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New Details Concerning the Reactions of Nitric Oxide with Vanadium Tetrachloride

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The slow addition of NO to a CCl_4 solution of VCl_4 reproducibly forms the known polymer $[V(NO)_3Cl_2]_n$ as a dark brown powder. Treatment of a CH_2Cl_2 suspension of $[V(NO)_3Cl_2]_n$ with excess THF generates *mer*-$(THF)_3V(NO)Cl_2$ (**1**) which can be isolated as an orange crystalline material in 55% yield. The reaction of **1** with excess MeCN or 1 equiv of trimpsi (trimpsi = $^tBuSi(CH_2PMe_2)_3$) provides yellow-orange $(MeCN)_3V(NO)Cl_2$·MeCN (**2**·MeCN) and yellow (trimpsi)$V(NO)Cl_2$ (**3**), respectively. A black, crystalline complex formulated as $[NO][VCl_5]$ (**4**) is formed by the slow addition of NO to neat VCl_4 or by the reaction of excess ClNO with neat VCl_4. Complex **4** is extremely air- and moisture-sensitive, and IR spectroscopy suggests that in solutions and in the gas phase it dissociates back into VCl_4 and ClNO. Reaction of **4** with excess $[NEt_3(CH_2Ph)]Cl$ generates $[NEt_3(CH_2Ph)]_2[VCl_6]\cdot 2CH_2Cl_2$ (**5**·$2CH_2Cl_2$), which can be isolated as deep-red crystals in 51% yield. All new complexes have been characterized by conventional spectroscopic methods, and the solid-state molecular structures of **1**, **2**·MeCN, and **5**·$2CH_2Cl_2$ have been established by single-crystal X-ray diffraction analyses.

Introduction

We have recently been investigating the properties of a new class of vanadium nitrosyl complexes, namely (trimpsi)$V(NO)X_2$ species (trimpsi = $^tBuSi(CH_2PMe_2)_3$; X = halide, carboxylate, alkyl, etc.).[1,2] To date we have discovered that treatment of (trimpsi)$V(NO)Cl_2$ with $Mg(CH_2SiMe_3)_2\cdot x$ dioxane provides high isolated yields of (trimpsi)V(NO)(CH_2SiMe_3)Cl, the first alkyl complex of a group 5 nitrosyl. Related complexes such as (trimpsi)$V(NO)(OTf)_2$ and (trimpsi)$V(NO)(\eta^1\text{-}O_2C\text{-}4\text{-}C_6H_4Me)_2$ are also preparable from the dichloro precursor by metathetical routes.[2] During the course of these investigations we began to wonder whether there might be a more convenient (and higher yielding) preparative route to the (trimpsi)$V(NO)Cl_2$ starting material than the four-step procedure from $[V(CO)_6]^-$ that we had previously developed.[1] Our initial search of the literature revealed the 1975 report of $(THF)_2V(NO)Cl_2$ which contains the requisite $V(NO)Cl_2$ fragment.[3] This complex can evidently be formed in two steps by treating VCl_4 in CCl_4 with NO to form the coordination polymer $[V(NO)_3Cl_2]_n$ and then reacting the polymer with THF.

We soon learned that the reactions between VCl_4 and NO have a relatively long history. For instance, Whittaker and Yost reported in 1949 that insoluble $V(NO)Cl_4$ is formed when NO is passed into a dilute CCl_4 solution of VCl_4.[4] However, in 1965 Beck and co-workers utilized similar methodology to form polymeric $[V(NO)_3Cl_2]_n$.[5] Furthermore, Yost also noted in his 1949 report that purple compounds with the empirical formulas $V_2(NO)Cl_7$ and $V_2(NO)_5Cl_8$ are formed by the reaction of NO with *neat* VCl_4 in the liquid and vapor phases, respectively.[4] As the first step in our studies with these systems, we therefore decided to reinvestigate the reactions of NO with VCl_4, and in this paper we present the results of these investigations. In our hands, the reaction in CCl_4 does indeed produce $[V(NO)_3Cl_2]_n$ whose derivative chemistry we find to be somewhat different than that described by Beck and co-workers in their 1975 report of $(THF)_2V(NO)Cl_2$. Most interestingly, and in contrast to the report by Whittaker and Yost, we have discovered that

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the slow addition of NO to neat VCl_4 results in the eventual isolation of black crystals of a material that we believe is best formulated as $[NO][VCl_5]$.

Results and Discussion

Reaction of NO with VCl_4 in CCl_4: Synthesis of $[V(NO)_3Cl_2]_n$. In agreement with the 1965 report by Beck and co-workers,[5] we find that treatment of a CCl_4 solution of VCl_4 with NO results in dehalogenation of the vanadium and the formation of polymeric $[V(NO)_3Cl_2]_n$ as a dark-brown solid in almost quantitative yield (eq 1).

