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New Tris(amido)vanadium(V) Imides: Iminoazavanadatranes

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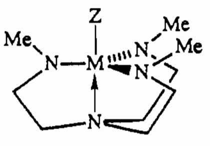
The synthesis of imidovanadium amides containing the tetradentate amine moiety $(MeNCH_2CH_2)_3N$ is reported. The facile transmetalation reaction of azastannatranes with N-substituted tris(siloxy)vanadium(V) imides was used to prepare $RN{=}V(NMeCH_2CH_2)_3N$ (**4**, R = $SiMe_3$; **5**, R = CMe_3) in high yields. The application of this transmetalation reaction to other transition metal fragments met with limited success. Compounds **4** and **5** were characterized by FT-IR, high-resolution mass, and solution and solid state heteronuclear NMR spectroscopic techniques. In the CP/MAS ^{13}C NMR spectrum of **4**, a quadrupolar coupling of vanadium with the carbon nucleus was observed.

Introduction

Whereas the past three decades have witnessed an extensive development of the chemistry of $M(NR_2)_n$ compounds,[1,2] this has not been true for tris(amido)metal(V) imides. In the case of V(V), considerable knowledge has been gained concerning a variety of trisalkoxy-, triaroxy-, and trialkylvanadium(V) imides,[3–8] and mixed species such as $(i\text{-PrO})_nV(O)[N(SiMe_3)_2]_{3-n}$ (n = 1, 2)[9] and $RN{=}V(OR)(NR_2)_2$ (R = $SiMe_3$)[9] were reported early on. In contrast to oxovanadium(V) compounds of the type $O{=}V(NR_2)_3$, which are well-known,[3,10,11] their imido analogues $RN{=}V(NR_2)_3$ do not seem to have been reported. Transition metal amides have recently enjoyed considerable attention as potential MOCVD precursors to metal nitride thin films.[12–14] Our interest in such compounds has centered on those derived from the tetradentate ligand system $(RNCH_2CH_2)_3N^{3-}$ (R = H, Me, $SiMe_3$), which by virtue of its C_3 symmetry confers volatility on a chelated metal as, for example, in **1** and **2**.[15] The related tetravalent metal species **6**[16] and $ZM(Me_3SiNCH_2CH_2)_3N$ (M = V, Ti; Z = Cl, R)[17] and trivalent metal derivatives $M(t\text{-}BuMe_2SiNCH_2CH_2)_3N$ (M = T, V, Cr, Mn, Fe)[18] were also recently described. Here we report the synthesis, from **3**, via a novel transmetalation reaction, of the tris(amido)vanadium(V) imides **4** and **5**, which feature a fifth V–N bond that forms by transannulation of the tertiary nitrogen. The five-coordinate structure of these complexes was confirmed earlier in the case of **2** by an X-ray-determined structure.[15]



