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Low-Coordinate (Arylimido)vanadium(V) Alkyls: Synthesis and Reactivity of $V(NAr)(CH_2Ph)_3$ (Ar = C_6H_3-2,6-Pr^i_2)

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Summary: The syntheses of a series of stable vanadium(V) alkyls have been achieved by the support of arylimido ligation. The (arylimido)vanadium(V) tribenzyl complex $V(NAr)(CH_2Ph)_3$ *(Ar =* C_6H_3*-2,6-*Pr^i_2*) has been prepared in high yield by the treatment of* $V(NAr)Cl_3{\cdot}THF$ *with* $PhCH_2MgCl$*. This compound, which represents the first structurally characterized vanadium(V) trialkyl complex, is a valuable synthetic precursor to a series of other vanadium(V) dialkyl derivatives with supporting alkoxide, aryloxide, and amido functionalities.*

In the area of homogeneous Ziegler−Natta olefin polymerization, classical vanadium catalyst systems have displayed a number of favorable performance characteristics.[1] These include (1) the preparation of high molecular weight polymers with narrow molecular weight distributions,[2] (2) the preparation of ethylene/α-olefin copolymers with high α-olefin incorporation,[2a,3] and (3) the preparation of syndiotactic polypropylene.[4] In view of the performances of these vanadium-based catalysts, and the distinctive advantages now offered by an impressive array of group IV single-site metallocene systems,[5] the synthetic development of well-defined single-site vanadium catalysts is an extremely desirable industrial goal.[6,7] Toward this goal, we describe the syntheses and structures of a rare series of low-coordinate vanadium(V) alkyls supported by arylimido ligation.[8]

The most common problem encountered in attempting to synthesize vanadium(V) alkyls is the reduction of the metal center upon alkylation.[9,10] In addition, the thermal instability of several vanadium(V) alkyl complexes and the formation of oils upon alkylation have often precluded full characterization and subsequent reactivity studies.[9−12] In order to surmount these problems, we have investigated the use of the sterically protected environment provided by bulky imido ligands, and in this regard, we have discovered that the (2,6-diisopropylphenyl)imido ligand[13] stabilizes the vanadium(V) center toward reduction and enables the formation of a series of thermally stable, crystalline vanadium(V) alkyl derivatives.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for ((2,6-Diisopropylaryl)imido)vanadium(V) Alkyls

compd	d(V–C)[a]	d(V–N$_{\mathrm{imido}}$)	d(V–O)	∠(C$_{ipso}$–N–V)
V(NAr)(CH$_2$C$_6$H$_5$)$_3$	2.061(7),[b] 2.079(7), 2.086(8)	1.641(6)		169.0(5)
V(NAr)(OC$_6$H$_3$-2,6-Pr$^i_2$)(CH$_2$C$_6$H$_5$)$_2$	2.048(7), 2.084(6)	1.669(5)	1.746(4)	161.7(4)
V(ArN)(OC(CF$_3$)$_3$)(CH$_2$C$_6$H$_5$)$_2$	2.026(7), 2.032(7)	1.638(5)	1.838(4)	172.9(4)
V(ArN)(NPhMe)(CH$_2$C$_6$H$_5$)$_2$	2.075(9),[b] 2.103(8)	1.658(7)		175.9(6)

[a] For Li[V(NSiBu$^t_3$)$_2$Me$_2$] d(V–C) = 2.043(8), 2.057(8)Å. [b] η^2-Coordinated benzyl ligand.