However, we have also found that the addition of the NO to the CCl_4 solution must be effected slowly over the course of several weeks to form $[V(NO)_3Cl_2]_n$ reproducibly. If the NO gas is introduced too quickly, the only isolable product is VCl_3 which can be readily identified by its distinctive purple color. The IR spectrum of $[V(NO)_3Cl_2]_n$ as a Nujol mull exhibits ν(NO) absorptions at 1924 (s) and 1764 (vs) cm^{-1}.

$$n\mathrm{VCl_4}\ (\text{in } \mathrm{CCl_4}) + 5n\mathrm{NO} \rightarrow [\mathrm{V(NO)_3Cl_2}]_n + 2n\mathrm{ClNO} \quad (1)$$

Reaction of $[V(NO)_3Cl_2]_n$ with THF: Synthesis and Characterization of *mer*-$(THF)_3V(NO)Cl_2$ (1). In 1975 Beck and co-workers reported the isolation of a complex formulated as $(THF)_2V(NO)Cl_2$ from the reaction of THF with $[V(NO)_3Cl_2]_n$.[3] This chloro nitrosyl complex was isolated as an orange crystalline material, and it exhibited a ν(NO) value of 1651 cm^{-1} in its Nujol-mull IR spectrum. In our hands the addition of excess THF to a CH_2Cl_2 suspension of $[V(NO)_3Cl_2]_n$ leads to the formation of an orange solution. Filtration of this solution, followed by removal of the volatiles from the filtrate in vacuo, provides an orange residue. Crystallization of this residue from THF/hexanes affords analytically pure *mer*-$(THF)_3V(NO)Cl_2$ (**1**) in 55% yield (eq 2).

$$[\mathrm{V(NO)_3Cl_2}]_n + 3\mathrm{THF} \rightarrow n\ mer\text{-}\mathrm{(THF)_3V(NO)Cl_2}\ (\mathbf{1}) + 2n\mathrm{NO} \quad (2)$$

Complex **1** exhibits a strong ν(NO) absorption at 1646 cm^{-1} in its Nujol-mull IR spectrum. Its room-temperature ^1H NMR spectrum in CD_2Cl_2 consists of several broad ($\nu_{1/2} \sim 125$ Hz) singlets. However, upon cooling of the sample to 200 K, these signals sharpen considerably and resonances attributable to THF in two magnetically inequivalent environments become evident. These ligand signals appear as singlets at δ 2.17 and 4.22 and δ 3.10 and 1.28, in a 2:1 ratio, respectively. In addition, two singlet resonances at δ 1.75 and 3.57 attributable to uncoordinated THF are also evident in the 200 K ^1H NMR spectrum of **1**.

mer-$(THF)_3V(NO)Cl_2$ (**1**) crystallizes in the monoclinic space group $P2_1/c$, and its solid-state molecular structure is shown in Figure 1. The V−N and N−O bond lengths are 1.689(2) and 1.182(3) Å, respectively, while the V1−N1−O1 angle is 178.4(2)°. These metrical parameters are typical for vanadium nitrosyls.[1,6] The V1−O3 bond length is 2.229(2) Å, significantly longer than the V−O2 and V1−O4 bond lengths (2.059(2) and 2.043(2) Å, respectively), thereby demonstrating the strong trans influence of the NO ligand.[7] Furthermore, the complex is distorted from an idealized octahedral geometry. Both chloro ligands and the two THF ligands cis to the nitrosyl group are deflected away from the NO ligand. Thus, the Cl1−V1−N1 bond angle is 94.53(7)°. This distortion is probably a manifestation of the strong π-accepting ability of the nitrosyl group.

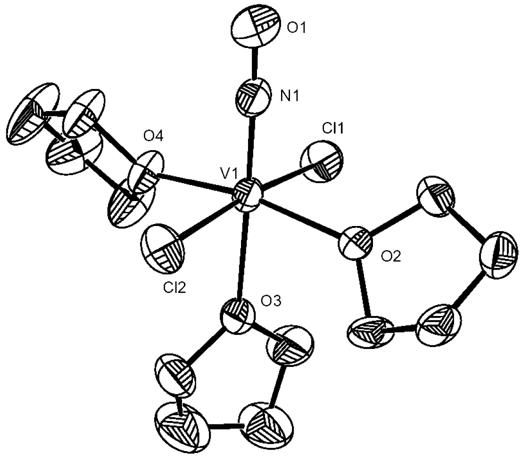

Figure 1. Solid-state molecular structure of *mer*-$(THF)_3V(NO)Cl_2$ (**1**) with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (deg): V1−N1 = 1.689(2), N1−O1 = 1.182(3), V1−Cl1 = 2.3447(7), V1−Cl2 = 2.3496(7), V1−O2 = 2.059(2), V1−O3 = 2.229(2), V1−O4 = 2.043(2); V1−N1−O1 = 178.4(2), Cl1−V1−Cl2 = 173.47(3), Cl1−V1−O2 = 89.56(6), Cl1−V1−O3 = 86.57(5), Cl1−V1−O4 = 90.03(5), Cl1−V1−N1 = 94.53(7), Cl2−V1−O2 = 89.59(5), Cl2−V1−O3 = 86.90(5), Cl2−V1−O4 = 89.52(5), Cl2−V1−N1 = 92.00(7), O2−V1−O3 = 84.31(6), O2−V1−O4 = 168.54(7), O2−V1−N1 = 96.50(8), O3−V1−O4 = 84.23(6), O3−V1−N1 = 178.63(8), O4−V1−N1 = 94.95(8).

