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

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Received May 11, 1994[⊗]

*Summary: One of the trimethylphosphine ligands in $CpV(NAr)(PMe_3)_2$ (**3**; Ar = 2,6-C_6H_3-i-Pr_2), obtained by magnesium reduction of $CpV(NAr)Cl_2$ (**2**), can be substituted by CO, ethylene, or diphenylacetylene to give the corresponding π-acceptor (L) complex $CpV(NAr)(L)(PMe_3)$ (L = CO, **4**; L = C_2H_4, **5**; L = $PhC{\equiv}Ph$, **6**). **3** reacts with $Ph_3P{=}CHPh$ to form the first vanadium(V) alkylidene, $CpV(NAr)({=}CHPh)(PMe_3)$ (**7**).*

Imido ligands have been widely used as stabilizing ligands in high-oxidation-state transition-metal complexes[1] and have played an important role in the development of well-defined olefin metathesis[2] and ring-opening metathesis polymerization[3] (ROMP) catalysts, i.e. alkylidenes. The use of imido ligands in organovanadium chemistry has allowed the isolation of thermally stable alkylvanadium(V) complexes[4] but did not lead to the isolation of vanadium(V) alkylidenes.[5] Half-sandwich vanadium imido complexes have received little attention,[4a–c,6] in spite of the potentially useful isolobal relationship between these complexes and titanocene derivatives.[7]

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) alkylidene.

In analogy with the established route to 4-substituted (phenylimido)vanadium complexes,[4a] reaction of $VOCl_3$ with ArNCO (Ar = 2,6-C_6H_3-*i*-Pr_2) in refluxing *n*-octane gave $V(NAr)Cl_3$ (**1**)[8] in a nearly quantitative yield (Scheme 1). **1** reacts cleanly with $CpSiMe_3$ to produce the moderately air sensitive half-sandwich imidovanadium dichloride $CpV(NAr)Cl_2$ (**2**)[9] in good yield (Scheme 1). Reduction of **2** with magnesium in the presence of trimethylphosphine (Scheme 1) yields the diamagnetic[9] vanadium(III) bis(trimethylphosphine) complex $CpV(NAr)(PMe_3)_2$ (**3**).[10]

An X-ray structure determination of **3**[11] (Figure 1) shows a nearly tetrahedral geometry about vanadium with a $Cp_{centroid}$—V(1)—N(1) bond angle of 129.99(11)°, P—V(1)—N(1) bond angles of 99° (average) and P—V(1)—$Cp_{centroid}$ bond angles of 114° (average). All such interligand angles are similar to those found in structurally characterized d^2 group 4 metallocene complexes

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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(5) One "Schrock-type" vanadium(III) alkylidene ((5a) Hessen, B.; Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Helgesson, G.; Håkansson, M.; Jagner, S.; Spek, A. L. *Organometallics* **1993**, *12*, 2268–2276) and several "Fischer-type" vanadium carbenes ((5b) Berlekamp, M.; Erker, G.; Petersen, J. L. *J. Organomet. Chem.* **1993**, *458*, 97–103 and references therein) are known.

(6) (a) Preuss, F.; Becker, H.; Kaub, J.; Sheldrick, W. S. *Z. Naturforsch.* **1988**, *43B*, 1195–1200. (b) Preuss, F.; Wieland, T.; Perner, J.; Heckmann, G. *Z. Naturforsch.* **1992**, *47B*, 1355–1362. (c) Preuss, F.; Wieland, T.; Günther, B. *Z. Anorg. Allg. Chem.* **1992**, *609*, 45–50.

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(8) All complexes gave satisfactory elemental analyses and have also been characterized by ^1H, ^{13}C, and ^{51}V NMR and IR. Full details may be found in the supplementary material.

(9) To a solution of $VCl_3[N\text{-}2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2]$ (7.50 g, 22.5 mmol) in 60 mL of CH_2Cl_2 was added $CpSiMe_3$ (3.12 g, 22.5 mmol). After the mixture was stirred for 48 h at 40 °C, the color had changed from green to golden brown and the mixture was filtered. After removal of the solvent in vacuo 15 mL of pentane was added to the residue and removed in vacuo, yielding 6.59 g (18.2 mmol; 81%) of product as a brown powder: ^1H NMR δ 6.82 (d, 2H, $^3J_{HH}$ = 7 Hz, NAr H_m), 6.72 (t, 1H, $^3J_{HH}$ = 7, NAr H_p), 5.89 (s, 5H, Cp), 3.91 (sept, 2H, $^3J_{HH}$ = 6.8, C*H*Me_2), 1.19 (d, 12H, $^3J_{HH}$ = 6.8, CH*Me_2*); ^{13}C NMR δ 159 (br, NAr C_{ipso}), 150.5 (NAr C_o), 129.3 (NAr C_p), 122.8 (NAr C_m), 116.6 (Cp), 28.2 ($CHMe_2$), 24.4 (CH*Me_2*); ^{51}V NMR δ −183 ($\Delta\nu_{1/2}$ = 875 Hz).

