $CHCl_3$ solution of about 10 times the volume of the total CH_3CN solution volume above. After the addition was completed, the resulting solution was stirred for another $^1/_2$ h or until the precipitate appeared as a fine powder. If necessary, periodic trituration of the solid may be employed to assist in the formation of such powder. Filtration, followed by air drying, typically resulted in complete metathesis to the new alkylammonium ion as indicated by ^1H NMR. If necessary, the process was repeated until ^1H NMR indicated complete conversion. This approach was utilized successfully to prepare the Pr_4N^+, $HexylNMe_3^+$, and $BuNMe_3^+$ salts, respectively, of $[CpTi·SiW_9V_3O_{40}]^{4-}$. In all cases, ^1H NMR shows the characteristic resonances of the alkylammonium ion together with the Cp resonance unshifted from that observed for $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$. The ^{51}V NMR for each of the above salts is also unchanged with respect to $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$.

Approaches towards Growing X-ray-Quality Crystals for $[CpTi·SiW_9V_3O_{40}]^{4-}$. Multiple attempts by two of us over several years were aimed at growing X-ray-quality crystals of $[CpTi·SiW_9V_3O_{40}]^{4-}$. The following sets of conditions were tried with multiple attempts for each set of conditions cited performed. Using vapor diffusion methods, initial attempts involved heteropolyanion solutions at concentrations of ca. 1 g/5 mL of solvent, although more dilute initial concentrations were also tried. Alkylammonium salts other than Bu_4N^+ were prepared as described above.

A. One Countercation Experiments. For the Bu_4N^+ and Pr_4N^+ salts, slow cooling of hot, saturated DMF or CH_3CN solutions to −22 °C over several days yielded either no observable precipitate or orange powders. Slow cooling of DMF solutions of $BuNMe_3^+$ or $HexylNMe_3^+$ salts yielded similar results. Vapor diffusion of either THF, benzene, or $CHCl_3$ into either DMF or CH_3CN solutions of the Bu_4N^+ or Pr_4N^+ salts or DMF solutions of the Hex_4N^+ or $BuNMe_3^+$ salts was attempted. The heteropolyanions typically formed oils under these conditions. Crystals of the Bu_4N^+ salts could be obtained from the DMF or $CH_3CN/CHCl_3$ 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 diffract in an X-ray beam or, in a couple of cases for the Bu_4N^+ salt (Professor V. Day, private communication), a weakly diffracting crystal in a large ca. ~5500-Å unit cell and cubic crystal system was produced.

B. Multiple Cation Experiments. Vapor diffusion of the Bu_4N^+ salt of $[CpTi·SiW_9V_3O_{40}]^{4-}$ in the presence of 1 equiv of cesium triflate/DMF or potassium triflate/CH_3CN or $ZnBr_2/CH_3CN$ 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 Bu_4N^+ salt. In the case of the K^+/Bu_4N^+ system, however, a crystalline product whose morphology appeared different than the Bu_4N^+ salt alone was observed, but all material of sufficient size to be used for X-ray crystallography was comprised of unusable aggregates.

Preparation of $(Bu_4N)_6[CpTi·P_2W_{15}V_3O_{62}]$. [This preparation was carried out with the same precautions for dry solvent, 150 °C and vacuum dried glassware, and $CpTiCl_3$ purity (noncommercial; sublimed) as detailed in the *Inorg. Synth.* preparation of $(Bu_4N)_4[CpTi·SiW_9V_3O_{40}]$, a procedure which should be read before performing the following synthesis.] In the drybox 11.22 g (1.8 mmol) of $(Bu_4N)_9P_2W_{15}V_3O_{62}$ was dissolved in 200 mL of dried acetonitrile using dried glassware. [It is important to get a C, H, N analysis on the starting $(Bu_4N)_{6-x}H_{3+x}[P_2W_{15}V_3O_{62}]$ (x = 0.1),[8b] since one must know the number of H^+ countercations in order to add the correct the number of $Bu_4N^+OH^-$ needed to make clean, H^+-free (or, alternatively, excess OH^- free) $(Bu_4N)_9P_2W_{15}V_3O_{62}$; see footnote 30 elsewhere for additional information.[8b]] Separately, 0.93 g (5.5 mmol) of silver nitrate was dissolved in 2.5 mL of dried acetonitrile and this mixture then added to 5 mL of a rapidly stirring solution of 0.40 g (1.8 mmol) of $CpTiCl_3$ in 5 mL of dried acetonitrile. Stirring was continued for 15 min, followed by filtration using a medium glass frit; ≥96% of the expected 3.0 equiv of AgCl precipitate (washed with CH_3CN and dried before weighing) is formed in this step. The yellow filtrate of $CpTi(CH_3CN)_x(NO_3)_3$) was introduced into a vigorously stirred solution of the heteropolyanion causing an appreciable deepening in color. (Similar results to those that follow have been obtained in preliminary experiments if $CpTiCl_3$ alone is used as the "$CpTi^{3+}$" source.) After the addition of the titanium solution was complete, the reaction solution was refluxed for 8–20 h while still in the drybox, followed by rotary evaporation to dryness leaving a light-brown solid. (Control experiments omitting the reflux step gives a less clean product by ^{31}P NMR.) This solid is a mixture containing not only the supported heteropolyanion but also 3 equiv of $Bu_4N^+NO_3^-$ (all attempts at recrystallization proved unsuccessful). Yield: 6.7 g (66.3%), red-brown powder. The crude material was purified further, *vide infra*, but because it might prove satisfactory in some applications, the crude material was also characterized.