1 M-Z = $Mo{\equiv}N$
2 M-Z = $V{=}O$
3 M-Z = Sn-*n*-Bu
4 M-Z = $V{=}NSiMe_3$
5 M-Z = $V{=}NCMe_3$
6 M-Z = $TiNMe_2$

Experimental Section

All manipulations were carried out under strict exclusion of moisture with standard vacuum-line techniques in an atmosphere of dry argon. Solvents were dried by standard methods[19] and distilled prior to use. Samples for IR and solid-state NMR experiments were prepared in a drybox with a dry and oxygen-free nitrogen atmosphere. $(MeHNCH_2CH_2)_3N$ (Me-tren) was prepared from $(H_2NCH_2CH_2)_3N$ (tren) by using a standard procedure.[20] Azastannatrane **3**,[21] $Me_3SiN{=}V(OSiMe_3)_3$,[22] and $Me_3CN{=}V(OSiMe_3)_3$[23] were prepared according to published procedures. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN. Mass spectra were recorded on a Kratos MS50 (EI, 70 eV) mass spectrometer, and high-resolution data were obtained by peak matching. IR spectra were recorded on an IBM98 FT-IR spectrometer. The samples were prepared as KBr pellets (4000–600 cm^{-1}) and as Nujol mulls between polyethylene plates (650–150 cm^{-1}), respectively. Solution NMR spectra were recorded on a Varian VXR300 (^1H, 299.95 MHz; ^{13}C, 75.43 MHz; ^{29}Si, 59.59 MHz; ^{51}V, 78.86 MHz) instrument using deuterated solvents as internal lock and TMS (^1H, ^{13}C) and $O{=}VCl_3$ as external standards. For low-temperature experiments, toluene-d_8 was used as the solvent. Temperature calibration of the NMR probe was carried out as described in the literature.[24] For the measurement of solid-state NMR spectra, polycrystalline samples (ca. 300–400 mg) were packed either into an airtight insert or directly into a ZrO_2 rotor, which was sealed by a threaded Teflon plunger. Spectra were obtained on a Bruker MSL300 spectrometer (^{13}C, 75.47 MHz; ^{29}Si, 59.63 MHz; ^{51}V, 78.90 MHz) under proton decoupling for the ^{13}C and ^{29}Si spectra using the CP/MAS technique, with sweep widths of 25, 50, and 125 kHz for the ^{13}C, ^{29}Si, and ^{51}V spectra, respectively. A 90° pulse was employed with mixing times for polarization transfer of 2–3 ms followed by a recycle delay. The ^{51}V spectra were obtained by means of the MAS technique, using high-power proton decoupling. Spinning rates were in the range of 2.5–4.5 kHz. Spectra were rerun at a different speed to establish the position of the centerband. The magic angle was set using the ^{79}Br resonance of KBr.[25]

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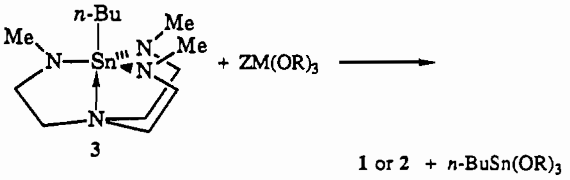
((Trimethylsilyl)imino)-*N,N,N'*-trimethylazavanadatrane (4). 1-*n*-Butyl-*N,N',N''*-trimethylazastannatrane (3.33 g, 9.20 mmol) was added to a solution of ((trimethylsilyl)imido)tris(trimethylsiloxy)vanadium(V) (3.74 g, 9.20 mmol) in 50 mL of toluene. The mixture was heated to 50 °C and stirred for 5 h at this temperature. After the solvent was evaporated in vacuo, the residue was washed twice with 1 mL of *n*-pentane to remove the tin byproduct. The residue was dissolved in 15 mL of *n*-pentane and crystallized at –15 °C. Sublimation of the crude product at 60–70 °C (5 mTorr) afforded 1.81 g (5.60 mmol, 61%) of red microcrystalline **4**, mp >65 °C dec. Compound **4** slowly decomposes at room temperature over a period of ca. 2 weeks, but it is stable over several months at –15 °C. Due to its thermal instability, no satisfactory elemental analysis could be obtained for **4**. MS (70 eV, EI), *m/e*: 323.170 54, 100% (calcd for $C_{12}H_{30}N_5SiV$ (M^+), 323.171 01); 280.128 15/278.112 65, 52/26% (calcd for $C_{10}H_{25}N_4SiV/C_{10}H_{23}N_4SiV$, $[M - NMe_2 \pm H]^+$, 280.128 82/278.113 17); 264.097 41, 13% (calcd for $C_9H_{21}N_4SiV$, $[M - HNMeEt]^+$, 264.097 42); 237.086 66/235.071 42, 38/92% (calcd for $C_8H_{20}N_3SiV/C_8H_{18}N_3SiV$, $[M - 2NMe_2 + 2/0H]^+$, 237.086 61/235.070 96); 234.104 91, 5% (calcd for $C_9H_{19}N_4V$, $[M - H_2NSiCMe_3]^+$, 234.104 93). IR (cm^{-1}): 303 (vw), 342 (vw), 381 (vw), 414 (w), 442 (vw), 562 (m), 615 (vw), 633 (w), 685 (w), 750 (w), 833 (vs), 897 (m), 939 (m), 980 (vw), 1016 (m), 1051 (s), 1067 (vw), 1096 (vs), 1119 (sh), 1134 (m), 1182 (w), 1194 (w), 1242 (m), 1269 (m), 1279 (w), 1348 (vw), 1377 (w), 1402 (m), 1441 (m), 1464 (w), 2660 (w), 2675 (m), 2777 (s), 2827 (s), 2851 (m), 2895 (m), 2959 (m). ^1H NMR (C_6D_6): δ 3.96 (s, 9 H, NCH_3), 3.11 (t, 6 H, $VNCH_2$, $^3J_{HH} = 5.7$ Hz), 2.44 (t, 6 H, $VNCH_2CH_2$, $^3J_{HH} = 5.7$ Hz), 0.38 (s, 9 H, $VNSi(CH_3)_3$, $^2J_{SiH} = 6.6$ Hz). ^{13}C NMR (C_6D_6): δ 60.9 (broad due to $^2J_{VC}$, $VNCH_2$, $\Delta\nu_{1/2} = 32$ Hz), 58.0 (broad due to $^2J_{VC}$, $VNCH_3$, $\Delta\nu_{1/2} = 42$ Hz), 52.0 ($VNCH_2CH_2$, $\Delta\nu_{1/2} = 5$ Hz), 2.12 ($VNSi(CH_3)$, $\Delta\nu_{1/2} = 0.8$ Hz). ^{29}Si NMR (toluene-d_8, 213 K): δ –11.3 ($\Delta\nu_{1/2} = 292$ Hz). ^{51}V NMR (C_6D_6): δ –273 ($\Delta\nu_{1/2} = 133$ Hz).