Derivative Chemistry of $(THF)_3V(NO)Cl_2$ (1). Compound **1** is an excellent starting material for the synthesis of other vanadium nitrosyl complexes. For instance, dissolution of **1** in MeCN results in a yellow solution from which $(MeCN)_3V(NO)Cl_2$ (**2**) can be isolated in 24% yield as yellow-orange crystals (eq 3).

$$mer\text{-}\mathrm{(THF)_3V(NO)Cl_2} + 3\mathrm{MeCN} \rightarrow \mathrm{(MeCN)_3V(NO)Cl_2}\ (\mathbf{2}) + 3\mathrm{THF} \quad (3)$$

Complex **2** exhibits a strong ν(NO) absorption at 1651 cm^{-1} in its Nujol-mull IR spectrum. This spectral feature is identical with that reported by Beck et al. for $[(MeCN)_4V(NO)Cl]Cl$, a complex reportedly formed by the reaction of $[V(NO)_3Cl_2]_n$ with MeCN.[5] However, this reaction is evidently more complex than originally described. In 1982 Herberhold and Trampisch utilized IR spectroscopy to demonstrate that MeCN solutions of $[V(NO)_3Cl_2]_n$ also contain *cis*-dinitrosylvanadium compounds, and they succeeded in isolating brick-red $[(MeCN)_2V(NO)_2Cl]_x$ by treating these solutions with 1% sodium amalgam.[8] The related vanadium dinitrosyl complexes $[L_4V(NO)_2]Br$ (L = Lewis

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(8) Herberhold, M.; Trampisch, H. *Inorg. Chim. Acta* **1983**, *70*, 143−146.

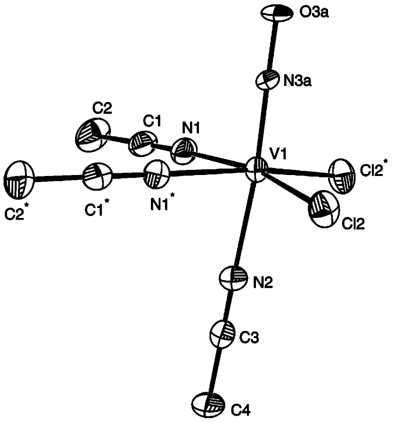

Figure 2. Solid-state molecular structure of the most abundant form of $(MeCN)_3V(NO)Cl_2$ (**2**) in crystals of **2**·MeCN. Selected bond lengths (Å) and angles (deg) of the principal form: V1−N1 = 2.140(1), V1−N2 = 2.158(2), V1−Cl2 = 2.2927(8), V1−Cl1 = 2.254(3), V1−N3 = 1.701(6), N3−O3 = 1.247(6), V1−N3−O3 = 177(2), Cl1−V1−Cl2 = 96.97(7), N1−V1−Cl1 = 90.64(8), N1−V1−Cl2 = 167.53(5), N1−V1−Cl2* = 90.32(5), Cl2−V1−Cl2* = 98.51(5), N1−V1−N2 = 83.57(6), N1−V1−N1* = 79.69(8).

base) and $(RNC)_3V(NO)_2X$ (X = Cl, Br, I) were subsequently described by Näumann and Rehder in 1984.[9]

X-ray-quality crystals of **2** can be grown readily from MeCN/Et_2O. Complex **2** crystallizes in the orthorhombic space group *Pbcm* as an acetonitrile solvate, **2**·MeCN. Interestingly, this is a different connectivity than that proposed by Beck and co-workers for $[(MeCN)_4V(NO)Cl]Cl$ in 1975,[5] yet it is an identical composition. An ORTEP diagram of the solid-state molecular structure of **2**·MeCN is shown in Figure 2. As in the structure of (trimpsi)V(NO)Cl_2,[1] the nitrosyl ligand in **2**·MeCN is disordered between the three ligand sites which are trans to an acetonitrile ligand, the relative occupancies of the three sites being 0.6, 0.2, and 0.2. In addition, a crystallographically imposed mirror plane relates the two halves of the molecule (Figure 2).

Unlike the three THF ligands in **1**, the three MeCN ligands in $(MeCN)_3V(NO)Cl_2$ **(2)** are arranged in a facial geometry. Consequently, the two chloro ligands are in a cis arrangement. The principal nitrosyl V−N bond length in **2** (V1−N3 = 1.701(6) Å) is typical of vanadium nitrosyls, but the N−O bond length (N3−O3 = 1.247(6) Å) is somewhat longer than expected. This latter feature may well be a result of the disorder extant in the crystals of **2**·MeCN.

Complex **1** readily reacts with phosphine donors as well. For instance, the reaction of **1** in CH_2Cl_2 with 1 equiv of trimpsi (trimpsi = $^tBuSi(CH_2PMe_2)_3$) generates deep blue solutions from which (trimpsi)V(NO)Cl_2, identified by a comparison of its IR and NMR spectral properties with those exhibited by an authentic sample, can be isolated as yellow crystals in 78% yield (eq 4).

The deep blue color observed during this formation of (trimpsi)V(NO)Cl_2 probably indicates the presence of small amounts of (trimpsi)V(THF)Cl_3 resulting from the reaction between $(THF)_3VCl_3$ and trimpsi.[6] This observation suggests that during the synthesis of $[V(NO)_3Cl_n]_n$ a small amount of VCl_3 is formed as well, and it is subsequently transformed into $(THF)_3VCl_3$ upon addition of THF.

$$mer\text{-}(THF)_3V(NO)Cl_2 + \text{trimpsi} \rightarrow (\text{trimpsi})V(NO)Cl_2\ (\mathbf{3}) + 3THF \quad (4)$$

