Reactivity of (trimpsi)V(NO)X_2 Complexes (X = Cl, Br, I; trimpsi = $^tBuSi(CH_2PMe_2)_3$). Synthesis of the First Group 5 Alkyl Nitrosyls

Trevor W. Hayton, Brian O. Patrick, and Peter Legzdins*

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia, Canada V6T 1Z1

Received October 9, 2003

Treatment of (trimpsi)V(NO)Cl_2 (trimpsi = $^tBuSi(CH_2PMe_2)_3$) in NEt_3 with 2 equiv each of *p*-toluic acid and Proton Sponge affords lemon yellow (trimpsi)V(NO)(η^1-O_2C-4-C_6H_4Me)$_2$ (**1**) in 47% isolated yield. Similarly, reaction of (trimpsi)V(NO)Cl_2 with 2 equiv of AgOTf in CH_2Cl_2 provides lemon yellow (trimpsi)V(NO)(OTf)$_2$ (**2**) in a comparable yield. Alternatively, **2** can be obtained directly in 40% yield by treating CH_2Cl_2 solutions of (trimpsi)V(CO)$_2$(NO) at −60 °C with 2 equiv of AgOTf. Likewise, both benzoyl peroxide and diphenyl disulfide are capable of oxidizing (trimpsi)V(CO)$_2$(NO) under similar conditions to form (trimpsi)V(NO)X_2-type complexes, namely (trimpsi)V(NO)(O_2CPh)$_2$ (**3**) and (trimpsi)V(NO)(SPh)$_2$ (**4**), respectively. The reactions of (trimpsi)V(NO)X_2 (X = Cl, Br) with $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane) (either 0.5 equiv or an excess) in THF afford the orange-red alkyl complexes (trimpsi)V(NO)(CH_2SiMe_3)X (X = Cl (**5**), Br (**6**)) in reasonable yields. Other members of this family of complexes such as (trimpsi)V(NO)(CH_2CMe_3)Cl (**7**) and (trimpsi)V(NO)(Me)Cl (**8**) can also be obtained by employing similar metathetical methodology, but all attempts to synthesize (trimpsi)V(NO)(alkyl)$_2$ complexes have to date been unsuccessful. All new complexes have been fully characterized by standard methods, and the solid-state molecular structures of **1**·1.5C_6H_5Me and **5**·2C_4H_8O have been established by single-crystal X-ray diffraction analyses.

Introduction

In recent years we have been exploring the chemical properties of 16-valence-electron Cp′M(NO)R_2 complexes (Cp′ = Cp, Cp*; M = Mo, W; R = alkyl, aryl), and in the process we have developed a very diverse chemistry of these compounds,[1,2] especially in the area of C−H bond activation.[3−5] These discoveries suggest that these organometallic nitrosyl complexes may well be employed one day as agents for the conversion of hydrocarbon feedstocks into industrially important compounds.[6] This exciting possibility was the original motivation for our development of the related (trimpsi)V(NO)X_2 complexes (X = Cl, Br, I; trimpsi = $^tBuSi(CH_2PMe_2)_3$).[7,8] In this contribution we describe our further investigations of (trimpsi)V(NO)-containing complexes, specifically our attempts to synthesize and characterize the first group 5 alkyl nitrosyl complexes.

The organometallic complexes considered in this report are formally vanadium(I) compounds. Interestingly, low-valent vanadium complexes, namely those which formally contain V(−I), V(0), or V(I), are relatively rare. Indeed, much of the low-valent chemistry of vanadium reported thus far has focused on the photolytic substitution of the carbonyl ligands of $[V(CO)_6]^-$ with Lewis bases to form $[V(CO)_{6-n}L_n]^-$-type complexes.[9,10] These complexes are formally d^6 V(−I) and are surprisingly stable, both to heat and in the presence of moisture. For instance, the preparation of $[Et_4N]$-$[V(CO)_6]$ employs water as a solvent.[11] As with the V(−I) complexes, most of the V(0) complexes have the general formula $V(CO)_{6-n}L_n$.[12−14] Unlike their V(−I) congeners, however, these octahedral 17e vanadium species are all very reactive and tend to be air and moisture sensitive. Complexes of this type are generally formed by replacement of the carbonyl ligands in $V(CO)_6$ with Lewis bases, transformations that proceed without photolysis.[12,14]

Vanadium(I) complexes also tend to be very reactive. Many are thermally unstable at ambient conditions,

---

* To whom correspondence should be addressed. E-mail: legzdins@chem.ubc.ca.

[1] Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223−233.

[2] Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41−48.

[3] Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035−7048.

[4] Ng, S. H. K.; Adams, C. S.; Legzdins, P. *J. Am. Chem. Soc.* **2002**, *124*, 9380−9381.

[5] Adams, C. S.; Legzdins, P.; Tran, E. *J. Am. Chem. Soc.* **2001**, *123*, 612−624.

[6] Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.

[7] Hayton, T. W.; Daff, P. J.; Legzdins, P.; Patrick, B. O. *Inorg. Chem.* **2002**, *41*, 4114−4126.

[8] Hayton, T. W.; Legzdins, P.; Patrick, B. O. *Inorg. Chem.* **2002**, *41*, 5388−5396.

[9] Müller, I.; Rehder, D. *J. Organomet. Chem.* **1977**, *139*, 293−304.

[10] Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1971**, *31*, 239−247.

[11] Barybin, M. V.; Pomije, M. K.; Ellis, J. E. *Inorg. Chim. Acta* **1998**, *269*, 58−62.

[12] Wells, F.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 1351−1360.

[13] Ellis, J. E.; Faltynek, R. A.; Rochfort, G. L.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* **1980**, *19*, 1082−1085.

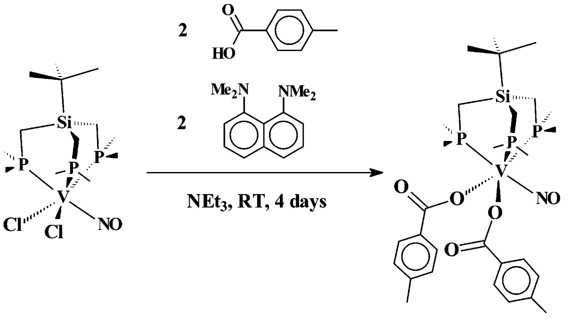
[14] Barybin, M. V.; Young, V. G., Jr.; Ellis, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 4678−4691.