Anal. Calculated (found; repeat trials) (from Pascher) for $(Bu_4N)_6[CpTi·P_2W_{15}V_3O_{62}]·3Bu_4N^+NO_3^-$: C, 27.76 (28.17; 28.15); H, 5.17 (5.57; 5.57); N, 2.61 (2.92; 2.97); W, 42.78 (39.6; 39.6). Calcd (found) (from E+R) for $(Bu_4N)_6[CpTi·P_2W_{15}V_3O_{62}]·3Bu_4N^+NO_3^-$: C, 27.76 (29.19); H, 5.17 (5.43); N, 2.61 (2.78). (Note, of course, that, in the absence of the purification step given below, these analyses do little more that confirm the weighing precision for the reactants that are mixed together.)

IR (KBr, cm^{-1}): 1080 (m); 1035 (w); 940 (sh); 930 (s); 900 (m); 880 (sh); 780 (s, br).

^{51}V (21 °C, 0.031 M, CD_3CN), δ (multiplicity, no. of V, $\Delta\nu_{1/2}$) (Figure 5): −519 (s, 1, 211 ±9 Hz), −544 (s, 2, 454 ± 11 Hz).

^{31}P (21 °C, 0.031 M, CD_3CN), δ (Figure 4): −8.9 , −13.6.

^{183}W (21 °C, 0.031 M, CD_3CN), δ (multiplicity, no. of W): −90.4 (s, 2), −138.6 (s, 2), −171.9 (s, 2), −171.9 (s, 2), −173.7 (s, 2), −174.5 (s, 1), −246.8 (s, 2); −291.9 (s, 2). The lines at −138.6 and −246.9 ppm are considerably broadened.

^{1}H NMR (21 °C, 0.033 M, CD_3CN), δ: 6.85. ^{1}H NMR (21 °C, 0.033 M, d_6-DMSO), δSPCLN 6.71.

A positive ion FAB mass spectrum (supplementary material, Figure F) does not show a parent $(M + H)^+$ ion at *m*/*e* = 5533 but shows a good intensity envelope at *m*/*e* = 5501 $(M + H - 2O)^+$ and 5547 $(M + H - 6O)^+$. Loss of the $CpTi^{3+}$ fragment, $(M - CpTi^{3+} + 2H)^+$ = *m*/*e* 5422, was not observed.

To remove the 3 equiv of $Bu_4N^+NO_3^-$, the solid $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]\cdot 3\ Bu_4N^+NO_3^-$ was dissolved in a minimum amount of acetonitrile and the mixture filtered through Whatman No. 2 filter paper. The filter paper was washed with a small amount of acetonitrile, and the heteropolyanion was then reprecipitated by addition of 400 mL of dry ethyl acetate (control experiments show that $Bu_4N^+NO_3^-$ is soluble in both acetonitrile and ethyl acetate). After the suspension was stirred for 30 min, the precipitate was collected on a medium glass frit and washed with 50 mL of ether. To completely remove the contaminating $Bu_4N^+NO_3^-$, the reprecipitation was repeated two more times. Yield: 6.2 g (62%, calculated relative to the amount of starting 1.0 equiv of $(Bu_4N)_9P_2W_{15}V_3O_{62}$).

Anal. Calcd (found) (from Pascher) for $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$: C, 21.93 (21.42); H, 4.03 (4.05); N, 1.52 (1.66); W, 49.84 (50.7); Ti, 0.87 (0.92); P, 1.12 (1.10); V, 2.76 (2.74); O 17.93 (17.2); total 100.0 (99.79).