Addition of excess PMe_3 to a CD_2Cl_2 solution of **1** generates a bright yellow solution. The ^1H NMR spectrum of this solution at room temperature displays a broad singlet at δ 0.99, while the $^{31}P\{^1H\}$ NMR spectrum also exhibits a broad singlet at δ −61. Upon cooling of the sample to 223 K, two new peaks appear in the ^1H NMR spectrum: a triplet at δ 1.41 (J_{PH} = 3.9 Hz) and a doublet at δ 0.77 (J_{PH} = 5.8 Hz) in a ratio of 2:1, respectively. A large singlet consistent with the presence of uncoordinated PMe_3 is also evident in this spectrum. Both the doublet and the triplet appear as singlets in the $^1H\{^{31}P\}$ NMR spectrum at the same temperature. The $^{31}P\{^1H\}$ NMR spectrum of this sample at 223 K exhibits two broad singlets at δ −2.5 and −26.2 in a 2:1 ratio, respectively. There is also a broad singlet at δ −61 in this spectrum. These NMR data are fully consistent with the presence of the expected $(Me_3P)_3V(NO)Cl_2$. Unfortunately, all attempts to isolate and further characterize this material have been unsuccessful to date. Solutions of $(Me_3P)_3V(NO)Cl_2$ slowly decompose under ambient conditions, as evidenced by the gradual loss of all signals in their $^{31}P\{^1H\}$ NMR spectra, thereby suggesting that the final product of decomposition is a paramagnetic species.

The generation of $(THF)_3V(NO)R_2$ (R = alkyl) complexes by reacting **1** with alkylating agents is another intriguing possibility. However, all our attempts to form such dialkyl compounds have so far been unsuccessful. For instance, addition of 1 equiv of $Mg(CH_2SiMe_3)_2 \cdot x$ dioxane or $Mg(CH_2Ph)_2 \cdot x$ dioxane to an orange THF solution of **1** quickly generates orange-brown solutions whose IR spectra are devoid of ν(NO) absorptions. Furthermore, no tractable products have yet been isolated from the final reaction mixtures.

Reaction of NO with Neat VCl_4: Synthesis and Characterization of $[NO][VCl_5]$. As noted in the Introduction, Yost and Whittaker reported in 1949 that passage of NO into liquid VCl_4 resulted in the precipitation of the compound $V_2(NO)Cl_7$ as dark purple, opaque crystals. In our hands, however, the slow addition of NO to neat VCl_4 results in the eventual isolation of black crystals (in 50% yield based on vanadium) of a material that we formulate as $[NO][VCl_5]$ (**4**) (eq 5).[10] Also formed during the course of the reaction is a purple powder whose properties are consistent with it being VCl_3. If the addition of NO is performed too quickly, then very little **4** is formed and the majority of the material isolated is VCl_3. Consequently, slow addition of NO to VCl_4 over the course of several weeks affords the best yields of **4**.

$$2VCl_4 + NO \rightarrow [NO][VCl_5]\ (\mathbf{4}) + VCl_3 \qquad (5)$$

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[9] Näumann, F.; Rehder, D. *Z. Naturforsch., B: Chem. Sci.* **1984**, *39*, 1654−1661.

[10] Given that the highest possible yield is 50%, this is essentially a quantitative conversion.

It appears that the initial step during the above conversion is the reduction of VCl_4 to VCl_3 by NO, a process that results in the formation of ClNO.[11] The ClNO then reacts with the remaining VCl_4 to form the nitrosonium salt. Consistent with this view is the fact that **4** can also be formed by reacting VCl_4 with ClNO (eq 6), and it can eventually be isolated in 76% yield. The formation of **4** by the route outlined in eq 6 is a far superior method of preparation than is the route outlined in eq 5. First, the reaction does not need to stand for several weeks; instead, it can be completed in about 1 h. Second, the preparation of **4** via eq 6 is atom economic since no VCl_3 is generated. It should also be noted that **4** is the only nitrosyl product isolated during our studies with neat VCl_4; we have also not been able to detect any other species that would fit the description of the products reported by Yost and Whittaker in 1949. It is interesting, though, that the sum of the product masses resulting from conversion (5) is $V_2(NO)Cl_8$, somewhat close to the $V_2(NO)Cl_7$ formulation by Yost and Whittaker.

$$VCl_4 + ClNO \rightarrow [NO][VCl_5]\ (\mathbf{4}) \qquad (6)$$

To confirm the composition of **4**, a preweighed sample of VCl_4 has been exposed to a 10-fold excess of ClNO. The weight of the powder that remains after removal of the unreacted ClNO reveals an increase in mass that corresponds to the capture of exactly 1 equiv of ClNO by the vanadium tetrachloride. Hence, the empirical composition of **4** is clearly $V(NO)Cl_5$.

Complex **4** is extremely volatile, and a brown haze surrounds its crystals even at atmospheric pressure under a dinitrogen atmosphere. It dissolves in pentane and CH_2Cl_2 to form yellow solutions, in arene solvents to give dark brown solutions, and in Et_2O, THF, or DME to produce deep red solutions.[12] In addition, complex **4** is extremely air- and moisture-sensitive, a fact that has so far precluded its satisfactory elemental analysis. It is light sensitive as well. When exposed to sunlight, its yellow CH_2Cl_2 solutions are quickly bleached colorless, concomitant with the deposition of a light-brown powder. Most importantly, the solventless syntheses of **4** are important factors leading to its successful isolation. Once dissolved in any solvent, solid $[NO][VCl_5]$ has never been recovered from any of these solutions.

