Synthesis, Molecular Structure, and Reactivity of a Half-Sandwich Vanadium(III) Imido Complex: The First Vanadium(V) Alkyldiene

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Summary: One of the trimethylphosphine ligands in CpV(NAr)(PMes)2; Ar = 2,6-C6H3-i-Pr2, obtained by magnesium reduction of CpV(NAr)Cl2, can be substituted by CO, ethylene, or diphenylacetylene to give the corresponding N-acceptor (L) complex CpV(NAr)(L)-Ph (Scheme 1). Reduction of 2 with magnesiun in the presence of trimethylphosphine (Scheme 1) yields the diamagnetically non-splitting bis(trimethylphosphine) complex CpV(NAr)(PMes)2 (3).

An X-ray structure determination of 311 (Figure 1) shows a nearly tetrahedral geometry about vanadium with a C(centroid)-V(1)-N(1) bond angle of 129.99(11)°, P(1)-V(1)-N(1) bond angles of 99° (average) and P(2)-V(1)-C(centroid) bond angles of 114° (average). All such interligand angles are similar to those found in structurally characterized d2 group 4 metalloene complexes.

Here we wish to report the synthesis and characterization of a simple half-sandwich imidovanadium(III) complex, as well as some aspects of its reactivity, including the synthesis and molecular structure of the first vanadium(V) alkyldiene.

In analogy with the established route to 4-substituted (phenylimido)/vanadium complexes,4 reaction of VOCl3 with ArNCO (Ar = 2,6-C6H3-i-Pr2) in refluxing n-octane gave V(NAr)Cl3 (1) in a nearly quantitative yield (Scheme 1). 1 reacts cleanly with CsPPh3 to produce the moderately air sensitive half-sandwich imidovanadium dichloride CpV(NAr)Cl2 (2) in good yield (Scheme 1). Reduction of 2 with magnesium in the presence of trimethylphosphine (Scheme 1) yields the diamagnetically non-splitting bis(trimethylphosphine) complex CpV(NAr)(PMes)2 (3).

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3 For a list of references, see ref 2.

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V(W) or V(V) systems (usually A)

![Figure 1. ORTEP diagram of 3. The thermal ellipsoids are drawn at the 30\% probability level. Selected bond distances (\text{\AA})/ (20): V(1)-N(1) = 1.698(2), V(1)-P(1) = 2.3994(9), V(1)-P(2) = 2.3868(10), V(1)-C(19) = 2.357(4), V(1)-C(20) = 2.340(5), V(1)-C(21) = 2.228(3), V(1)-C(22) = 2.187(4), V(1)-C(23) = 2.268(4). Selected bond angles (deg): V(1)-N(1)-C(1) = 170.7(2), P(1)-V(1)-P(2) = 92.60(4), P(1)-V(1)-N(1) = 101.66(6), P(2)-V(1)-N(1) = 96.69(9), C_{\text{centroid}}-V(1)-N(1) = 129.99(11), P(1)-V(1)-C(21) = 113.24(6), P(2)-V(1)-C_{\text{centroid}} = 115.49(7).

Scheme 1. Synthesis and Reactivity of 3

such as Cp$_2$Ti(PMe$_3$)$_2$. The V-N distance of 1.698(2) A is characteristic of V-N multiple bonding but is relatively long compared to most known V-N bonds in V(IV) or V(V) systems (usually 1.60-1.68 A) and similar to the one found in the comparatively electron rich V(III) complex Cp(V=NC(CMe$_3$)=CHCMe$_3$)(dmpe) (1.707(2) A). The V-N-V angle is almost linear (170.7(2) A). Three short and two long V-C$_{\text{Cp}}$ bond distances indicate a trend toward $\eta^3$ coordination of the cyclopentadienyl moiety. Similar behavior has been observed for several cyclopentadienyl imido complexes of group 5 metals.4,13

One of the trimethylphosphate ligands in 3 can be substituted by CO, ethylene, or diphenylacetylene to give the corresponding $\pi$-acceptor (L) complex CpV(NAr)(L)(PMe$_3$) (L = CO, 4; L = C$_2$H$_4$, 5; L = Ph=C=CPh, 6; Scheme 1). The reactions proceed under conditions (25-50 °C, 1 atm) milder than those reported for the analogous niobium complex (C$_5$Me$_5$)(NAr)(PMe$_3$)$_2$.14 and no disubstitution, as has been reported for tittancene complex Cp$_2$Ti(PMe$_3$)$_2$.12,15 is observed. The products can be obtained in good yields as crystalline solids.