10.1021/om034227p CCC: $27.50
Publication on Web 01/21/2004

even under an inert atmosphere.[15−17] For instance, hydrides such as $VH(CO)_4(dmpe)$ tend to decompose at room temperature by releasing H_2.[18−20] Similarly, the halide complexes $[CpV(CO)_3X]^-$ (where X = Cl, Br, I) disproportionate to $CpV(CO)_4$ and other unisolated vanadium-containing species.[21] A few vanadium(I) alkyls such as $[CpV(CO)_3Me]^-$ and $VMe(CO)_4(L_2)$ (L_2 = dppe, diars) are known,[21,22] and each of these complexes can be synthesized by adding an alkyl halide to an anionic vanadium carbonyl complex. Metathetical routes to low-valent vanadium alkyls are rare, since there are few suitable halide or pseudohalide precursors, but V−Me linkages in a Schiff-base complex have been formed in this manner.[23]

Results and Discussion

Synthesis of (trimpsi)V(NO)(η^1-O_2C-4-C_6H_4Me)$_2$ (1). Suspensions of (trimpsi)V(NO)Cl_2 in NEt_3 react with 2 equiv each of *p*-toluic acid and Proton Sponge (1,8-bis(dimethylamino)naphthalene) to generate (trimpsi)V(NO)(η^1-O_2C-4-C_6H_4Me)$_2$ (**1**) (eq 1). Crystallization of the reaction residue from THF/hexanes provides **1** as a lemon yellow solid in 47% yield.



(1)

1

Complex **1** is both air- and moisture-sensitive; furthermore, upon exposure to vacuum, yellow crystals of **1** turn light brown after a few hours. Possibly because of this, an acceptable elemental analysis of **1** has not been obtained. Nevertheless, a single-crystal X-ray crystallographic analysis of **1** has established its identity. The requisite crystals of **1** were obtained from toluene as the solvate **1**·1.5C_6H_5Me. An ORTEP diagram of the solid-state molecular structure of **1** as it occurs in these crystals is shown in Figure 1.

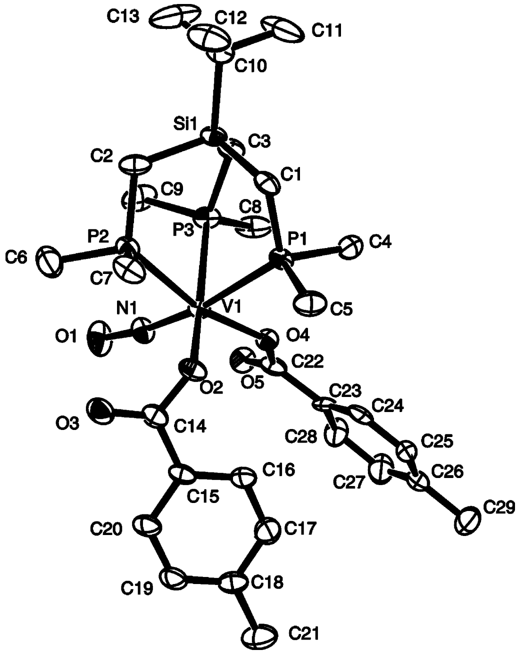


Figure 1. ORTEP diagram of **1** with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (deg): V1−N1 = 1.704(6), V1−O2 = 1.938(5), V1−O4 = 1.969(5), V1−P1 = 2.594(2), V1−P2 = 2.511(2), V1−P3 = 2.517(2), N1−O1 = 1.226(8); V1−N1−O1 = 171.1(6), N1−V1−O2 = 99.0(2), N1−V1−O4 = 102.3(3), N1−V1−P1 = 171.6(2), N1−V1−P2 = 90.2(2), N1−V1−P3 = 89.0(2), O2−V1−O4 = 99.0(2), O2−V1−P1 = 86.3(2), O2−V1−P2 = 85.8(2), O2−V1−P3 = 167.3(2), O4−V1−P1 = 83.1(2), O4−V1−P2 = 165.6(2), O4−V1−P3 = 88.9(2), P1−V1−P2 = 83.70(7), P1−V1−P3 = 84.70(7), P2−V1−P3 = 84.30(8).

In the solid state **1** possesses an η^3-trimpsi ligand and two η^1-benzoato ligands. The three V−P bond lengths are 2.594(2), 2.511(2), and 2.517(2) Å, and the linear nitrosyl ligand exhibits V−N and N−O distances of 1.704(6) and 1.226(8) Å, respectively. The N−O distance, in particular, is quite long relative to those extant in other nitrosyls[24] and nicely demonstrates the strong metal→NO back-bonding interaction that is present in many early-transition-metal nitrosyls.

The ^1H NMR spectrum of **1** in CD_2Cl_2 at −60 °C exhibits signals due to the trimpsi ligand that are similar to those of (trimpsi)V(NO)Cl_2,[8] thereby indicating that the low-temperature solution structure of the complex resembles that found in the solid state (vide supra). For instance, at −60 °C the ^1H NMR spectrum of **1** displays two virtual triplets due to the PMe_2 groups at 1.65 and 1.97 ppm which are diagnostic of the trimpsi ligand being in a C_s-symmetric environment. In accord with the ^1H NMR data, the $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 at −60 °C consists of two broad singlets at −20.7 and −3.7 ppm in a 1:2 ratio, respectively. In contrast, the room-temperature ^1H NMR spectrum of **1** in CD_2Cl_2 consists of several broad peaks with no fine structure, while the room-temperature $^{31}P\{^1H\}$ NMR spectrum in the same solvent exhibits four broad resonances from 24 to −23 ppm and a sharp resonance at −54 ppm. The latter signal at −54 ppm is indicative of an uncoordinated phosphorus atom.[25] These variable-temperature NMR data thus suggest that **1** undergoes a structural change upon warming. In particular, the $^{31}P\{^1H\}$ NMR spectra suggest that upon warming the trimpsi ligand in **1** changes from an η^3 to an η^2 bonding mode. To maintain an octahedral coordination geometry

---

(15) Calderazzo, F.; De Benedetto, G. E.; Pampaloni, G.; Mössmer, C. M.; Strähle, J.; Wurst, K. *J. Organomet. Chem.* **1993**, *451*, 73−81.