(*tert*-Butylimino)-*N,N,N'*-trimethylazavanadatrane (5). A solution of 1-*n*-butyl-N,N',N''-trimethylazastannatrane (7.48 g, 19.2 mmol) and (*tert*-butylimido)tris(trimethylsiloxy)vanadium(V) (6.93 g, 19.20 mmol) in 50 mL of toluene was heated to 65 °C and stirred at this temperature for 20 h. After removal of the volatiles in vacuo, the resulting mixture was washed twice with 1 mL of *n*-pentane to remove the majority of the tin byproduct. The crude product was recrystallized from *n*-pentane at –15 °C, affording 5.09 g (16.6 mmol, 86%) of well-shaped deep orange crystals, mp 95–96 °C. Compound **5** can be sublimed at 80–100 °C at 5 mTorr. Anal. Calcd (found) for $C_{13}H_{30}N_5V$: C, 50.80 (49.80); H, 9.84 (9.76); N, 22.79 (22.14). MS (70 eV, EI), *m/e*: 307.193 99, 100% (calcd for $C_{13}H_{30}N_5V$ (M^+), 307.194 08); 264.151 75/262.136 35, 19/52% (calcd for $C_{11}H_{25}N_4V/C_{11}H_{23}N_4V$, $[M - NMe_2 \pm H]^+$, 264.151 89/262.136 24); 248.120 76, 30% (calcd for $C_{10}H_{21}N_4V$, $[M - HNMeEt]^+$, 248.120 58); 236.121 06/234.105 32, 9/5% (calcd for $C_9H_{21}N_4V/C_9H_{19}N_4V$, $[M - C_4H_{10}N \pm H]^+$, 236.120 59/234.104 93); 221.109 67/219.093 04, 47/14% (calcd for $C_9H_{20}N_3V/C_9H_{18}N_3V$, $[M - 2NMe_2 + 2/0H]^+$, 221.109 68/219.094 04). IR (cm^{-1}): 347 (vw), 401 (vw), 424 (vw), 527 (w), 588 (m), 604 (vw), 623 (vw), 750 (w), 804 (w), 845 (m), 895 (m), 937 (m), 1015 (m), 1051 (vs), 1069 (w), 1126 (s), 1140 (m), 1180 (m), 1205 (m), 1236 (vs), 1263 (w), 1281 (vw), 1354 (m), 1377 (w), 1402 (m), 1456 (m), 2658 (w), 2765 (m), 2783 (m), 2807 (m), 2827 (s), 2852 (m), 2897 (m), 2924 (m), 2966 (s). ^1H NMR (C_6D_6): δ 3.90 (s, 9 H, NCH_3), 3.19 (t, 6 H, $VNCH_2$, $^3J_{HH} = 5.8$ Hz), 2.53 (t, 6 H, $VNCH_2CH_2$, $^3J_{HH} = 5.8$ Hz), 1.56 (t, 9 H, $VNC(CH_3)_3$, $^3J_{NH} = 1.2$ Hz). ^{13}C NMR (C_6D_6): δ 60.8 (broad due to $^2J_{VC}$, $VNCH_2$, $\Delta\nu_{1/2} = 18$ Hz), 56.7 (broad due to $^2J_{VC}$, $VNCH_3$, $\Delta\nu_{1/2} = 37$ Hz), 52.4 ($VNCH_2CH_2$, $\Delta\nu_{1/2} = 3$ Hz), 31.8 ($VNC(CH_3)$, $\Delta\nu_{1/2} = 7$ Hz). ^{51}V NMR (C_6D_6): δ –433 (t, $^1J_{VN} = 101$ Hz).