$$[NO][VCl_5]\ (\mathbf{4}) \leftrightarrow VCl_4 + ClNO \qquad (7)$$

The solution- and gas-phase IR spectra of **4** are consistent with it dissociating to some extent to ClNO and VCl_4 in various media (eq 7). For instance, the gas-phase IR spectrum of **4** exhibits a strong doublet centered at 1800 cm^{-1}, a feature that shifts to 1765 cm^{-1} in the gas-phase IR spectrum of **4**-^{15}N. Another doublet is also evident in these spectra at 595 and 580 cm^{-1} for **4** and **4**-^{15}N, respectively. Both features are consistent with the presence of ClNO,[13] the N−O and N−Cl stretches being doublets since the fundamentals show PQR structure with the Q-branch maxima being fairly broad.[13a] Complex **4** exhibits $\nu(NO)$ absorptions at 1805 cm^{-1} in its IR spectra both in Nujol and in hexanes, at 1844 cm^{-1} in CH_2Cl_2, and 1872 cm^{-1} in $MeNO_2$. IR spectra of its benzene solutions are devoid of vibrations assignable to the NO group, but in Et_2O a strong $\nu(NO)$ band is evident at 1844 cm^{-1}. These spectroscopic data strongly suggest that **4** does not exist as discrete ions in these phases.[14] Consistently, complex **4** is essentially nonconducting in CH_2Cl_2, while in $MeNO_2$ it exhibits a molar conductivity of 28.5 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ that is well below the value expected for a 1:1 electrolyte.[15] The lack of conductivity in CH_2Cl_2 and the low conductivity in $MeNO_2$ are also consistent with the view that in solutions **4** exists predominantly as VCl_4 and ClNO.

A parent ion peak for **4** is not detectable in its mass spectrum, but a molecular weight determination by the Signer method in pentane provides a value of 261 g/mol[16] that is remarkably close to the theoretical value of 258 g/mol for an associated species. Furthermore, **4** exhibits a μ_{eff} of 1.79, a value very close to that expected for a compound having one unpaired electron.[17]

Even though **4** evidently sublimes as a tight ion pair and forms large crystals when sublimed at 50 °C, its solid-state molecular structure has not yet been established by an X-ray crystallographic analysis. The crystals of **4** apparently consist of individual crystallites that afford diffraction data that have not been successfully interpreted by any of the crystallographic methods tried to date. Nevertheless, the formulated anionic component of **4**, namely $[VCl_5]^-$, has been characterized twice previously in the solid state in crystals of $[PPh_4]_2[V_2Cl_9][VCl_5]\cdot CH_2Cl_2$[18] and in crystals of $[PCl_4][VCl_5]$.[19] Interestingly, $[PCl_4][VCl_5]$, like $[NO][VCl_5]$, is a black volatile solid.[20,21] The $[VCl_5]^-$ anion can also be formed by reacting 1 equiv of $[AsPh_4]Cl$ with VCl_4.[22]

In summary, possible formulations of **4** include the nitrosonium salt, $[NO][VCl_5]$, the d^1 octahedral species, $V(NO)Cl_5$, and the Lewis acid/Lewis base adduct, $VCl_4\cdot ClNO$. We favor the first over the latter two (which also have no precedents in the chemical literature)[11,23] for several reasons. First, in aromatic solvents the complex is dark brown in color, possibly reflecting the formation of a nitrosonium

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(11) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

(12) The reaction between $[NO][VCl_5]$ and ethereal solvents most likely involves the irreversible formation of VCl_4L_2 and ClNO. Complexes of the type VCl_4L_2 (where L is an ether) are known, and they tend to be red in color. See: Bridgland, B. E.; Fowles, G. W. A.; Walton, R. A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 383−389.

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(14) Also, the reported $\nu(NO)$ value for NO^+ is 2100 cm^{-1}. See ref 11.

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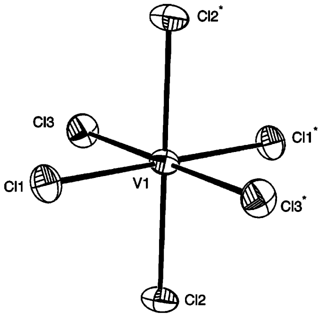

Figure 3. ORTEP diagram of the $[VCl_6]^{2-}$ dianion as it occurs in **5**·$2CH_2Cl_2$ with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (deg): V1−Cl1 = 2.2849(5), V1−Cl2 = 2.3479(5), V1−Cl3 = 2.2995(5), Cl1−V1−Cl2 = 89.60(2); Cl1−V1−Cl3 = 90.33(2), Cl1−V1−Cl2* = 90.40(2), Cl1−V1−Cl3* = 89.67(2), Cl2−V1−Cl3 = 90.57(2), Cl2−V1−Cl3* = 89.43(2).

charge-transfer complex.[24] Second, the anion $[VCl_5]^-$ is a well-known, structurally characterized entity. Third, the existence of the equilibrium presented in eq 7 best accounts for the physical properties of the complex. So, while our formulation of $[NO][VCl_5]$ is not definitive, we believe that it is chemically reasonable and that it provides a good working hypothesis for the further investigations of the chemistry of this complex.

Derivative Chemistry of $[NO][VCl_5]$ (4). The addition of excess $[NEt_3(CH_2Ph)]Cl$ to a CH_2Cl_2 solution of $[NO][VCl_5]$, followed by crystallization from CH_2Cl_2/pentane, provides analytically pure red crystals of $[NEt_3(CH_2Ph)]_2[VCl_6]$ (**5**) in 51% yield (eq 8).