Molecular weight (sedimentation equilibrium method, in 0.1 M $Bu_4N^+PF_6^-/CH_3CN$): $\bar{M}_r$(calc for $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$) 5532, $\bar{M}_r$(found) 5770 ± 600 (supplementary material, Figure E).

^{31}P (21 °C, 0.031 M, CD_3CN), δ (multiplicity, no. of P, $\Delta\nu_{1/2}$): −8.6 (s, 1 ± 1, 1.86 ± 0.6 Hz), −13.3 (s, 3 ± 1, 11.22 ± 3.7 Hz). ^{31}P (21 °C, 0.031 M, d_6-DMSO), δ: −8.8, −13.5.

^{51}V (21 °C, 0.031 M, CD_3CN), δ (multiplicity, no. of V, $\Delta\nu_{1/2}$): −524 (s, 1, 232 ± 6 Hz), −550 (s, 2, 506 ± 25 Hz). ^{51}V (21 °C, 0.031 M, d_6-DMSO), δ: −532, −559.

^{183}W (21 °C, 0.031 M, CD_3CN) (supplementary material, Figure 1), δ: −86.2, −135.2, −168.6 , −169.7, −171.4; −173.2, −240.9; −286.8. The lines at −135.2 and −240.9 ppm are considerably broadened.

^{1}H (21 °C, 0.033 M, CD_3CN), δSPCLN 6.69 (for Cp–H).

In two preparations, following the reflux step, a green solution instead of a light-brown one was obtained. This green solution subsequently yielded a green powder, instead of a light-brown colored one, in the ethyl acetate precipitation step. Even though a ^{51}V NMR spectrum of this green powder showed the expected two-line spectrum (integrated intensities 1:2), ^{31}P NMR did not give a clean spectrum but showed numerous peaks flanking the two ^{31}P NMR resonances expected. The source of this discrepancy is not completely understood, although a solution of $CpTiCl_3$ in dry and degassed acetonitrile (water contents < 0.02%) changes from clear-yellow to green over the course of 2 d; however, the ^{1}H NMR remains unchanged. To confirm that the reported synthesis is reliable, one more independent repeat of this preparation *exactly as written up above* was performed prior to submitting this paper, and it gave authentic material exhibiting clean ^{51}V and ^{31}P NMR spectra.

Metathesis of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ to Other Alkylammonium Salts. Passing the compound through a cation-exchange resin in the Pr_4N^+ form, $P\text{-}SO_3^-\text{-}Pr_4N^+$, followed by precipitation of the product from a concentrated CH_3CN solution by addition of excess Pr_4N^+, yielded the Pr_4N^+ salt only as indicated by ^{1}H NMR. Crystallization of this product from $CH_3CN/CHCl_3$ using vapor diffusion techniques resulted in a small amount of decomposition as indicated by the appearance of additional resonances in the ^{51}V NMR (the exact amount of decomposition was not quantifiable due to overlapping resonances).

Cation-Exchange Resin Tests of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$. A solution of 0.5 g of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ was passed down an Amberlyst 15 acidic cation-exchange resin in the Bu_4N^+ form, $P\text{-}SO_3^-\text{-}Bu_4N^+$, as described above for $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$. As expected, if no $CpTi^{3+}$ dissociation for the complex occurred, no retention of the dark orange solution was noted, and the colored eluant was unchanged (by ^{1}H and ^{51}V NMR).

Experiments Probing Whether or Not the *C*$_s$ Symmetry Isomer of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ Is the Kinetic or Thermodynamic Product (Isomer). Variable-Temperature ^{51}V NMR. Variable-temperature ^{51}V NMR of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ (0.031 M, CD_3CN) between 5 and 45 °C showed an increase in line-broadening at lower temperatures [δ (sample temperature, $\Delta\nu_{1/2}$) −524 (25 °C, 372 ± 31 Hz) (5 °C, 473 ± 52 Hz); −550 (25 °C, 842 ± 29 Hz) (5 °C; 1053 ± 56 Hz)]. Unsurprisingly, upon subjection of the sample to elevated temperature, a sharpening of the resonances (a decrease in the line-broadening) was observed [δ (sample temperature, $\Delta\nu_{1/2}$) −524 (25 °C, 372 ± 31 Hz) (45 °C, 292 ± 28 Hz); −550 (25 °C, 842 ± 29 Hz) (45 °C; 692 ± 12 Hz)]. Returning the sample to 25 °C demonstrated that these line width changes are completely reversible. Note that in all cases that two ^{51}V NMR lines are seen requiring that the *C*$_s$ symmetry of the complex be maintained (at least up to the 45 °C examined).