Results and Discussion

Transmetalation Reaction. Because tris(amido)vanadium(V) imides were unknown, the well-known transamination reaction of transition metal amides[26] (in this case $RN{=}V(NR'_2)_3$) with tren and its substituted methyl derivative $(HMeNCH_2CH_2)_3N$ (Me-tren) could not be applied to the synthesis of imidoazavanadatranes **4** and **5**. Moreover, transamination reactions involving tren and Me-tren with a variety of transition metal tris(amido) derivatives gave only intractable polymeric materials.[27] Since the synthesis of transition metal azatranes is of current interest in our laboratories, we have been exploring extensions of our recently described transmetalation reaction 1 to other transition metal fragments. Although reports on methathetical reactions of organostannanes with boron alkoxides were reported in the late 1960s by Lappert and co-workers,[28] analogous reactions with transition metal alkoxides have been unexplored.



(1)

By applying transmetalation reagent **3** to tris(alkylsiloxy)vanadium(V) imides, we were able to synthesize the first fully nitrogen-ligated vanadium(V) compounds, namely, **4** and **5**. As in the previously described cases of **1** and **2**,[15] a clean and quantitative reaction was observed by monitoring the ^1H NMR spectra. Unoptimized isolated yields of 61 and 86% for **4** and **5**, respectively, were obtained. Both **4** and **5** are highly moisture-sensitive, colored solids (red and orange, respectively) showing good volatility. The lack of significant polymeric side products in our transmetalation reaction may be attributed to the steric restrictions of the Me-tren ligand imposed on the binding of all four of its nitrogens to a common center, namely, *n*-BuSn. Thus polymer formation is expected to be inhibited by the Sn atom's ability in **3** to keep the nitrogens in close proximity to one another, so that a second and a third amido nitrogen is more likely to react with the first transition metal reagent molecule to exchange its second and third ligands than with a fresh (more distant) TM reagent molecule. Unfortunately, this steric restriction does not apply to tren as a ligand for the RSn moiety in the transmetalation reaction, since polymeric material is formed, presumably because of the presence of second reactive site on each amido nitrogen (*i.e.*, N–H).[15]