(16) Calderazzo, F.; Pampaloni, G.; Pelizzi, G.; Vitali, F. *Organometallics* **1988**, *7*, 1083−1092.

(17) Calderazzo, F.; Pampaloni, G.; Vitali, D. *Gazz. Chim. Ital.* **1981**, *111*, 455−458.

(18) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 131−136.

(19) Davison, A.; Reger, D. L. *J. Organomet. Chem.* **1970**, *23*, 491−496.

(20) Süssmilch, F.; Glöckner, W.; Rehder, D. *J. Organomet. Chem.* **1990**, *388*, 95−104.

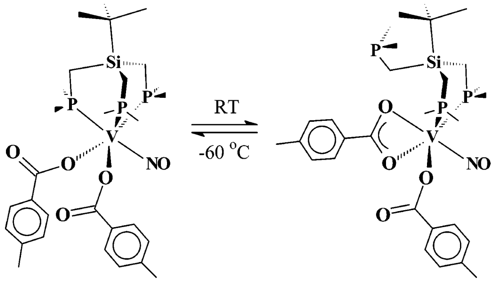
(21) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902−7915.

(22) Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* **1975**, *93*, 205−217.

(23) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318−9325.

(24) Feltham, R. D.; Enemark, J. H. *Top. Stereochem.* **1981**, *12*, 155−215.

at the metal center, one of the benzoato ligands could undergo a concomitant change from monodentate to bidentate coordination (eq 2).



(2)

Synthesis of (trimpsi)V(NO)(OTf)$_2$ (2). The reaction of (trimpsi)V(NO)Cl$_2$ with 2 equiv of AgOTf in CH$_2$Cl$_2$ affords yellow solutions of (trimpsi)V(NO)(OTf)$_2$ (**2**) (eq 3). Complex **2** can be isolated in 40% yield by

$$\text{(trimpsi)V(NO)Cl}_2 + 2\text{AgOTf} \rightarrow \underset{\mathbf{2}}{\text{(trimpsi)V(NO)(OTf)}_2} + 2\text{AgCl} \quad (3)$$

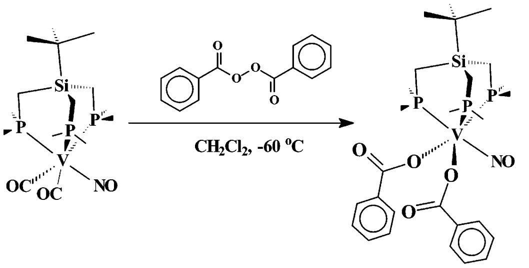
crystallization from CH$_2$Cl$_2$/hexanes as a lemon yellow powder. The Nujol-mull IR spectrum of **2** exhibits a ν(NO) value of 1642 (s) cm^{-1}, approximately 50 cm^{-1} higher than those displayed by (trimpsi)V(NO)X$_2$ (X = Cl, Br, I), a feature reflecting the strongly electron-withdrawing nature of the triflate ligand. As expected, the room-temperature ^{1}H NMR spectrum of **2** in CD$_2$Cl$_2$ is similar to that of (trimpsi)V(NO)Cl$_2$ and indicates the presence of an η^3-trimpsi ligand, while its room-temperature ^{19}F{^{1}H} NMR spectrum in CD$_2$Cl$_2$ exhibits the anticipated singlet at −77 ppm.

Alternatively, **2** can be obtained directly from (trimpsi)V(CO)$_2$(NO). Thus, 2 equiv of AgOTf reacts with CH$_2$Cl$_2$ solutions of (trimpsi)V(CO)$_2$(NO) at −60 °C to generate yellow solutions of **2** with the concomitant evolution of CO (eq 4). When it is synthesized from

$$\text{(trimpsi)V(CO)}_2\text{(NO)} + 2\text{AgOTf} \rightarrow \underset{\mathbf{2}}{\text{(trimpsi)V(NO)(OTf)}_2} + 2\text{Ag} + 2\text{CO} \quad (4)$$

(trimpsi)V(CO)$_2$(NO) in this manner, analytically pure **2** can be isolated in 40% yield. Even though conversions 3 and 4 afford **2** in identical isolated yields, the formation of **2** by reaction 4 is more efficient than its formation by reaction 3, since the synthesis and purification of (trimpsi)V(NO)Cl$_2$ can be completely avoided.

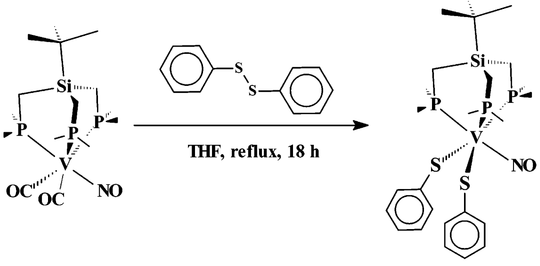
Reactions of (trimpsi)M(CO)$_2$(NO) (M = V, Nb, Ta) with Benzoyl Peroxide and Diphenyl Disulfide. Like AgOTf, both benzoyl peroxide and diphenyl disulfide are capable of oxidizing (trimpsi)V(CO)$_2$(NO) to form (trimpsi)V(NO)X$_2$-type complexes. For instance, solutions of (trimpsi)V(CO)$_2$(NO) in CH$_2$Cl$_2$ react with 1 equiv of benzoyl peroxide at −60 °C to generate yellow (trimpsi)V(NO)(η^1-O$_2$CPh)$_2$ (**3**) with concomitant evolution of CO (eq 5).[26] Crystallization of the reaction residue from toluene affords **3** as yellow crystals in 41% yield. Complex **3** as a KBr pellet exhibits ν(CO) peaks at 1654 and 1633 cm^{-1} and a ν(NO) absorption at 1592 cm^{-1} in its IR spectrum. Both the room-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra of **3** in CD$_3$CN reveal the expected signals for a η^3-trimpsi ligand in a C_s-symmetric environment, while the ^{1}H NMR spectrum displays the expected signals for two magnetically equivalent benzoato ligands. Interestingly, there is no evidence in the NMR spectra that **3** undergoes a structural transformation analogous to that shown for **1** in eq 2, even though there is a very close structural similarity between **1** and **3**.