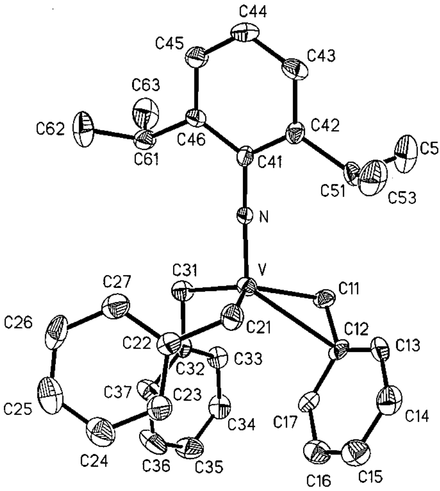


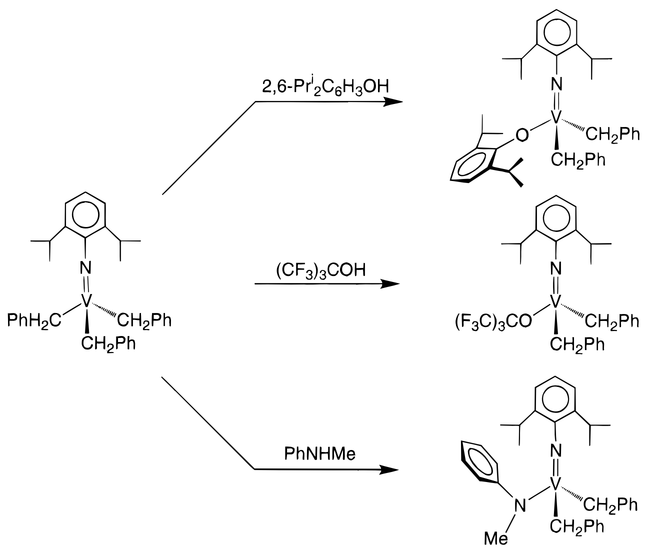
Figure 1. Molecular structure of V(NAr)(CH$_2$Ph)$_3$.

Significantly, the vanadium(V) tribenzyl complex V(NAr)(CH$_2$Ph)$_3$ (Ar = C$_6$H$_3$-2,6-Pr$^i_2$) can be readily obtained in high yield by treatment of V(NAr)Cl$_3$·THF[7] with PhCH$_2$MgCl in hexane (eq 1).[14,15]

$$\mathrm{V(NC_6H_3\text{-}2,6\text{-}Pr^i_2)Cl_3{\cdot}THF} \xrightarrow{\mathrm{3C_6H_5CH_2MgCl}} \mathrm{V(NC_6H_3\text{-}2,6\text{-}Pr^i_2)(CH_2Ph)_3} \quad (1)$$

An X-ray structure determination for V(NAr)(CH$_2$Ph)$_3$ reveals a monomeric structure with a pseudo-tetrahedral geometry at the metal center (Figure 1).[16-18] Selected bond lengths and angles are displayed in Table 1. Importantly, the isolation of a monomeric vanadium(V) complex demonstrates that the choice of the supporting ligand is critical, since Floriani has reported that treatment of V(Ntol)Cl$_3$·THF with PhCH$_2$MgCl and 2,4,6-Me$_3$C$_6$H$_2$MgBr leads to the formation of the vanadium(IV) dimers [V(Ntol)(CH$_2$Ph)$_2$]$_2$ and [V(Ntol)(C$_6$H$_2$-Me$_3$)$_2$]$_2$.[10a,c] In addition, the reactions between V(NAr)CpCl$_2$ and a wide variety of alkylating agents are reported to yield only complex oily mixtures.[19,20] Moreover, other attempts to prepare organometallic derivatives from V(NR)Cl$_3$ (R = Bu$^t_3$Si, C$_6$H$_3$-2,6-Me$_2$[21]) have led either to the formation of oils or to the reduction of the metal center.[9,10]

Scheme 1



Significantly, V(NAr)(CH$_2$Ph)$_3$ is also a valuable synthetic precursor to a series of new (arylimido)vanadium(V) dialkyls (Scheme 1). Treatment of V(NAr)(CH$_2$Ph)$_3$ with 2,6-Pr$^i_2$C$_6$H$_3$OH, (CF$_3$)$_3$COH, and *N*-methylaniline leads, in each case, to the elimination of toluene and formation of the arylimido–dibenzyl derivatives V(NAr)(OR′)(CH$_2$Ph)$_2$ (R′ = –C$_6$H$_3$-2,6-Pr$^i_2$, –C(CF$_3$)$_3$) and V(NAr)(NPhMe)(CH$_2$Ph)$_2$.[14,15]

As revealed by X-ray diffraction studies, these complexes all possess monomeric structures with pseudo-tetrahedral geometries at the vanadium metal centers.[22] Table 1 provides a list of selected bond lengths and angles for comparison. The V–C bond lengths span the range 2.026(7)–2.103(8) Å. For comparison, the average V–C bond length in Li[(Bu$^t_3$SiN)$_2$VMe$_2$] is 2.050(11) Å.[11a] The relatively short V–N bond lengths (1.638(5)–1.669(5) Å) and the C–N–V bond angles (161–176°) suggest that for these complexes the vanadium-nitrogen bond orders are likely to be close to three.[23] Of this series of compounds V(NAr)(OAr)(CH$_2$Ph)$_2$ possesses the longest V–N bond length (1.669(5) Å) and the smallest C–N–V bond angle (161.7(4)°), possibly reflecting competing V–N/V–O π-interactions.[24] In contrast, V(NAr)-

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(14) Murphy, V. J.; Turner, H. U.S. Patent Pending.