Using $p\text{-}MeC_6H_4N{=}V(O\text{-}t\text{-}Bu)_3$, transmetalation reaction 1 is observed at temperatures above 110 °C. Unfortunately ^1H NMR spectroscopy reveals considerable decomposition as the reaction proceeds. The product (ca. 20%) which was detected by NMR spectroscopy, could not be isolated from the reaction mixture, owing to physical properties very similar to those of the decomposition products. The difference in reactivities among the three imidovanadium(V) reagents discussed here may be due to the variation in electronic properties of the imido as well as of the alkoxy ligands. To further probe the synthetic potential of transmetalation reaction 1, we also attempted the preparation of azatitanatranes by reacting $(i\text{-}PrO)_4Ti$ with three 1-R-*N,N',N''*-trimethylazastannatranes (R = Me (**7**),[21] *n*-Bu (**3**), and Ph (**8**)[21]). However, even under rather harsh conditions (refluxing xylene), no reactions were observed. It is tempting to attribute the failure of these reactions to an increasing oxygen affinity of the transition metal with respect to tin in going from vanadium to titanium. Whereas the metathetical reaction of TiF_4 with Me_3SnNMe_2 yields $Ti(NMe_2)_4$,[28] the reactions of TiF_4 with **3**, **7**, or **8** failed. It is possible, however, to substitute the apical dimethylamino group in 1-(dimethylamino)-*N,N',N''*-trimethylazastannatrane with flourine by reacting it with TiF_4.[21] Thus there is a substantial difference in reactivity between the apical tin–nitrogen bond in an azastannatrane cage and those in the cage of these pentacoordinate tin compounds.

Another challenge for the synthetic potential of transmetalation reaction 1 is the Mo≡Mo fragment, since simply reacting $Mo_2(NMe_2)_6$ with Me-tren in a transamination reaction was found to give only intractable products. The coordinative requirements of molybdenum upon addition of Lewis bases are oxidation-state

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dependent. Thus for molybdenum(VI) fragments, trigonal bipyramidal coordination is favored,[15,29] whereas the distorted tetrahedral dimolybdenum(III) core becomes a square pyramid with additional donor ligands.[30,31] We also tested $Mo_2(O\text{-}t\text{-}Bu)_6$ and $Mo_2(OCH_2CMe_3)_6$ in transmetalation reaction 1. However, $Mo_2(O\text{-}t\text{-}Bu)_6$ reacts neither with azastannatrane **7** nor with **8** (28-h reflux in xylene). With $Mo_2(OCH_2CMe_3)_6$, a reaction with these azastannatranes in refluxing toluene was observed, affording a complex mixture of products.

The examples tested here clearly show that the success of our transmetalation reaction is quite dependent on steric factors, on the coordination requirements of the specific metal center, and on electronic effects. This question, as well as the extension of the transmetalation concept to the synthesis of other metallatranes, is currently under investigation.

Infrared Spectra of 4 and 5. The V=N stretching vibrations of **4** and **5** are found at 1236 and 1096 cm^{-1}, respectively. The rather large difference between these stretching frequencies is not unprecedented in the literature. Almost the same frequencies were found for $Cl_3V{=}N{-}R$ where R = *tert*-butyl (1205 cm^{-1})[23] and trimethylsilyl (1104 cm^{-1}).[32] These differences in V=N stretching frequencies can be attributed to coupling with the Si—N stretching vibration, which is enhanced by the collinear arrangement of the V=N—Si skeleton.[33] Since this effect for the V=N— X fragment is more pronounced the smaller the energy difference between the V=N and the N—X stretching vibration becomes,[32] the high-frequency shift for the *tert*-butyl derivative **4** compared with that of the trimethylsilyl-substituted **5** becomes reasonable. Aside from the V=N stretching frequencies, the infrared spectra of both azavanadatranes **4** and **5** are very similar. The two additional Si—C stretching frequencies observed for compound **4** (expected for its approximate C_{3v} molecular symmetry) are assigned at 633 and 685 cm^{-1}.