(10) A mixture of $CpVCl_2[N\text{-}2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2]$ (**2**; 1.09 g, 3.01 mmol), PMe_3 (0.46 g, 6.02 mmol), and magnesium (1.0 g, 41.1 mmol) in 20 mL of THF was stirred for 16 h under argon at room temperature. After removal of the solvent in vacuo, the dark residue was extracted with 40 mL of pentane. Concentrating and cooling the green extract to −25 °C gave 0.90 g (2.03 mmol, 67%) of product as dark green crystals in two crops: ^1H NMR δ 7.13 (d, 2H, $^3J_{HH}$ = 7 Hz, NAr H_m), 7.00 (t, 1H, $^3J_{HH}$ = 7, NAr H_p), 4.81 (t, 5H, J_{PH} = 2.1, Cp), 4.55 (sept, 2H, $^3J_{HH}$ = 6.8, C*H*Me_2), 1.22 (d, 12H, $^3J_{HH}$ = 6.8, CH*Me_2*), 0.99 (virtual t, 18H, P*Me_3*); ^{13}C NMR δ 142.9 (NAr C_{ipso}), 129.3 (NAr C_o), 122.7 (NAr C_p), 121.1 (NAr C_m), 94.1 (Cp), 26.8 ($CHMe_2$), 24.4 (CH*Me_2*), 22.6 (dd, $^1J_{PC}$ = 9.2 Hz, $^3J_{PC}$ = 6.1); ^{51}V NMR δ 265 (t, J_{PV} = 380 Hz).

(11) **3** crystallizes in the monoclinic space group $P2_1/c$ (No. 14), with a = 9.0608(3) Å, b = 19.0538(6) Å, c = 16.0943(5) Å, β = 110.466(3)°, V = 2603.18(15) Å^3, Z = 4, 6788 reflections measured, 5360 unique reflections, 298 K, Cu Kα radiation, $2.32° < \theta < 75.0°$. The structure was solved by automated Patterson methods (DIRDIF-92). Refinement on F^2 (SHELXL-93), with H atoms at calculated positions, gave $wR2$ = 0.115, $R1$ = 0.047, and S = 1.01.

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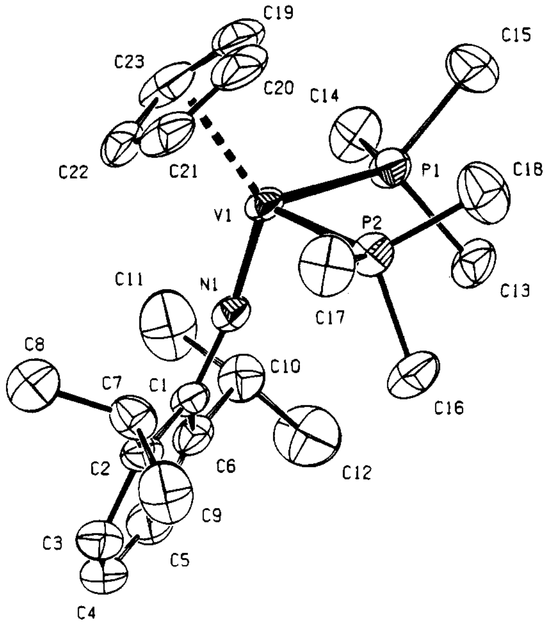
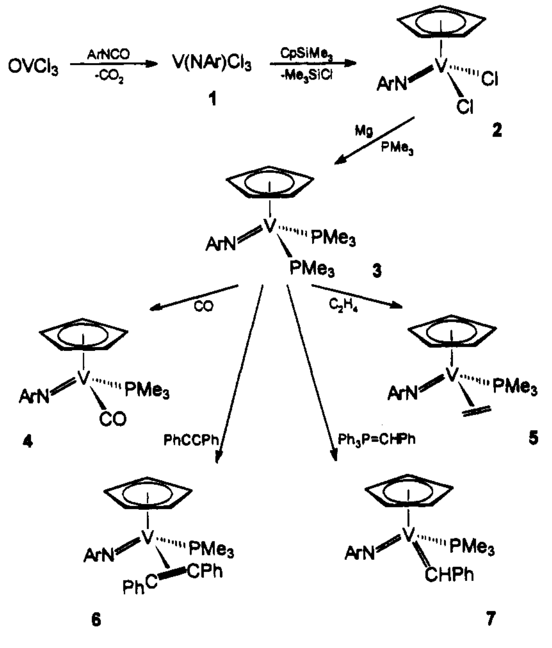