The solid-state molecular structure of **5** has been established by an X-ray crystallographic analysis. Complex **5** crystallizes in the triclinic space group $P\bar{1}$ as a bis(dichloromethane) solvate, **5**·$2CH_2Cl_2$. An ORTEP diagram of the anionic portion of **5**·$2CH_2Cl_2$ is shown in Figure 3, which also illustrates that the $[VCl_6]^{2-}$ dianion resides on a crystallographic inversion center.

$$[NO][VCl_5] + 2[NEt_3(CH_2Ph)]Cl \rightarrow [NEt_3(CH_2Ph)]_2[VCl_6]\ (\mathbf{5}) + ClNO \quad (8)$$

The octahedral $[VCl_6]^{2-}$ anion in **5**·$2CH_2Cl_2$ exhibits a slight Jahn−Teller distortion, with V1−Cl2 (2.3479(5) Å) being somewhat longer than V1−Cl1 (2.2849(5) Å) and V1−Cl3 (2.2995(5) Å). This is not surprising given that the vanadium center has a d^1 electronic configuration.[25] What is somewhat surprising, however, is that the $[VCl_6]^{2-}$ species has not been previously characterized by single-crystal X-ray diffraction. The only crystallographic data reported for a $[VCl_6]^{2-}$-containing species are the unit-cell parameters for Cs_2VCl_6 as determined by powder diffraction.[26] The complex $[EMIM]_2[VCl_6]$ (EMIM = 1-ethyl-3-methylimidazolium) has been synthesized but not structurally characterized.[27] On the other hand, the trianion, $[VCl_6]^{3-}$, has been structurally characterized in crystals of $[NMeH_3]_4[VCl_6]Cl$,[28] and as expected, it exhibits slightly longer V−Cl bond lengths (average 2.38 Å) than those extant in **5**·$2CH_2Cl_2$.

Finally, a DME solution of $[NO][VCl_5]$ (**4**) was kept at −30 °C while being exposed to air and moisture. After several months, red-orange crystals had deposited on the sides of the flask. These crystals have been shown to be $[(DME)VCl_2(O)]_2(\mu\text{-}O)$ (**6**) by an X-ray crystallographic analysis. Full details of the isolation and characterization of this complex are provided in the Supporting Information.

Summary

In this report we have provided full details of a viable alternate route to the (trimpsi)$V(NO)X_2$ class of complexes via *mer*-$(THF)_3V(NO)Cl_2$ (**1**) that should facilitate our future investigations of the chemistry of the trimpsi complexes. In addition, we have found that complex **1** is an interesting precursor molecule in its own right. We have only briefly explored its characteristic chemistry during the current study, and we note that more work could be done in this area. For instance, reactions of **1** with isocyanides, sulfides, amines, and other monodentate, neutral two-electron donors could provide a number of new, unique vanadium nitrosyls, as could the reactions between **1** and potentially tridentate ligands such as triazacyclononane. Finally, a high-yielding, reproducible method for synthesizing $[NO][VCl_5]$ (**4**) has been developed, a fact that should make the study of this intriguing complex much easier.

Experimental Section

General Methods. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of dinitrogen or argon. Pentane, hexanes, and benzene were dried and distilled from sodium or sodium/benzophenone ketyl. Tetrahydrofuran was distilled from molten potassium, while dichloromethane, MeCN, and DME were distilled from calcium hydride. CD_2Cl_2 was dried by standing over activated 4 Å molecular sieves for 2 days, and it was degassed prior to use. $MeNO_2$ was purified by the published procedure.[29] NO, ^{15}NO, and VCl_4 were purchased from commercial suppliers and were used as received. $[NEt_3CH_2Ph][Cl]$ was recrystallized from CH_2Cl_2 before use. The trimpsi ligand was prepared by the published procedure.[6] ClNO was generated by the method of Pass and Sutcliffe and was used immediately upon preparation.[30]

NMR spectra were recorded on a Bruker AMX 500 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{31}P spectra are referenced to external 85% H_3PO_4. Magnetic susceptibility measurements were performed on a Johnson Matthey MSB-1 magnetic susceptibility balance, while conductivity measurements were performed using a VWR 2052 conductivity meter equipped with a Au dip cell. IR spectra were recorded on a BOMEM MB-100 FT-IR spectrometer or a Mattson

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Genesis FT-IR spectrometer. Elemental analyses were performed by Mr. M. Lakha of this department.

Preparation of $[V(NO)_3Cl_2]_n$. Polymeric $[V(NO)_3Cl_2]_n$ was prepared by a modification of the published procedure.[5] In a typical experiment, a yellow solution of VCl_4 (0.5 mL, 0.91 g, 4.7 mmol) in CCl_4 (60 mL) in a 100-mL Schlenk tube was connected via a glass bridge to a glass-walled bomb (1 L) filled with NO (1 atm). A brown solid began precipitating from the CCl_4 solution after about 1 h. After 11 days, the supernatant CCl_4 solution was removed by cannulation, and the remaining solid was dried in vacuo to obtain $[V(NO)_3Cl_2]_n$ (0.68 g, 70%) as a brown powder. The product was identified by its appearance, and its characteristic ν(NO) absorptions at 1924 (s) and 1764 (vs) cm^{-1} in its Nujol-mull IR spectrum.

Preparation of *mer*-$(THF)_3V(NO)Cl_2$ (1). To a stirred suspension of $[V(NO)_3Cl_2]_n$ (0.609 g, 2.87 mmol) in CH_2Cl_2 (40 mL) was added THF (1.9 mL, 23 mmol). The brown powder characteristic of $[V(NO)_3Cl_2]_n$ was gradually replaced by a purple powder, and the initially colorless solution became bright orange. This mixture was filtered through a plug of Celite (2 × 2 cm). The volatiles were removed from the filtrate in vacuo, and the remaining residue was dissolved in THF (15 mL) to obtain a clear orange solution. Pentane (15 mL) was added, and the solution was cooled to −30 °C overnight to induce the deposition of orange crystals of **1** (0.58 g, 55%). Anal. Calcd for $C_{12}H_{24}Cl_2NO_4V$: C, 39.15; H, 6.57; N, 3.80. Found: C, 38.85; H, 6.66; N, 3.97. IR (Nujol mull): ν(NO) 1646 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 500 MHz, 200 K): δ 1.28 (4H, OCH_2CH_2), 2.17 (8H, OCH_2CH_2), 3.10 (4H, OCH_2CH_2), 4.22 (8H, OCH_2CH_2). MS (LSIMS, thioglycerol matrix): *m*/*z* 369, $[P^+]$.