A normal-coordinate analysis performed for silatranes showed that the normal modes for the tricyclic atrane cage are highly mixed.[34,35] An analysis of the IR spectra for a series of apically substituted azastannatranes, particularly those with F, Cl, Br, and I, indicates similar behaviors.[36] Therefore an assignment of such cage vibrations to single stretching, bending, etc. modes is impossible. Nevertheless a comparison of the infrared spectra of **4** and **5** lead us to tentatively assign the bands at 414 and 562 cm^{-1} for **4** and 528 and 588 cm^{-1} for **5** as having predominantly V—N stretching character. The higher frequency band in each case is close to that for a V—N stretching frequency of 612 cm^{-1} reported for $O{=}V(NEt_2)_3$.[11] The larger difference (114 cm^{-1}) for the low-frequency A_1 band in approximate C_{3v} molecular symmetry between **4** and **5** can be attributed to symmetry-allowed mixing with stretching vibrations of the V=N—Si fragment in **4**, whereas the high-frequency E vibrations are within 26 cm^{-1} of one another. The larger difference in the A_1 bands of **4** and **5** is consistent with our assignment of the Si—N stretching frequency at the unusually low value of 442 cm^{-1}. Although this value lies outside the normal range for nonlinear silylimides (550–600 cm^{-1} [37]), a value of 477 cm^{-1} was assigned to this vibration for $Cl_3V{=}N{-}SiMe_3$.[32]

Mass Spectra. The identity of compounds **4** and **5** was confirmed by high-resolution mass spectroscopy. In both cases the molecular ion peak (M^+) is observed to be the base peak. For **5** the intensities of the peaks decrease as the mass decreases, and the second intense peak ($[M - NMe_2 + H]^+$) has only half the height of the M^+ peak. The situation is quite different for the vanadium(V) imide **4**, for which the second most intense peak is about 90% of the M^+ peak. These observations are in agreement with the less pronounced thermal stability of **4** (which decomposes above 65 °C) compared with **5** (which melts without decomposition above 95 °C). In contrast to other atranes,[21,36] fragmentation due to the loss of the apical group (here N—R) is rather small (**4**, 5%; **5**, 5%), indicating considerable stability of the V=N—R moiety.

NMR Spectra. The ^1H NMR spectra of **4** and **5** show the typical pattern observed for azatranes.[15,21] For the protons of the *tert*-butyl group in **5**, a three-bond coupling of 1.2 Hz to the ^{14}N of the imido substitutent is observed. In contrast to **2**,[15] both sets of virtual triplets for the AA'XX' spin system (virtual point group C_{3v} at room temperature) in **4** and **5** are well resolved. Only a slight broadening for the methylene cage protons and the methyl protons adjacent to the equatorial nitrogen atoms is observed, indicating residual coupling to the ^{51}V nucleus. The energies of the free enthalpies for racemization of the metallatrane framework (point group C_3 at lower temperatures) are 42.0 and 42.8 kJ/mol for **4** and **5**,[38] respectively. These values are somewhat higher than those observed for **1** (40.8 kJ/mol) and **2** (41.0 kJ/mol),[15] reflecting the increased rigidity of the azametallatrane skeleton in **4** and **5** owing to π bonding of the equatorial nitrogens to the transition metal.

Compounds **4** and **5** display ^{51}V chemical shifts in solution of -273 ($\Delta\nu_{1/2}$ = 133 Hz) and -433 ppm ($\Delta\nu_{1/2}$ = 278 Hz), respectively. Direct comparison to similar species is not possible, since acyclic tris(amido)vanadium(V) imides are not known. For $O{=}V(NEt_2)_3$ a $\delta(^{51}V)$ value of -389 ppm was reported,[10] which is in the range of the chemical shifts found here. Imidovanadium(V) compounds in general show a very broad range of chemical shift values, from +1000 to −800 ppm.[39–41] The resonances of **4** and **5** are both upfield from the corresponding oxoazavanadatrane **2** (−241 ppm[15]). For **5**, the resonance is split into a 1:1:1 triplet with a coupling constant of 100 Hz due to vanadium–nitrogen spin coupling, which is within the usually observe range for imidovanadium(V) compounds.[39,40] Although the line width for **4** increased upon raising the temperature[42] (205 Hz at 378 K), no splitting was resolved. From the observed shoulders, a coupling constant of about 80 Hz was estimated.