Figure 1. ORTEP diagram of **3**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): V(1)—N(1) = 1.698(2), V(1)—P(1) = 2.3994(9), V(1)—P(2) = 2.3859(10), V(1)—C(19) = 2.357(4), V(1)—C(20) = 2.340(5), V(1)—C(21) = 2.228(3), V(1)—C(22) = 2.187(4), V(1)—C(23) = 2.268(4). 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(8), P(2)—V(1)—N(1) = 96.69(9), $Cp_{centroid}$—V(1)—N(1) = 129.99(11), P(1)—V(1)—$Cp_{centroid}$ = 113.24(6), P(2)—V(1)—$Cp_{centroid}$ = 115.49(7).

Scheme 1. Synthesis and Reactivity of 3



such as $Cp_2Ti(PMe_3)_2$.[12] The V—N distance of 1.698(2) Å 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 Å)[1] and similar to the one found in the comparatively electron rich V(III) complex CpV[═NC(CMe$_3$)═CHCMe$_3$](dmpe) (1.707(2) Å).[5a] The V—N—Ar bond angle is almost linear (170.7(2)°). Three short and two long V—C_{Cp} bond distances indicate a trend toward η^3 coordination of the cyclopentadienyl moiety. Similar behavior has been observed for several cyclopentadienyl imido complexes of group 5 metals.[4b,13]

One of the trimethylphosphine ligands in **3** can be substituted by CO, ethylene, or diphenylacetylene to give the corresponding π-acceptor (L) complex CpV(NAr)(L)(PMe$_3$) (L = CO, **4**; L = C_2H_4, **5**; L = PhC≡CPh, **6**; Scheme 1). The reactions proceed under conditions (25–50 °C, 1 atm) milder than those reported for the analogous niobium complex $(C_5Me_5)Nb(NAr)(PMe_3)_2$,[14] and no disubstitution, as has been reported for titanocene complex $Cp_2Ti(PMe_3)_2$,[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] (δ 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]-**4**,[18] prepared from **3** and ^{13}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 ^2H NMR spectrum of [$^2H_4$]-**5**,[19] prepared from **3** and C_2D_4, shows resonances at 1.92, 1.76, and 0.75 ppm, which correspond to partially hidden multiplets in the ^1H NMR of **5**. The relatively high IR frequency of the $\nu_{C\equiv C}$ vibration (1778 cm^{-1}) in alkyne complex **6** indicates that the alkyne acts as a two-electron donor, in contrast with the alkyne acting as a four-electron donor in structurally characterized CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$[20] ($\nu_{C\equiv C}$ = 1600 cm^{-1}).

Alkylidene transfer from phosphoranes to reduced transition-metal complexes has been reported for Cp_2Zr[21] and Cp_2TaMe systems[22] and recently for W(IV) imido complexes.[23] Reaction of **3** with Ph$_3$P═CHPh (Scheme 1) proceeds with loss of PMe$_3$ and PPh$_3$ to produce the first vanadium(V) alkylidene, CpV(NAr)-

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(16) Selected spectroscopic data for **4**: ^1H NMR (toluene-d_8) δ 7.06 (d, 2H, $^3J_{HH}$ = 7 Hz, NAr H_m), 6.96 (t, 1H, $^3J_{HH}$ = 7, NAr H_p), 5.01 (d, 5H, J_{PH} = 2.1, Cp), 4.22 (sept, 2H, $^3J_{HH}$ = 6.8, C*H*Me$_2$), 1.32 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 1.26 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 0.82 (d, 9H, $^2J_{PH}$ = 7.1, PMe$_3$); ^{13}C NMR (toluene-d_8) NAr C_{ipso} not observed, δ 144.0 (NAr C_o), 123.1 (NAr C_p), 122.4 (NAr C_m), 95.3 (Cp), 27.7 (*C*HMe$_2$), 24.5, 23.3 (CH*Me*$_2$), 19.6 (d, $^1J_{PC}$ = 20.6); ^{51}V NMR (toluene-d_8) δ −548 (d, J_{PV} = 390 Hz).