Preparation of $(MeCN)_3V(NO)Cl_2\cdot MeCN$ (2). Complex **1** (0.15 g, 0.40 mmol) was dissolved in MeCN (3 mL) to obtain a yellow solution that was filtered through a plug of Celite (0.5 × 2 cm). Et_2O (1 mL) was added to the filtrate, and the resulting solution was cooled to −30 °C overnight to induce the deposition of yellow-orange crystals of **2**·MeCN (0.030 g, 24%). IR (Nujol mull): ν(NO) 1651 (s) cm^{-1}.

Preparation of (trimpsi)$V(NO)Cl_2$ (3). To an orange solution of $(THF)_3V(NO)Cl_2$ (0.100 g, 0.27 mmol) in CH_2Cl_2 was added trimpsi (0.1 mL, 0.38 mmol). The solution immediately turned intense blue. Pentane (10 mL) was added, and the solution was cooled to −30 °C for several days to induce the deposition of yellow crystals (0.098 g, 78%). This material was determined to be (trimpsi)$V(NO)Cl_2$ (**3**) by its characteristic NMR and IR spectra.[1]

Preparation of $[NO][VCl_5]$ (4): Method A. VCl_4 (5.0 mL, 9.1 g, 47 mmol) in a 100-mL Schlenk tube was connected via a glass bridge to a glass-walled bomb (1 L) filled with NO (1 atm). The bridge and headspace above the VCl_4 were filled with Ar (1 atm), and the Kontes Rotoflo valve of the bomb was slowly opened. The apparatus was allowed to stand undisturbed at ambient temperatures for 1 month, after which time the bridge was replaced with a coldfinger, and all of the volatiles were sublimed onto the sublimation probe by placing the Schlenk tube under vacuum and warming it to 50 °C. In this manner black crystals of $[NO][VCl_5]$ (6.2 g, 50% based on vanadium) were obtained. A purple ashlike material (4.2 g) remained in the reaction flask after the sublimation had been completed. $[^{15}NO][VCl_5]$ was generated similarly using ^{15}NO. Anal. Calcd for Cl_5NOV: C, 0.00; H, 0.00; N, 5.42; Cl, 68.65. Found: C, <0.3; H, <0.3; N, 6.73; Cl, 58.46. IR (gas phase): $[^{14}NO][VCl_5]$, 1806, 1788, 605, 585 cm^{-1}; $[^{15}NO][VCl_5]$, 1776, 1757, 590, 570 cm^{-1}. IR (Nujol): ν(NO) 1805 cm^{-1}. IR (hexanes): ν(NO) 1805 cm^{-1}. IR (CH_2Cl_2): ν(NO) 1844 cm^{-1}. IR ($MeNO_2$): ν(NO) 1872 cm^{-1}. IR (Et_2O): ν(NO) 1844 cm^{-1}. MS (Signer method in pentane, hexamethylbenzene as standard): 261 g/mol; theoretical for $[NO][VCl_5]$, 258 g/mol. Magnetic susceptibility: $\mu_{eff} = 1.79$. Λ_M (CH_2Cl_2, 23 °C, 1.52 mM) = 0.20 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. Λ_M ($MeNO_2$, 23 °C, 1.25 mM) = 28.5 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

Method B. ClNO (4.2 mL, 5.9 g, 90.6 mmol) was vacuum transferred into a glass Schlenk tube containing VCl_4 (1.8 mL, 3.28 g, 17.0 mmol). The Schlenk tube was connected to an oil bubbler and was allowed to warm slowly to room temperature. The excess ClNO was quickly evolved to leave a purple-black solid. The stopper of the Schlenk tube was replaced with a coldfinger, and all of the volatiles were sublimed onto the sublimation probe by placing the Schlenk tube under vacuum and warming it to 50 °C. In this manner black crystals of **4** were obtained (3.34 g, 76%). A nonvolatile gray ashlike material (0.52 g) remained in the reaction flask. The spectroscopic properties of the black crystals were identical with those of $[NO][VCl_5]$ obtained from VCl_4 and NO.

Determination of the Stoichiometry of $[NO][VCl_5]$ (4). To VCl_4 (0.8322 g, 4.32 mmol) in a preweighed glass bomb was added ClNO (2.3 mL, 3.2 g, 49.6 mmol) by vacuum transfer. The bomb was connected to an oil bubbler and was allowed to warm to room temperature. ClNO was quickly evolved, and 1.1121 g of a purple-black solid was left behind. The increase in weight of the reaction flask was 0.2799 g, which corresponds to 4.27 mmol, or 1 equiv, of ClNO.