Thus far very little information about solid-state ^{51}V NMR spectra has appeared. A recent report[43] deals mainly with metavanadate or vanadium oxides deposited on surfaces. In a previous communication[15] we reported the observation of the ^{51}V solid-state NMR spectrum of **2** featuring an isotropic chemical shift at −206 ppm which is 35 ppm downfield from the solution value. In the solid-state ^{51}V NMR spectra of **4** and **5**, the central ($-^1/_2$, $+^1/_2$) transitions are observed at −278 and −437 ppm, respectively. The line broadening due to second-order quadrupolar interaction is about 1 kHz, whereas the chemical shift anisotropy is about 15 and 20 kHz in **4** and **5**, respectively. Unfortunately, the characteristic quadrupolar line shape was not well resolved, therefore precluding graphic analysis.[44] On the other hand, the sideband pattern indicated a highly axially symmetric chemical shift tensor. Assuming the same high symmetry for the electronic

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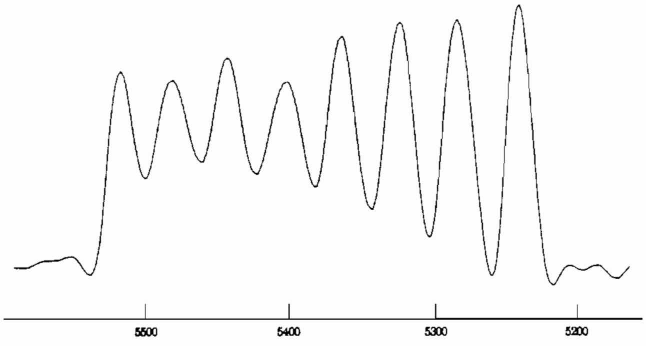

Figure 1. Resonance of the quaternary carbon of **5** in the ^{13}C CP/MAS NMR spectrum (rotor frequency = 4170 Hz, 8952 scans).

field gradient ($\eta = 0$), then the shoulder on the downfield side of each of the central resonance lines suggests that the isotropic chemical shift values may be 4 or 5 ppm higher than the observed maxima.[44] In any case, the solid-state chemical shift values resemble those found in solution (**4**, –273 ppm; **5**, –433 ppm).

In the room-temperature solution ^{29}Si NMR spectrum of **4**, no resonance is observed owing to coupling with the quadrupolar nuclei ^{51}V ($I = {}^7/_2$) and ^{14}N ($I = 1$). Lowering the temperature to 213 K, and thus increasing the relaxation rate for the quadrupolar nuclei,[42] led to the observation of a still rather broad resonance at –11.3 ppm ($\Delta\nu_{1/2}$ = 292 Hz). In the room-temperature solid-state ^{29}Si NMR spectrum, this resonance appears at –11 ppm and the absence of spinning sidebands indicates a small chemical shift anisotropy.

The ^{13}C resonances for **4** and **5** were assigned by means of J-modulated spin-echo (APT)[45] and selective proton-decoupling experiments, respectively. In contrast to the ^{13}C NMR spectral results for **2** reported earlier,[15] no resolved ^{51}V–^{13}C coupling was detected. The observed chemical shift values for the two methylene cage carbons are virtually the same in **2**, **4**, and **5**. On the other hand, the resonances for the methyl carbons on the equatorial nitrogens are shifted progressively downfield in the order **2**, **5**, **4**. The largest ^{51}V–^{13}C couplings indicated by the observed line broadening are found for the two carbon atoms directly bound to each equatorial nitrogen. As expected from other (*tert*-butylimido)vanadium(V) compounds,[40] the resonance line for the quaternary carbon atom is almost within the baseline ($\Delta\nu_{1/2}$ = 140 Hz) at room temperature. As was the case for the ^{29}Si resonance of **4**, lowering the temperature of **5** decreased the breadth of the quaternary carbon peak attributable to the coupling of the ^{51}V and ^{14}N quadrupolar nuclei[42] until, at 203 K, its chemical shift could be clearly observed at 70.0 ppm ($\Delta\nu_{1/2}$ = 39 Hz).