(17) Selected spectroscopic data for **5**: ^1H NMR δ 6.93 (d, 2H, $^3J_{HH}$ = 7 Hz, NAr H_m), 6.85 (t, 1H, $^3J_{HH}$ = 7, NAr H_p), 5.14 (d, 5H, J_{PH} = 2.5, Cp), 3.60 (sept, 2H, $^3J_{HH}$ = 6.8, C*H*Me$_2$), 2.00 (m, 2H, C_2H_4), 1.80 (m, 1H, C_2H_4), 1.22 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 1.17 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 0.90 (d, 9H, $^2J_{PH}$ = 7.3, PMe$_3$), 0.81 (m, 1H, C_2H_4); ^{13}C NMR NAr C_{ipso} not observed, δ 145.4 (NAr C_o), 122.7 (NAr C_p), 122.6 (NAr C_m), 99.8 (Cp), 40.8, 38.8 (br s, C_2H_4), 27.0 (*C*HMe$_2$), 24.6, 24.4 (CH*Me*$_2$), 17.3 (d, $^1J_{PC}$ = 19.8); ^{51}V NMR δ −702 (d, J_{PV} = 272).

(18) Selected spectroscopic data for [^{13}C]-**4**: ^{13}C NMR (C_6D_6) δ 306 (*C*O, $\Delta\nu_{1/2}$ = 1230 Hz).

(19) Selected spectroscopic data for [$^2H_4$]-**5**: ^2H NMR (C_6D_6) δ 1.92 (br s, 2D, $\Delta\nu_{1/2}$ = 9 Hz), 1.76 (br s, 1D, $\Delta\nu_{1/2}$ = 11), 0.75 (br s, 1D, $\Delta\nu_{1/2}$ = 7).

(20) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925–1936.

(=CHPh)(PMe$_3$) (**7**).[24] Transfer of the alkylidene moiety from phosphorus to vanadium is clearly indicated by the downfield shift of the alkylidene H$_\alpha$ (13.45 ppm) and C$_\alpha$ (304 ppm) resonances. Nuclear Overhauser effect experiments[25] 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 study[26] (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 (C$_5$Me$_5$)Nb(NAr)(=CHPh)PMe$_3$,[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 undistorted[29] 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(CHCMe$_3$)(dmpe).[5a]

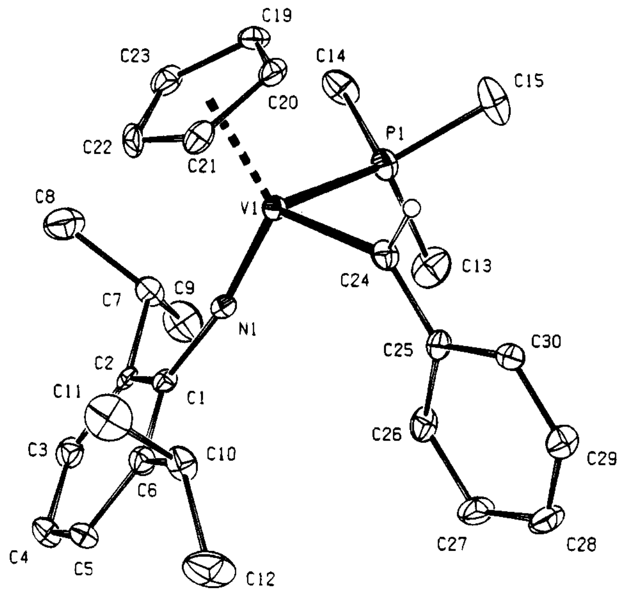

Figure 2. ORTEP diagram of **7**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): V(1)–N(1) = 1.679(5), V(1)–P(1) = 2.4010(19), V(1)–C(24) = 1.922(6), V(1)–Cp$_{centroid}$ = 1.990(3). Selected bond angles (deg): V(1)–N(1)–C(1) = 169.5(4), P(1)–V(1)–C(24) = 87.62(17), P(1)–V(1)–N(1) = 99.24(15), N(1)–V(1)–C(24) = 105.1(2), Cp$_{centroid}$–V(1)–N(1) = 126.96(16), P(1)–V(1)–Cp$_{centroid}$ = 113.12(9), V(1)–C(24)–C(25) = 136.9(4), V(1)–C(24)–H(24) = 113(3).