(15) (a) See the Supporting Information. (b) Elemental analyses performed on V(NAr)(CH$_2$Ph)$_3$ and V(NAr)(NPhMe)(CH$_2$Ph)$_2$ consistently gave results ~1–2% low in carbon.

(16) V(NAr)(CH$_2$Ph)$_3$ is triclinic, space group $P\bar{1}$, (No. 2), with a = 9.943(2) Å, b = 11.911(5) Å, c = 13.568(3) Å, α = 96.28(2)°, β = 110.56(2)°, γ = 104.46(3)°, V = 1422.0(7) Å^3, and Z = 2.

(17) One of the benzyl ligands is bound in an η^2-fashion with a V–C$_{ipso}$ bond length of 2.527(8) Å. This type of interaction has been previously encountered with electronically unsaturated metal centers. See ref 13 and: (a) Jordan, R. F.; Lapointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892–2903. (b) Jordan, R. F.; Lapointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539–1545.

(18) The C11–C12 bond length (1.452(10) Å) is not significantly shortened as a consequence of the V–C$_{ipso}$ interaction. For comparison d(C21–C22) = 1.461(11) Å and d(C31–C32) = 1.493(10) Å.

(19) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1995**, *497*, 161–170.

(20) V(NBu^t)CpMe$_2$ is reported as a red oil which decomposes in solution at 20°C.[9f]

(21) Murphy, V. J.; Turner, H. Unpublished results.

(22) V(NAr)(OC$_6$H$_3$-2,6-Pr$^i_2$)(CH$_2$Ph)$_2$ is orthorhombic, space group $P2_12_12_1$ (No. 19), with a = 9.883(1) Å, b = 18.156(4) Å, c = 19.265(8) Å, V = 3457(2) Å^3, and Z = 4. V(NAr)(OC(CF$_3$)$_3$)(CH$_2$Ph)$_2$ is monoclinic, space group $P2_1/n$ (No. 14), with a = 10.104(3) Å, b = 18.502(6) Å, c = 16.451(5) Å, β = 90.93(2)°, V = 3075(2) Å^3, and Z = 4. V(NAr)(NPhMe)(CH$_2$Ph)$_2$ is rhombohedral, space group $R\bar{3}$ (No. 148), with a = 25.546(2) Å, c = 23.686(5) Å, V = 13387(3) Å^3, and Z = 18.

(23) (a) The mean V=N$_{\mathrm{imido}}$ bond length listed in the Cambridge Structural Database (Version 5.11) is 1.675(9) Å. (b) For structural comparisons with other vanadium(V) complexes containing the (2,6-diisopropylphenyl)imido ligand, see ref 7 and: Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922–2924.

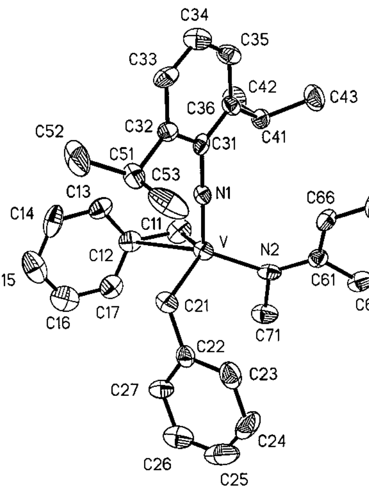

Figure 2. Molecular structure of $V(NAr)(NPhMe)(CH_2Ph)_2$.

$(OC(CF_3)_3)(CH_2Ph)_2$, containing the powerfully electron withdrawing perfluoroalkoxide substituent, possesses an essentially linear imido ligand in addition to the shortest V−N (d(V−N) = 1.638(5) Å) and V−C (d_{av}(V−C) = 2.030(10) Å) bond lengths for this series of vanadium(V) alkyl derivatives.[25]

The ^1H NMR spectra for the series of arylimido−dibenzyl derivatives display AB patterns for the methylene protons of the benzyl ligands, consistent with the structures as determined by X-ray diffraction. For $V(NAr)(NPhMe)(CH_2Ph)_2$, the observation of equivalent benzyl ligands in solution implies (1) that interconversion between η^2 and η^1 coordination is facile[26] and (2) that the amido (−NPhMe) ligand must rotate about the V−N bond. In the solid state $V(NAr)(NPhMe)(CH_2Ph)_2$ possesses C_1 symmetry with the phenyl group of the amido ligand adopting a *syn* position with respect to the position of the arylimido ligand (Figure 2).[27]