(5)

3

Similarly, refluxing a THF solution containing equimolar amounts of (trimpsi)V(CO)$_2$(NO) and diphenyl disulfide for 18 h gives deep purple solutions of (trimpsi)V(NO)(SPh)$_2$ (**4**) (eq 6).[27] Crystallization from THF/hexanes (1:1) provides deep red crystals of **4** as a THF solvate in 29% yield. Complex **4** exhibits a ν(NO) band at 1570 cm^{-1} in its IR spectrum as a KBr pellet, while its ^{1}H NMR spectrum in C$_6$D$_6$ contains resonances attributable to trimpsi and to two phenyl sulfide ligands.



(6)

4

Having established that the oxidation of (trimpsi)V(CO)$_2$(NO) with benzoyl peroxide or diphenyl disulfide gives tractable (trimpsi)V(NO)X$_2$-type products, we next attempted the formation of the congeneric Nb and Ta species in a similar manner. Disappointingly, (trimpsi)M(NO)X$_2$ (M = Nb, Ta, X = pseudohalide) complexes do not result from reactions analogous to those portrayed for vanadium in eqs 5 and 6 (see Experimental Section for details).

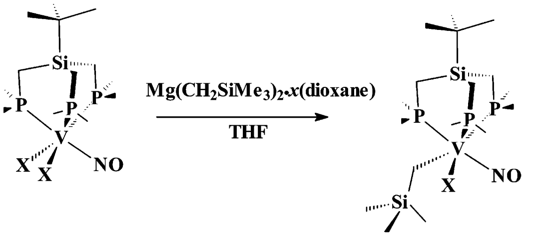
Syntheses of (trimpsi)V(NO)(R)X Complexes (X = Cl, Br; R = Me, CH$_2$SiMe$_3$, CH$_2$CMe$_3$). The reactions of (trimpsi)V(NO)X$_2$ (X = Cl, Br) with Mg(CH$_2$SiMe$_3$)$_2$·*x*(dioxane) (either 0.5 equiv or an excess) in THF at low temperature, followed by warming to ambient temperatures, generate orange solutions containing (trimpsi)V(NO)(CH$_2$SiMe$_3$)X (X = Cl (**5**), Br (**6**)) (eq 7). Crystallization from THF/hexanes affords the alkyl complexes as orange-red crystals in reasonable yields (**5**, 50%; **6**, 48%). Compounds **5** and **6** represent the first

---

(25) Gardner, T. G. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1989.

(26) Albano, V. G.; Monari, M.; Orabona, I.; Panunzi, A.; Roviello, G.; Ruffo, F. *Organometallics* **2003**, *22*, 1223−1230.

(27) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4860−4861.



(7)

X = Cl, Br

X= Cl, **5**
X= Br, **6**

isolated group 5 alkyl nitrosyl complexes. These orange crystalline materials are soluble in Et_2O, toluene, THF, and CH_2Cl_2, and both are thermally stable in the solid state and in solutions for indefinite periods of time. Both **5** and **6** have nitrosyl-stretching absorptions at ca. 1550 cm^{-1} in their Nujol-mull IR spectra; these features are lower in energy than those of their parent halo complexes. The room-temperature ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of both **5** and **6** are consistent with the proposed formulation and expected C_1 molecular symmetry. Thus, their ^1H NMR spectra reveal six doublets attributable to the six inequivalent methyl groups of the trimpsi ligand, while their $^{31}P\{^1H\}$ NMR spectra each consist of three broad singlets. The α carbon signals for the Me_3SiCH_2 ligands in the room-temperature $^{13}C\{^1H\}$ NMR spectra occur as broad singlets at 72.9 and 77.9 ppm for **5** and **6**, respectively.

Crystals of **5** suitable for X-ray diffraction analysis have been obtained from saturated THF solutions as the solvate **5**·2THF. The solid-state molecular structure of **5** as it occurs in these crystals is shown in Figure 2. Complex **5** contains a linear nitrosyl ligand with V1−N1 and N1−O1 distances of 1.755(8) and 1.117(8) Å, respectively. The V1−C14 distance of 2.123(7) Å is comparable to other vanadium(I) V−C single-bond lengths.[23] The three vanadium−phosphorus distances give an indication of the π-acceptor ability of the trimpsi ligand. For instance, the phosphorus atom trans to the nitrosyl ligand, P3, exhibits the longest bond to vanadium (2.604(2) Å vs 2.533(2) and 2.546(2) Å for the V−P bonds trans to the chloro and the alkyl ligands, respectively). This is as expected, since NO is a much better π-acceptor, and the trimpsi ligand cannot compete efficiently for the available electron density. Consistently, the phosphorus atom trans to the π-donating chloro ligand, P1, exhibits the shortest bond to vanadium.[28]

Other alkyl nitrosyl complexes in this family can also be prepared by metathetical methods. For instance, the reaction of $(trimpsi)V(NO)Cl_2$ with 0.5 equiv of $Mg(CH_2CMe_3)_2{\cdot}x(dioxane)$ in THF generates a red-purple solution of $(trimpsi)V(NO)(CH_2CMe_3)Cl$ (**7**) (eq 8). Complex

$$\begin{aligned}&(trimpsi)V(NO)Cl_2 + \\ &\quad 0.5Mg(CH_2CMe_3)_2{\cdot}x(dioxane) \rightarrow \\ &\underset{\mathbf{7}}{(trimpsi)V(NO)(CH_2CMe_3)Cl} + 0.5MgCl_2{\cdot}x(dioxane)\end{aligned} \tag{8}$$

7 can be isolated analytically pure from THF/hexanes solutions in 30% yield. It displays an NO-stretching frequency at 1530 cm^{-1} in its Nujol-mull IR spectrum, while its ^1H and $^{31}P\{^1H\}$ NMR spectra are similar to those exhibited by **5** and **6**. The signal due to the α carbon of the CH_2CMe_3 ligand in **7** occurs at 110 ppm in its $^{13}C\{^1H\}$ NMR spectrum.