In an initial reactivity study, benzylidene complex **7** shows no activity in ROMP of norbornene[30] and no reaction with acetone,[31] presumably due to its electronic and coordinative saturation and lack of dissociation of PMe$_3$ 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.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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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[23] Johnson, L. K.; Frey, M.; Ulibarry, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167–8177.

[24] A mixture of CpV[N-2,6-C$_6$H$_3$-(*i*-Pr)$_2$](PMe$_3$)$_2$ (0.81 g, 1.82 mmol) and PhCH=PPh$_3$ (0.65 g, 1.82 mmol) in 20 mL of toluene was stirred at 70 °C for 16 h. Occasionally a vacuum was applied to remove PMe$_3$ liberated during reaction. After the mixture was cooled to room temperature, solid CuCl (0.18 g, 1.82 mmol) was added to coordinate free PPh$_3$ and the resulting mixture was stirred at room temperature for 20 h. Removal of the solvent in vacuo gave a sticky, brown residue, which was extracted two times with 50 mL of pentane. Concentrating and cooling the combined extracts to −25 °C yielded 0.41 g (1.11 mmol, 61%) of red crystals in two crops: ^{1}H NMR δ 13.45 (d, 1H, $^3J_{PH}$ = 7.5 Hz, H$_\alpha$), 7.65 (d, 2H, $^3J_{HH}$ = 7.9, Ph H$_o$), 7.11 (t, 2H, $^3J_{HH}$ = 7.9, Ph H$_m$), 7.00 (m, 3H, NAr H$_m$, Ph H$_p$), 6.83 (t, 1H, $^3J_{HH}$ = 7, NAr H$_p$), 5.58 (d, 5H, J_{PH} = 2.5, Cp), 4.27 (sept, 2H, $^3J_{HH}$ = 6.8, C*H*Me$_2$), 1.18 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 1.15 (d, 6H, $^3J_{HH}$ = 6.8, CH*Me*$_2$), 0.81 (d, 9H, $^2J_{PH}$ = 8.0, PMe$_3$); ^{13}C NMR (toluene-*d*$_8$) δ 304 ($\Delta\nu_{1/2}$ = 600 Hz, C$_\alpha$), 148.5 (NAr C$_{ipso}$), 144.8 (NAr C$_o$), 137.8 (Ph C$_{ipso}$), 127.8 (Ph C$_o$), 126.4 (Ph C$_p$), 125.1 (Ph C$_m$), 123.1 (NAr C$_p$), 122.5 (NAr C$_m$), 101.4 (Cp), 26.8 (*C*HMe$_2$), 24.4, 24.1 (CH*Me*$_2$), 18.0 (d, $^1J_{PC}$ = 22.5); ^{51}V NMR δ −630 (s, $\Delta\nu_{1/2}$ = 1000).

[25] In a 2D-NOESY of **7** an interaction between H$_\alpha$ and the Cp protons is observed, whereas NOE's between this proton and the *i*-Pr protons are absent. Calculations on the molecular structure of **7** support the observed NOE: H(24)–H(20) = 2.430 Å.

[26] **7** crystallizes in the monoclinic space group *P*2$_1$/*c* (No. 14), with *a* = 8.8870(12) Å, *b* = 15.816(2) Å, *c* = 18.719(2) Å, β = 104.930(10)°, *V* = 2542.3(6) Å^3, *Z* = 4, 8455 reflections measured, 3950 unique reflections, 150 K, Mo Kα radiation, 1.13° < θ < 24.2°. The structure was solved by automated Patterson methods (DIRDIF-92). Refinement on *F*^{2} (SHELXL-93), with H atoms at calculated positions, except H24 (which was located on a difference Fourier map), gave *wR*2 = 0.131, *R*1 = 0.063, and *S* = 0.94.

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[28] Crystal ionic radii are V(V) = 0.59 Å and Nb(V) = 0.69 Å: *Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1980; pp F214–215.

[29] See ref 1, p 155.

[30] A 0.035 M solution of **7** in C$_6$D$_6$ was allowed to react with 34 equiv of norbornene at 75 °C. No polymerization of norbornene or decomposition of **7** was observed after 72 h (NMR).

[31] **7** can be dissolved in acetone-*d*$_6$ without decomposition (NMR).