The ^{51}V chemical shifts for the series of compounds span the range δ 289−1008.[28] The low-field chemical shift observed for $V(NAr)(CH_2Ph)_3$ (δ 1008) is in good agreement with low-field chemical shifts reported for $V(Ntol)(CH_2SiMe_3)_3$ (δ 1028)[9a] and $V(NBu^t)(CH_2SiMe_3)_3$ (δ 877).[10b] Substitution of a single benzyl group leads to upfield chemical shifts in the order $-OC(CF_3)_3$ (δ 835) < $-OC_6H_3$-2,6-$Pr^i{}_2$ (δ 548) < −NPhMe (δ 289).[29]

In summary, we have demonstrated a convenient synthetic route to a range of vanadium(V) alkyls. The (arylimido)vanadium(V) tribenzyl derivative $V(NAr)(CH_2Ph)_3$ can be synthesized in high yield by the addition of $PhCH_2MgCl$ to $V(NAr)Cl_3{\cdot}THF$. The (2,6-diisopropylaryl)imido ligand imparts a high degree of stability with respect to the reduction of the vanadium(V) metal center. As a consequence, $V(NAr)(CH_2Ph)_3$ is a valuable precursor to a series of new (arylimido)vanadium(V) dibenzyl derivatives with supporting alkoxide, aryloxide, and amido functionalities.

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Supporting Information Available: Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for $V(NAr)(CH_2Ph)_3$ (Ar = C_6H_3-2,6-$Pr^i{}_2$), $V(NAr)(NPhMe)(CH_2Ph)_2$, $V(NAr)(OC(CF_3)_3)(CH_2Ph)_2$, and $V(NAr)(OAr)(CH_2Ph)_2$, ORTEP drawings for $V(NAr)(OC(CF_3)_3)(CH_2Ph)_2$ and $V(NAr)(OAr)(CH_2Ph)_2$, and experimental details and tables of analytical and spectroscopic data (33 pages). Ordering information is given on any current masthead page.

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[24] In support of this argument, the V−O bond length in this complex (1.746(4) Å) is slightly shorter than the value reported for the terminal aryloxide in $[V(Ntol)(OC_6H_3\text{-}2,6\text{-}Me_2)_2Cl]_2$ (1.797(3) Å).[9a]

[25] (a) The V−O bond length in this complex (1.838(4) Å) is significantly longer than the values reported for $V(NR)(OSiMe_3)_3$ (1.764(3) Å, R = 1-adamantyl),[25b] and $[V(CH_2Bu^t)(OBu^t)(\mu\text{-}NBu^t)]_2$ (1.736(4) Å) and $[V(CH_2SiMe_3)(OBu^t)(\mu\text{-}NBu^t)]_2$ (1.745(13) Å).[10b] (b) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 342−343.

[26] Consistent with observations made for $Cr(NR)_2(CH_2C_6H_5)_2$ (R = Bu^t, C_6H_3-2,6-$Pr^i{}_2$).[13a]

[27] For $V(NAr)(NPhMe)(CH_2Ph)_2$ V−C(12) = 2.503(10) Å, C(11)−C(12) = 1.437(13) Å, and C(21)−C(22) = 1.478(12) Å. For $V(NAr)(OC(CF_3)_3)(CH_2Ph)_2$ and $V(NAr)(OC_6H_3\text{-}2,6\text{-}Pr^i{}_2)(CH_2Ph)_2$ $V-C_{ipso}$ interactions are not observed.

[28] ^{51}V NMR data (in C_6D_6 relative to $VOCl_3$): $V(NAr)Cl_3{\cdot}THF$ δ 435 ($\Delta v_{1/2}$ = 1200 Hz); $V(NAr)(CH_2Ph)_3$ δ 1008 ($\Delta v_{1/2}$ = 300 Hz); $V(NAr)(OC_6H_3\text{-}2,6\text{-}Pr^i{}_2)(CH_2Ph)_2$ δ 548 ($\Delta v_{1/2}$ = 360 Hz); $V(NAr)(OC(CF_3)_3)(CH_2Ph)_2$ δ 838 ($\Delta v_{1/2}$ = 400 Hz); $V(NAr)(NPhMe)(CH_2Ph)_2$ δ 289 ($\Delta v_{1/2}$ = 370 Hz).

[29] For a discussion of ^{51}V chemical shift trends, see ref 9a and: Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33−83. Rehder, D. *Coord. Chem. Rev.* **1991**, *110*, 161−210. Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125−237.