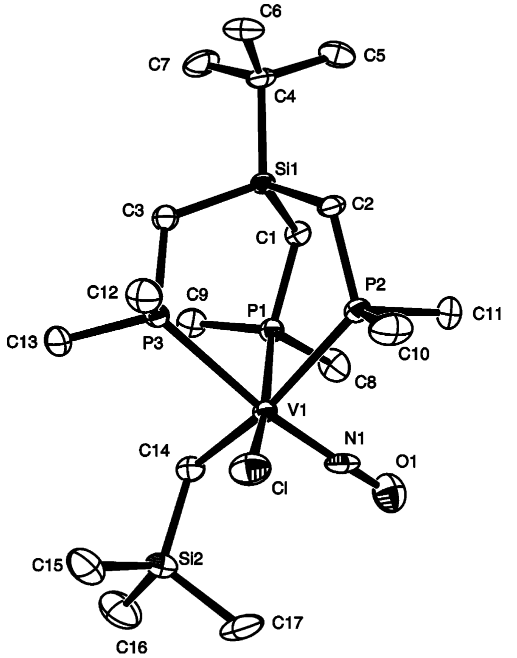


Figure 2. ORTEP diagram of **5** with 50% probability ellipsoids being shown. Selected bond lengths (Å) and angles (deg): V1−P1 = 2.533(2), V1−P2 = 2.546(2), V1−P3 = 2.604(2), V1−N1 = 1.755(8), V1−Cl = 2.364(2), V1−C14 = 2.123(7), N1−O1 = 1.117(8); Cl−V1−P1 = 167.86(9), Cl−V1−P2 = 89.57(7), Cl−V1−P3 = 86.13(8), Cl−V1−N1 = 99.8(2), Cl−V1−C14 = 106.3(2), P1−V1−P2 = 83.28(6), P1−V1−P3 = 83.47(7), P1−V1−N1 = 90.0(2), P1−V1−C14 = 80.3(2), P2−V1−P3 = 84.79(7), P2−V1−N1 = 89.9(2), P2−V1−C14 = 163.4(2), P3−V1−N1 = 172.0(2), P3−V1−C14 = 91.3(2), N1−V1−C14 = 92.1(3), V1−N1−O1 = 174.1(6).

In a similar manner, the reaction of $(trimpsi)V(NO)Cl_2$ with 0.5 equiv of $MgMe_2{\cdot}x(dioxane)$ in THF generates a yellow solution containing $(trimpsi)V(NO)(Me)Cl$ (**8**) (eq 9). Complex **8** may be obtained analytically pure

$$\begin{aligned}&(trimpsi)V(NO)Cl_2 + 0.5MgMe_2{\cdot}x(dioxane) \rightarrow \\ &\quad \underset{\mathbf{8}}{(trimpsi)V(NO)(Me)Cl} + 0.5MgCl_2{\cdot}x(dioxane)\end{aligned} \tag{9}$$

by crystallization from THF/hexanes in 25% yield. Again, the spectroscopic properties of **8** are similar to those exhibited by the other monoalkyl complexes. The signal due to the carbon atom of the methyl ligand in **8** appears as a broad singlet at 60.5 ppm in its $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2), while in the ^1H NMR spectrum the resonance attributable to the methyl protons occurs at 1.94 ppm as a doublet of triplets. This latter signal collapses to a singlet in the $^1H\{^{31}P\}$ NMR spectrum.

Attempts to prepare the bromo analogue, (trimpsi)V(NO)(Me)Br, by utilizing the same methodology employed for the synthesis of **8** have so far failed. ^1H NMR spectroscopy of the final reaction mixture shows that small amounts of (trimpsi)V(NO)(Me)Br are formed in the reaction between $(trimpsi)V(NO)Br_2$ and $MgMe_2{\cdot}x(dioxane)$. However, it is a minor constituent of any

---

[28] Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5−80.

isolated material, and it cannot be separated from the other products.

Attempted Syntheses of (trimpsi)V(NO)R_2 (R = Alkyl) Complexes. Given our success with the preparation of the monoalkyl complexes, (trimpsi)V(NO)(R)X (X = Cl, Br), we next turned our attention to the synthesis of the bis(alkyl) complexes, (trimpsi)V(NO)-R_2, the original target molecules of this research. The first synthetic attempts simply consisted of treating the dihalo precursors, (trimpsi)V(NO)X_2 (X = Cl, Br), with 1.0 equiv of $MgR_2 \cdot x$(dioxane) (i.e. 2.0 equiv of R^-). The reactions of (trimpsi)V(NO)Cl_2 or (trimpsi)V(NO)Br_2 with 1.0 equiv of $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane) afford **5** and **6**, respectively, as the only isolable products, and an additional metathesis event to form (trimpsi)V(NO)-$(CH_2SiMe_3)_2$ is not observed. In contrast, if (trimpsi)V-(NO)Cl_2 is reacted with 1.0 equiv of $Mg(CH_2CMe_3)_2 \cdot x$(dioxane) in THF, the reaction mixture quickly turns yellow-brown. The IR spectrum of the final reaction mixture is devoid of a ν(NO) absorption, and no tractable products can be isolated. The reaction of (trimpsi)V(NO)-Cl_2 with 1.0 equiv of $MgMe_2 \cdot x$(dioxane) proceeds similarly.

Attempted alkylation of (trimpsi)V(NO)$(OTf)_2$ (**2**) with 1.0 equiv of $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane) results in the formation of a red-brown solution whose IR spectrum is devoid of ν(NO) absorptions. Similar reactions between **2** and $Mg(CH_2CMe_3)_2 \cdot x$(dioxane) or $MgMe_2 \cdot x$(dioxane) also fail to generate tractable nitrosyl-containing species. The reaction of (trimpsi)V(NO)-(CH_2SiMe_3)Cl (**5**) with 1.0 equiv of AgOTf in CH_2Cl_2, in an attempt to form (trimpsi)V(NO)(CH_2SiMe_3)(OTf), leads only to the isolation of **2** in very low yields.

The addition of 1.0 equiv of (Me_3SiCH_2)Li to a THF solution of **5** at −30 °C results in the formation of an orange-brown solution. An IR spectrum of this solution reveals a single ν(NO) band at 1524 cm^{-1}. However, even at −30 °C, the intensity of this absorption diminishes with time, and the attempted isolation of this material by crystallization only produces an intractable red-brown precipitate. Similarly, the reaction of **5** with 1.0 equiv of MeLi generates a yellow solution which exhibits a ν(NO) absorption at 1526 cm^{-1} in its IR spectrum. On standing at −30 °C, though, the solution turns orange, and no tractable material has yet been isolated from it. It thus appears that the initial products from the reactions between **5** and alkyllithium salts are indeed nitrosyl-containing complexes, but they are thermally unstable even at low temperatures and cannot be isolated. It is not yet known whether these initial products are in fact bis(alkyl) complexes.