Preparation of $[NEt_3(CH_2Ph)]_2[VCl_6]$ (5). To a yellow solution of $[NO][VCl_5]$ (0.096, 0.37 mmol) in CH_2Cl_2 (15 mL) was added a solution of $[NEt_3(CH_2Ph)]Cl$ (0.275 g, 1.21 mmol) in CH_2Cl_2 (15 mL) whereupon the solution immediately became deep red. Pentane (20 mL) was added, and the resulting solution was cooled to −30 °C for several days to induce the deposition of deep-red crystals of **5** (0.124 g, 51%). Anal. Calcd for $C_{26}H_{44}N_2VCl_6$: C, 48.17; H, 6.84; N, 4.32. Found: C, 48.67; H, 6.85; N, 4.34. IR (Nujol mull): 1260 (m), 1079 (m), 1005 (m), 792 (m), 753 (m), 707 (m) cm^{-1}.

X-ray Crystallography. Data collection for each structure was performed on a Rigaku/ADSC CCD diffractometer using graphite-monochromated Mo Kα radiation.

Data for **1** were collected at −75 ± 1 °C to a maximum 2θ value of 56.3° in 0.50° oscillations with 23.0 s exposures. The structure was solved by direct methods[31] and expanded using Fourier techniques.[32] The THF ligand comprised of carbon atoms C1, C2, C3, and C4 was found to be disordered, and C3 and C4 were modeled in two distinct orientations with equal relative populations. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3639 observed reflections and 199 variable parameters.

Data for **2**·MeCN were collected at −100 ± 1 °C to a maximum 2θ value of 55.8° in 0.50° oscillations with 51.0 s exposures. The structure was solved by direct methods[31] and expanded using Fourier techniques.[32] The nitrosyl ligand was found to be disordered over the three coordination sites trans to the acetonitrile ligands, with relative occupancies of 0.6, 0.2, and 0.2. Constraints were applied making the two V−N distances equivalent. The N−O and V−Cl distances were handled similarly. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement

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Table 1. X-ray Crystallographic Data for Complexes **1**, **2**·MeCN, and **5**·$2CH_2Cl_2$

param	**1**	**2**·MeCN	**5**·$2CH_2Cl_2$
Crystal Data			
empirical formula	$C_{12}H_{24}NO_4Cl_2V$	$C_8H_{12}N_5OCl_2V$	$C_{28}H_{48}Cl_{10}N_2V$
cryst habit, color	block, orange	block, orange	Block, red
cryst size (mm)	0.40 × 0.40 × 0.20	0. 25 × 0.15 × 0.10	0.40 × 0.20 × 0.20
cryst system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	*Pbcm*	$P\bar{1}$
V (Å^3)	1697.4(1)	1479.54(4)	936.7(2)
a (Å)[a]	8.7782(5)	8.2923(12)	9.0570(12)
b (Å)	12.8637(6)	11.8720(17)	9.2441(13)
c (Å)	15.0745(9)	15.0289(19)	13.1457(15)
α (deg)	90	90	107.333(3)
β (deg)	94.322(4)	90	93.278(3)
γ (deg)	90	90	114.325(4)
Z	4	4	1
fw	368.17	316.1	409.06
D(calcd) (Mg/m^3)	1.441	1.42	1.450
abs coeff (cm^{-1})	9.09	1.024	1.00
F_{000}	768	640	423
radiatn (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
Data Refinement			
final R indices[b]	$R_1 = 0.061$, $wR_2 = 0.108$	$R_1 = 0.028$, $wR_2 = 0.060$	$R_1 = 0.036$, $wR_2 = 0.105$
goodness-of-fit on F^2 [c]	1.26	0.906	1.012
largest diff peak and hole (e Å^{-3})	0.49 and −0.45	0.26 and −0.26	0.62 and −0.44

[a] Cell dimensions based on the following: **1**, 8060 reflections, 6.1° ≤ 2θ ≤ 56.3°; **2**·MeCN, 7580 reflections, 5.0 ≤ 2θ ≤ 55.8°, **5**·$2CH_2Cl_2$, 6688 reflections, 5.1° ≤ 2θ ≤ 55.8°. [b] Number of observed reflections: **1**, 2576 ($I_o > 3\sigma(I_o)$), $R_1 = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma wF_o{}^4]^{1/2}$, $w = [\sigma^2 F_o]^{-1}$; **2**·MeCN, 1728 ($I_o > 2\sigma(I_o)$), $R_1 = \Sigma|(|F_o| - |F_c|)\ |/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma wF_o{}^4]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0209P)^2]^{-1}$; **5**·$2CH_2Cl_2$, 3788 ($I_o > 2\sigma(I_o)$), $R_1 = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma wF_o{}^4]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0669P)^2]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$. [c] $\mathrm{GOF} = [\Sigma(w(F_o{}^2 - F_c{}^2|)^2)/\text{degrees of freedom}]^{1/2}$.

was based on 1728 observed reflections and 143 variable parameters.

Data for **5**·$2CH_2Cl_2$ were collected at −100 ± 1 °C to a maximum 2θ value of 55.8° in 0.50° oscillations with 35.0 s exposures. The structure was solved by direct methods[30] and expanded using Fourier techniques.[32] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3788 observed reflections and 190 variable parameters.

For each structure solution and refinement neutral-atom scattering factors were taken from Cromer and Waber.[33] Anomalous dispersion effects were included in F_c;[34] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[35] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[36] All calculations were performed using the CrystalClear software package of Rigaku/MSC[37] or SHELXL-97.[38] X-ray crystallographic data for **1**, **2**·MeCN, and **5**·$2CH_2Cl_2$ are collected in Table 1, and full details of all crystallographic analyses are provided in the Supporting Information.

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Supporting Information Available: Text, table, and a figure giving details of the isolation and characterization of **6** and complete details of the four X-ray crystallographic studies as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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