The CO stretch for carbonyl complex 4,16 at 1885 cm$^{-1}$, and the $^{13}$C NMR shifts of the vanadium-bonded ethylene carbons of 5$^{17}$ (40.7 and 38.8 ppm) are consistent with considerable back-donation from the vanadium(III) centers of 4 and 5. The $^{13}$C NMR spectrum of $^{[13]C}_2$-4,18 prepared from 3 and $^{12}$CO, shows a broad plateau-form resonance for the carbonyl carbon at 306 ppm, the broadening being caused by a combination of unresolved coupling to the $I = 7/2$ vanadium nucleus and quadrupolar relaxation effects.$^{4e}$ For the same reason no olefinic C-H coupling constants can be determined in the $^{13}$C NMR spectrum of 5. The $^2$H NMR spectrum of $^{[2H]}_2$-5,19 prepared from 3 and Cp$_2$D$_4$, shows resonances at 1.92, 1.76, and 0.75 ppm, which correspond to partially hidden multiplets in the $^1$H NMR of 5. The relatively high IR frequency of the $v_{CO}$ vibration (1778 cm$^{-1}$) in alkyn complex 6 indicates that the alkyn acts as a two-electron donor, in contrast with the alkyn acting as a four-electron donor in structurally characterized Cp$_2$V($\eta^2$-PhC=CPh)(PMe$_3$)$_2$.20 ($v_{CO}$ = 1600 cm$^{-1}$).

Alkylidene transfer from phosphoranes to reduced transition-metal complexes has been reported for Cp$_2$Zr$^{21}$ and Cp$_2$TaMe systems$^{22}$ and recently for W(IV) imido complexes.$^{23}$ Reaction of Ph$_3$P=CHPh (Scheme 1) proceeds with loss of PMe$_3$ and PPh$_3$ to give the corresponding macceptor (L) complex Cp$_2$V(NAr) eq

(16) Selected spectroscopic data for 4: $^1$H NMR (toluene-d$_6$) $\delta$ 7.06 (d, 2H, $v_{\text{NH}} = 7$ Hz, NAr H$_6$), 6.96 (t, 1H, $v_{\text{NH}} = 7$, NAr H$_7$), 5.01 (d, SH, $v_{\text{NH}} = 2.1$, Cp), 4.22 (sept, 2H, $v_{\text{NH}} = 6.8$, CHMe$_2$), 1.32 (d, 6H, $v_{\text{NH}} = 6.8$, CHMe$_2$), 0.82 (d, 6H, $v_{\text{NH}} = 7.1$, PMe$_3$); $^{13}$C NMR (toluene-d$_6$) $\delta$ 144.0 (NAr C$_1$), 123.1 (NAr C$_2$), 122.4 (NAr C$_3$), 95.3 (Cp), 27.7 (CHMe$_2$), 24.5, 23.3 (CHMe$_2$), 19.6 (d, $v_{\text{CH}} = 20.6$); $^{11}$V NMR (toluene-d$_6$) $\delta$ 348 (d, $v_{\text{NV}} = 220$ Hz).
(17) Selected spectroscopic data for 5: $^1$H NMR $\delta$ 7.06 (d, 2H, $v_{\text{NH}} = 7$, NAr H$_6$), 6.85 (t, 1H, $v_{\text{NH}} = 7$, NAr H$_7$), 5.14 (d, SH, $v_{\text{NH}} = 2.1$, Cp), 3.90 (sept, 2H, $v_{\text{NH}} = 6.8$, CHMe$_2$), 2.00 (m, 5H, CH$_2$), 1.80 (m, 1H, CMe$_2$), 1.17 (d, 6H, $v_{\text{NH}} = 6.8$, CHMe$_2$), 0.90 (d, 9H, $v_{\text{NH}} = 7.3$, PMe$_3$), 0.81 (m, 1H, CH$_2$); $^{13}$C NMR NAr C$_{\text{CN}}$ not observed, $\delta$ 145.4 (NAr C$_1$), 122.7 (NAr C$_2$), 122.6 (NAr C$_3$), 99.8 (Cp), 40.8, 38.8 (br s, CHMe$_2$), 27.0 (CHMe$_2$), 24.4, 23.7 (CH$_2$); $^{13}$C NMR $\delta$ 144.0 (NAr C$_1$), 123.1 (NAr C$_2$), 122.4 (NAr C$_3$), 95.3 (Cp), 27.7 (CHMe$_2$), 24.5, 23.3 (CHMe$_2$), 19.6 (d, $v_{\text{CH}} = 20.6$); $^{11}$V NMR (toluene-d$_6$) $\delta$ 348 (d, $v_{\text{NV}} = 220$ Hz).
(18) Selected spectroscopic data for $^{[13]C}_2$-4: $^{13}$C NMR (C$_6$D$_6$) $\delta$ 306 (CO, $v_{\text{CO}} = 1320$ Hz).
(19) Selected spectroscopic data for $^{[13]C}_2$-5: $^{13}$C NMR (C$_6$D$_6$) $\delta$ 306 (CO, $v_{\text{CO}} = 1320$ Hz).
Transfer of the alkylidene moiety from phosphorus to vanadium is clearly indicated by the downfield shift of the alkylidene H₆ (13.45 ppm) and C₆ (304 ppm) resonances. Nuclear Overhauser effect experiments²⁵ indicate a syn arrangement of the alkylidene ligand relative to the imido group in the single alkylidene rotamer that is formed.