In a further attempt to form the desired bis(alkyl) complexes, the reaction between **5** and $K(CH_2SiMe_3)$ has been effected, but again no identifiable material could be isolated. Finally, attempts to form a bis(methyl) complex by reacting (trimpsi)V(NO)Cl_2 with $ZnMe_2$ only result in the formation of mixtures of starting material and **8**.

Reaction of (trimpsi)V(NO)I_2 with H_2O and O_2. During the initial synthesis and characterization of (trimpsi)V(NO)I_2,[8] a CH_2Cl_2 solution of this compound was allowed to stand at −30 °C for several months, during which time several large orange-red crystals formed. An X-ray crystallographic analysis has revealed these crystals, typically isolable in 14% yield based on vanadium, to be $[(\eta^3\text{-trimpsiO}_3)(\eta^2\text{-trimpsiO}_3)\text{VO}][I_3]_2 \cdot CH_2Cl_2 \cdot H_2O$ ($\text{trimpsiO}_3 = {}^t\text{BuSi}(CH_2P(O)Me_2)_3$) (**9**·$CH_2Cl_2 \cdot H_2O$), a product of the decomposition of (trimpsi)V-(NO)I_2 by air and water.[29] Full details of the isolation and characterization of this complex are provided in the Supporting Information.

Summary

The preparation and isolation of the complexes (trimpsi)V(NO)$(\eta^1\text{-}O_2C\text{-}4\text{-}C_6H_4R)_2$ (R = H, Me), (trimpsi)-V(NO)$(OTf)_2$, (trimpsi)V(NO)$(SPh)_2$, and (trimpsi)V-(NO)R(Cl) (R = CH_2SiMe_3, CH_2CMe_3, Me) demonstrate that the (trimpsi)V(NO) fragment is thermally stable when bound to a variety of coligands. However, several attempts to isolate the corresponding bis(alkyl) complexes, (trimpsi)V(NO)R_2, have not been successful. There may be several plausible reasons for this fact. One possibility is that bis(alkyl) complexes are formed initially, but they then undergo facile α-H elimination to form (trimpsi)V(NO)(=CHR) and RCH_3, a process followed by decomposition of the alkylidene complex. Such α-H elimination occurs readily in Cp*W(NO)R_2 (R = alkyl) complexes.[5] Another possible explanation is that the vanadium center in a bis(alkyl) complex is simply too electron rich. That (trimpsi)V(NO)(CH_2SiMe_3)Cl (**5**) and the other mono(alkyl) species are already quite electron rich is indicated by their low ν(NO) values evident in their IR spectra. The bis(alkyl) complexes would be even more electron rich. A concomitant increase in electron density onto the nitrosyl ligand by V→NO π-back-donation would further weaken the N−O bond and might result in these complexes undergoing nitrosyl-ligand cleavage, a process for which there is literature precedent.[30]

Future studies with these systems will be directed toward the synthesis of alkoxide and amide complexes containing the (trimpsi)V(NO) fragment. In addition, the reactivity of the vanadium−carbon bonds in the mono(alkyl) complexes toward unsaturated organic molecules, CO, and isocyanides will also be explored.

Experimental Section

General Methods. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or under an atmosphere of dinitrogen or argon. Pentane, hexanes, toluene, and benzene-d_6 were dried and distilled from sodium or sodium/benzophenone ketyl. Tetrahydrofuran was distilled from molten potassium, and dichloromethane was distilled from calcium hydride. Both CD_3CN and CD_2Cl_2 were dried by standing over activated 4 Å molecular sieves for 2 days and degassed prior to use. $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane),[31,32] $Mg(CH_2CMe_3)_2 \cdot x$(dioxane),[5] $MgMe_2 \cdot x$(dioxane),[30] (trimpsi)V(NO)X_2 (X = Cl, Br, I),[8] and (trimpsi)M-$(CO)_2$(NO) (M = V, Nb, Ta)[7] were prepared by published procedures. All other reagents were purchased from commercial suppliers and were used as received.

NMR spectra were recorded on Bruker AMX 500, AVA 300, or AVA 400 instruments. ^1H and ^{13}C spectra are referenced to

---

(29) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991−3003.

(30) Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272−6282.

(31) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262−265.

(32) Andersen, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809−811.

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, while ^{19}F spectra are referenced to external trifluoroacetic acid. Where appropriate, NMR spectral assignments were supported by conventional homonuclear and heteronuclear correlation spectroscopy experiments. IR spectra were recorded on a BOMEM MB-100 FT-IR spectrometer or a Mattson Genesis FT-IR spectrometer. Elemental analyses were performed by Mr. M. Lakha of this department.