Experiments with Added $CpTi(CH_3CN)_3^{3+}$ as a Possible Isomerization Catalyst. In the drybox, 200 mg (0.036 mmol) of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ was dissolved in 0.6 mL of CD_3CN. To this solution was added 1 equiv of $[CpTi(CD_3CN)_3]^{3+}$ (0.2 mL (1 equiv) of a stock solution prepared by reaction of 0.158 g (0.72 mmol) of $CpTiCl_3$ and 0.367 g (2.16 mmol) of $AgNO_3$ in a total of 4 mL of d_3-acetonitrile, filtering off the AgCl precipitate, and adjusting to a final volume of 4.0 mL with d_3-acetonitrile). The ^{51}V NMR spectrum, collected immediately after the addition of 1 equiv of $[CpTi(CH_3CN)_3]^{3+}$, remains unchanged, showing the familiar two-line spectrum (*vide supra*) with δ −524, −554. Similarly, addition of a total of 2 and 5 equiv of $[CpTi(CH_3CN)_3]^{3+}$ to the above heteropolytungstate solution did not change the number or chemical shift of resonances in the ^{51}V NMR spectrum observed for $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$.

Preparation of $(Bu_4N)_4[ClTi\cdot SiW_9V_3O_{40}]$. In the drybox, a solution containing 5.0 grams (1.2 mmol) of $(Bu_4N)_7SiW_9V_3O_{40}$ in 30 mL of 1,2-dichloroethane was prepared. A 132-μL volume (1.0 equiv) of $TiCl_4$ was added by syringe. The resulting solution was refluxed for 1 h, and then all solvent was removed by rotary evaporation under reduced pressure. IR (CH_3CN): 970 cm^{-1} (m); 910 cm^{-1} (s), 820 cm^{-1} (m); 785 cm^{-1} (m). ^{183}W NMR (1 g/mL of CD_3CN, 60 000 transients, 13.67 h) showed a dominant five-line spectrum at −76.8 (2W, $\Delta\nu_{1/2}$ ca. 36 Hz), −94.3 (2W, $\Delta\nu_{1/2}$ = 2.6 ± 0.1 Hz), −104.0 (2W, $\Delta\nu_{1/2}$ = 3.4 ± 0.1 Hz), −114.0 (2W, $\Delta\nu_{1/2}$ = 3.0 ± 0.1 Hz), and −115.4 ppm (1W, $\Delta\nu_{1/2}$ = 7.4 ± 0.3 Hz). All recrystallization attempts (all under N_2) proved unsuccessful, yielding only an oily or gummy substance. The approach which proved successful for $(Bu_4N)_4CpTiSiW_9V_3O_{40}$, namely, MeOH or EtOH washing to remove impurities, followed by crystallization from $CH_3CN/CHCl_3$, was not explored with $[ClTi\cdot SiW_9V_3O_{40}]^{4-}$ due to the anticipated sensitivity of the now exposed titanium center. Repeating the synthesis using crystalline, sublimable $TiCl_4(CH_3CN)_2$[24] as an alternative source of $TiCl^{3+}$ yielded a product with a similar IR spectrum.

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Supplementary Material Available: Plot of ln absorbance (*A*) vs r_i^2 from the ultracentrifugation molecular weight measurement for $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$ (Figure A), positive ion FAB mass spectrum of $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$ in thioglycerol (Figure B), ^{51}V NMR spectra of $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$ following treatment with ca. 3 equiv of (A) Br_2, (B) $Et_3O^+BF_4^-$, and (C) $Bu_4N^+OH^-/H_2O$ (Figure C), cyclic voltammogram for 1 mM $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$ in 0.1 M $Bu_4N^+PF_6^-/CH_3CN$ (Figure D), plot of ln absorbance (*A*) vs r_i^2 from the ultracentrifugation molecular weight measurement for $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ (Figure E), positive ion FAB mass spectrum of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ in thioglycerol (Figure F), possible *C*$_s$ symmetry isomer of $[CpTi\cdot P_2W_{15}V_3O_{62}]^{6-}$ involving $CpTi^{3+}$ attachment to four polyoxometalate surface oxygens (Figure G), ^{183}W NMR of $(Bu_4N)_4[ClTi\cdot SiW_9V_3O_{40}]$ (Figure H), and ^{183}W NMR spectrum of $(Bu_4N)_6[CpTi\cdot P_2W_{15}V_3O_{62}]$ in CD_3CN, showing the expected 8-line spectrum for a *C*$_s$ symmetry heteropolyoxoanion-supported complex (Figure 1) (7 pages). Ordering information is given on any current masthead page.