The structure of 7 was confirmed by an X-ray diffraction study²⁶ (Figure 2), showing a slightly distorted tetrahedral geometry about the metal, similar to the geometry in 3. All interligand angles are similar to those found in the structurally characterized niobium analogue (C₆Me₆)Nb(NAr)(=CHPh)PMe₃,²⁷ whereas the differences in metal–ligand distances correlate well with the difference in ionic radii of V(V) and Nb(V)²⁸ (e.g. V= C = 1.922(6) Å versus Nb=C = 2.026(4) Å). The V(1)–C(24)–C(25) angle of 136.9(4)° is indicative of an undistorted²⁹ alkylidene ligand, which is in marked contrast with the very obtuse V= C–C angle of 173.3–(3)° that was observed in the only other structurally characterized 3d-metal alkylidene, CpV(CHCMe₃)₂(dmpehSa)²⁷.

Crystal ionic radii are drawn at the 30% probability level. Selected bond distances (Å): V(1)–N(1) = 1.679(5), V(1)–P(1) = 2.4010(19), V(1)–C(24) = 1.922(6), V(1)–C(24) = 1.990(3). Selected bond angles (deg): V(1)–N(1)–C(1) = 169.5(4), P(1)–V(1)–C(24) = 87.62(17), P(1)–V(1)–N(1) = 99.24(15), N(1)–V(1)–C(24) = 105.12(2), C₆P₃Me₃–V(1)–N(1) = 126.96–(16), P(1)–V(1)–C(24) = 113.12(9), V(1)–C(24)–C(25) = 138.9(4), V(1)–C(24)–H(24) = 113(3).

In an initial reactivity study, benzylidene complex 7 shows no activity in ROMP of norbornene³⁰ and no reaction with acetone,³¹ presumably due to its electronic and coordinative saturation and lack of dissociation of PMe₃ from the Lewis acidic metal center.

Currently we are investigating both the reactivity of the compounds mentioned here and the scope of alkylidene transfer from phosphoranes to low-valent vanadium complexes.

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Supplementary Material Available: Text giving experimental details and analytical and spectral data for all compounds and tables giving details of the structure determination, crystal data, positional and thermal parameters, bond distances and angles, and torsion angles for 3 and 7 (38 pages). Ordering information is given on any current masthead page.

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(31) 7 can be dissolved in acetone-d₆ without decomposition (NMR).