Preparation of (trimpsi)V(NO)(η^1-O_2C-4-C_6H_4Me)$_2$ (1). NEt_3 (15 mL) was cannulated onto an intimate mixture of (trimpsi)V(NO)Cl_2 (0.077 g, 0.17 mmol), *p*-toluic acid (0.045 g, 0.33 mmol), and Proton Sponge (0.071 g, 0.33 mmol). The resulting yellow suspension was stirred at ambient temperatures for 4 days. The still yellow suspension was then taken to dryness in vacuo, and the remaining solid was dissolved in toluene (15 mL). The yellow solution was filtered through a plug of Celite (2 × 2 cm) supported on a medium-porosity frit, which was subsequently washed with toluene (10 mL). The combined yellow filtrates were taken to dryness in vacuo, and the remaining solid was dissolved in THF (2 mL) and layered with hexanes (3 mL). The solution was cooled overnight at −35 °C, resulting in the deposition of lemon yellow crystals of **1** (36 mg). A second crop of crystals (16 mg) was obtained by further cooling of the solution to −35 °C overnight. Total yield: 52 mg (47%). IR (Nujol mull): ν(NO) 1585 (s) cm^{-1}, ν(CO) 1645 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 500 MHz, −60 °C): δ 0.43 (d, J_{PH} = 9.3 Hz, CH_2), 0.84 (s, CMe_3), 0.94 (m, 2 CH), 1.06 (d, J_{PH} = 5.7 Hz, PMe_2), 1.16 (m, 2 CH), 1.65 (vt, J_{PH} = 3.2 Hz, 2 PMe), 1.97 (vt, J_{PH} = 3.3 Hz, 2 PMe), 2.34 (s, 2 Me), 7.14 (d, J_{HH} = 7.9 Hz, 4 CH), 7.99 (d, J_{HH} = 7.9 Hz, 4 CH). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 500 MHz, −60 °C): δ 0.43 (s, CH_2), 0.84 (s, CMe_3), 0.95 (d, J_{HH} = 14.7 Hz, 2 CH), 1.07 (s, PMe_2), 1.16 (d, J_{HH} = 12.4 Hz, 2 CH), 1.65 (s, 2 PMe), 1.97 (s, 2 PMe), 2.34 (s, 2 Me), 7.14 (d, J_{HH} = 7.7 Hz, 4 CH), 7.99 (d, J_{HH} = 7.8 Hz, 4 CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, −60 °C): δ 5.0 (d, J_{CP} = 6.7 Hz, CH_2), 7.7 (s, 2 CH_2), 14.0 (d, J_{CP} = 7.6 Hz, PMe_2), 14.4 (m, 2 PMe), 16.6 (q, J_{CP} = 5.6 Hz, *C*Me_3), 18.9 (t, J_{CP} = 11.1, 2 PMe), 21.2 (s, 2 Me), 24.9 (s, C*Me*$_3$), 128.3 (s, 4 CH), 129.7 (s, 4 CH), 132.0 (s, *C*Me), 141.1 (s, O_2C*C*), 173.1 (d, J_{CP} = 6.3 Hz, O_2*C*C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, −60 °C): δ −20.7 (br s, 1P), −3.7 (br s, 2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 25 °C): δ 24.5 (br s), −4.3 (br s), −17.3 (br s), −23.1 (br s), −53.9 (s). MS (EI; *m*/*z*): 631 [P^+ − NO]. High-resolution MS (EI; *m*/*z*): found, 631.189 99; calcd for $C_{29}H_{47}O_4SiP_3V$, 631.189 62. Crystals of **1** suitable for an X-ray crystallographic analysis were obtained from toluene as the solvate **1**·1.5C_6H_5-Me.

Preparation of (trimpsi)V(NO)(OTf)$_2$ (2). Method A. To an intimate mixture of (trimpsi)V(NO)Cl_2 (0.105 g, 0.23 mmol) and $AgSO_3CF_3$ (AgOTf, 0.118 g, 0.46 mmol) was added CH_2Cl_2 (15 mL) via a syringe. The suspension was shielded from light and was stirred at ambient temperatures for 9 days. The mixture was then filtered through Celite (2 cm × 2 cm) supported on a medium-porosity frit to obtain a yellow solution. The volume of this solution was reduced to 5 mL in vacuo, and it was then cooled to −30 °C overnight to induce the precipitation of a yellow powder. This powder was collected by filtration and was dried under vacuum to obtain analytically pure **2** (0.063 g, 40% yield). Anal. Calcd for $C_{15}H_{33}F_6NO_7P_3S_2$-SiV: C, 26.13; H, 4.82; N, 2.03. Found: C, 26.20; H, 4.82; N, 1.92. IR (Nujol mull): ν(NO) 1642 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 0.27 (d, J_{PH} = 10.5 Hz, CH_2), 0.82 (d, J_{PH} = 6.5 Hz, PMe_2), 0.93 (s, CMe_3), 1.08 (m, 2 CH), 1.46 (m, 2 CH), 1.78 (vt, J_{PH} = 4.6 Hz, 2 PMe), 2.19 (vt, J_{PH} = 4.4 Hz, 2 PMe). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.27 (s, CH_2), 0.82 (s, PMe_2), 0.93 (s, CMe_3), 1.08 (d, J_{HH} = 9.0 Hz, 2 CH), 1.46 (d, J_{HH} = 9.0 Hz, 2 CH), 1.78 (s, 2 PMe), 2.19 (s, 2 PMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 7.3 (s, CH_2), 10.7 (s, 2 CH_2), 15.3 (d, J_{CP} = 12.5 Hz, PMe_2), 16.7 (br s, 2 PMe), 18.6 (br s, *C*Me_3), 20.2 (t, J_{CP} = 10.0 Hz, 2 PMe), 27.0 (s, C*Me*$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 25 °C): δ −21.2 (br s, 1P), 3.0 (br s, 2P). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): δ −77.6 (s). MS (EI, 150 °C; *m*/*z*): 659 [P^+ − NO].

Method B. To a solution of (trimpsi)V(CO)$_2$(NO) (0.79 g, 1.76 mmol) in CH_2Cl_2 (60 mL) at −60 °C was added powdered $AgSO_3CF_3$ (AgOTf, 0.91 g, 3.54 mmol). The stirred mixture was warmed to room temperature while being shielded from light. The mixture was then refluxed for 2 h, and the brown precipitate was separated from the yellow solution by filtration through Celite (2 cm × 2 cm) supported on a medium-porosity frit. The filtrate was reduced to 30 mL in vacuo, hexanes (10 mL) were added, and the mixture was cooled to −30 °C overnight to induce the precipitation of **2** as a yellow powder which was collected and dried under vacuum (0.48 g, 40% yield). This powder was recrystallized from CH_2Cl_2 to obtain analytically pure material.