For the (trimethylsilyl)imido derivative **4**, the solid-state ^{13}C NMR spectrum showed only two resonance peaks: one at 3 ppm ($Si(\mathit{C}H_3)_3$, $\Delta\nu_{1/2}$ = 40 Hz) and the other at 60 ppm ($\Delta\nu_{1/2}$ = 190 Hz). The rather broad downfield peak consists of resonances from the cage methylene carbons as well as the methyl carbon on the equatorial nitrogen, as was shown by an experiment utilizing a dipolar dephasing pulse sequence.[46] In the solid-state ^{13}C NMR spectrum of the *tert*-butyl derivative **5**, all the resonances are well separated, even though they show line widths up to 330 Hz. Except for the resonance at 32 ppm ($V{=}N{-}C(\mathit{C}H_3)_3$, $\Delta\nu_{1/2} < 20$ Hz), all the others have rather large line widths owing to interaction with the neighboring quadrupolar ^{51}V and ^{14}N nuclei (53 ppm, $\Delta\nu_{1/2}$ = 330 Hz, $VNCH_2\mathit{C}H_2$; 58 ppm, $\Delta\nu_{1/2}$ = 240 Hz, $VN\mathit{C}H_3$; 61 ppm, $\Delta\nu_{1/2}$ = 280 Hz, $VN\mathit{C}H_2CH_2$; 71 ppm, $\Delta\nu_{1/2}$ = 300 Hz, $V{=}N\mathit{C}(CH_3)_3$).

For the quaternary carbon of the *tert*-butyl group of **5**, it is possible to resolve the structure of the resonance line by applying a mathematical resolution enhancement (see Figure 1). The resonance consists of eight lines of nonequidistant intervals, suggestive of coupling with the quadrupolar vanadium ($I = {}^7/_2$) nucleus, and each of the eight lines has a line width of about 20–30 Hz (with a digital resolution of 1.5 Hz). Such a distortion of the multiplet can in principle be due to two types of effects, namely, anisotropy of the scalar coupling and the dipolar interaction, respectively, with the quadrupolar ^{51}V nucleus.[47] A first-order perturbation treatment[47] can be used to evaluate the isotropic scalar coupling constant J_{iso} and the parameter d characterizing the distortion of the multiplet. The values obtained from the spectrum in Figure 1 are J_{iso} = 40 Hz and d = –4.5 Hz. Assuming axial symmetry for the quadrupole tensor of the vanadium and orientation of the z axis of the quadrupole as well as that of the coupling tensor along the linear $V{=}N{-}C$ fragment in compound **5** allows a prediction of the d value by eq 2,[47] wherein

$$d = \frac{-\chi}{10Z_V}(-\Delta J + 3D) \qquad (2)$$

Z_V is the Zeeman frequency of ^{51}V in the applied field, ΔJ is the anisotropy of the scalar coupling, D is the dipolar coupling constant as given by $(\mu_0/4\pi)(\gamma_V\gamma_C/r_{V\text{-}C}{}^3)(h/4\pi^2)$, and χ is the quadrupolar coupling constant at the ^{51}V nucleus. From the V—C distance of 308 pm estimated from literature values,[3,4,48] it is possible to calculate the dipolar coupling constant D to be 275 Hz. With the assumptions made above, the quadrupolar coupling constant χ for a purely dipolar interaction can be estimated to be 4.3 MHz. This compares surprisingly well with the χ values found for metavanadates (2.88–4.36 MHz),[49] especially when the rather large uncertainty for the measured d value is considered. Moreover, it is obvious that the anisotropy of the scalar coupling makes only a minor contribution to the distortion of the multiplet.

Conclusions. Transmetalation reaction 1 is dependent not only on the metal used but also on the ligand that will occupy the apical site in the TBP structure. Moreover, there are indications that the nature of the alkoxy substituent in the metallic starting material may be important. The reactions presented here also show that the azametallatrane framework is quite stable. We have been able to show that it is possible to observe the coupling between ^{51}V and ^{13}C in the CP/MAS spectrum of **5**. The anisotropy of the observed coupling allowed an estimate of the ^{51}V quadrupolar coupling constant.

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