Preparation of (trimpsi)V(NO)(η^1-O_2CPh)$_2$ (3). A solution of $(PhCO_2)_2$ (0.047 g, 0.19 mmol) dissolved in CH_2Cl_2 (10 mL) was slowly added to a solution of (trimpsi)V(CO)$_2$(NO) (0.087 g, 0.19 mmol) in CH_2Cl_2 (10 mL) cooled to −60 °C, whereupon the color changed from red to yellow. The solution was allowed to warm to room temperature, and all the volatiles were removed in vacuo. The resulting brown-yellow oil was dissolved in toluene (3 mL), and this solution was filtered though a plug of Celite (2 × 0.5 cm) supported on glass wool. The volume of the resulting yellow-orange filtrate was reduced to 2 mL in vacuo, and this solution was cooled to −30 °C for several weeks to induce the deposition of yellow crystals of **3** (0.049 g, 41%). Anal. Calcd for $C_{27}H_{43}NO_5P_3SiV$: C, 51.18; H, 6.84; N, 2.21. Found: C, 51.24; H, 6.80; N, 2.52. IR (KBr): ν(CO) (s) 1654, (s) 1633 cm^{-1}; ν(NO) (s) 1592 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz, 25 °C): δ 0.54 (d, J_{PH} = 9.4 Hz, CH_2P), 0.90 (s, $SiCMe_3$), 1.05 (d, J_{PH} = 5.1 Hz, PMe_2), 1.13 (m, 2CH), 1.31 (m, 2CH), 1.70 (vt, 2PMe), 1.98 (vt, 2PMe), 7.31 (t, J_{HH} = 7.3 Hz, CH_p), 7.43 (t, J_{HH} = 6.7 Hz, CH_m), 8.15 (d, J_{HH} = 7.2, CH_o). $^1H\{^{13}P\}$ NMR (CD_3CN, 300 MHz, 25 °C): δ 0.54 (s, CH_2P), 0.91 (s, $SiCMe_3$), 1.06 (s, PMe_2), 1.13 (d, J_{HH} = 14.9 Hz, 2CH), 1.35 (d, J_{HH} = 14.7 Hz, 2CH), 1.70 (s, 2PMe), 1.98 (s, 2PMe), 7.28 (t, J_{HH} = 7.9 Hz, CH_p), 7.45 (t, J_{HH} = 7.4 Hz, CH_m), 8.18 (d, J_{HH} = 7.1, CH_o). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz, 25 °C): δ 5.84 (m, CH_2P), 9.13 (br s, 2CH), 14.3 (m, PMe_2), 15.3 (m, 2PMe), 17.5 (m, Si*C*Me_3), 19.8 (m,2PMe), 26.0 (s, SiC*Me*$_3$), 128.9 (CH_p), 130.9 (CH_o), 131.8 (CH_m). $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz, 25 °C): δ −2.4 (br s, 2P), −21.5 (br s, 1P). MS (EI, 200 °C; *m*/*z*): 603 [P^+ − NO].

Preparation of (trimpsi)V(NO)(SPh)$_2$ (4). A solution of (trimpsi)V(CO)$_2$(NO) (0.106 g, 0.23 mmol) and PhSSPh (0.052 g, 0.24 mmol) in THF (15 mL) was refluxed for 18 h, whereupon the color of the mixture changed from cherry red to purple. The THF was removed in vacuo, and the residue was dissolved in toluene (5 mL). This solution was filtered though Celite (2 × 0.5 cm) supported on glass wool. The filtrate was reduced in vacuo to 3 mL, and it was then cooled to −30 °C overnight to induce the deposition of a purple powder. This powder was recrystallized from THF/hexanes (1:1) to obtain deep red crystals of **4** (0.45 g, 29%). Anal. Calcd for $C_{25}H_{43}$-$NOP_3S_2SiV\cdot C_4H_8O$: C, 51.09; H, 7.54; N, 2.05. Found: C, 50.85; H, 7.52; N, 2.49. IR (KBr): ν(NO) 1570 (s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz, 25 °C): δ 0.22 (m, 4CH), 0.56 (s, $SiCMe_3$), 0.83 (d, J_{PH} = 12.8 Hz, CH_2P), 1.11 (vt, 2PMe), 1.26 (d, J_{PH} = 5.6 Hz, PMe_2), 1.42 (vt, 2PMe), 7.01 (t, J_{HH} = 8.9 Hz, CH_p), 7.31 (t, J_{HH} = 7.6 Hz, CH_m), 8.19 (d, J_{HH} = 7.0 Hz, CH_o). $^1H\{^{31}P\}$ NMR (C_6D_6, 500 MHz, 25 °C): δ 0.21 (overlapping d, 4CH), 0.56 (s, $SiCMe_3$), 0.83 (s, CH_2P), 1.11 (s, 2PMe), 1.26 (s, PMe_2), 1.42 (s, 2PMe), 7.01 (t, J_{HH} = 8.9 Hz, CH_p), 7.31 (t, J_{HH} = 7.6 Hz, CH_m), 8.19 (d, J_{HH} = 7.0 Hz, CH_o). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 9.2 (m, 2CH), 15.4 (m, 2PMe), 16.6 (m, CH_2P), 17.3 (d of t, J_{CP} = 11.3, 2.3 Hz, PMe_2), 25.3 (m, 2PMe), 25.5 (s, SiC*Me*$_3$), 124.0 (CH_p), 128.0 (CH_m), 133.4 (CH_o).

^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 25 °C): δ −10.3 (br s, 2P), −20.9 (br s, 1P). MS (EI, 200 °C; *m*/*z*): 609 [P^+].

Reactions of (trimpsi)M(CO)$_2$(NO) (M = Nb, Ta) with Benzoyl Peroxide and Diphenyl Disulfide. A THF solution of (trimpsi)Nb(CO)$_2$(NO) quickly reacts with 1 equiv of benzoyl peroxide at −30 °C, and a gas is evolved. Monitoring of the reaction by IR spectroscopy reveals the quick diminution of the peaks attributable to the starting material; however, no new ν(NO) absorptions appear, and no tractable materials can be isolated from the final orange reaction mixture. Similarly, the addition of 1 equiv of diphenyl disulfide to a THF solution of (trimpsi)Nb(CO)$_2$(NO) at −30 °C causes a gradual color change from red to orange-green. An IR spectrum of the final reaction solution is devoid of ν(NO) and ν(CO) absorptions, and no tractable materials can be isolated from the reaction mixture. Disappointingly, the same reactions with the tantalum congener afford similar results.

Preparation of (trimpsi)V(NO)(CH$_2$SiMe$_3$)Cl (5). THF (40 mL) was vacuum-transferred onto an intimate mixture of (trimpsi)V(NO)Cl$_2$ (1.025 g, 2.2 mmol) and Mg(CH$_2$SiMe$_3$)$_2$·*x*(dioxane) (0.325 g, 2.3 mmol of $CH_2SiMe_3^-$) at −196 °C. The reaction mixture was vigorously stirred for 72 h while being permitted to warm slowly to room temperature. The final orange suspension was taken to dryness in vacuo, and the remaining orange powder was dissolved in CH_2Cl_2 (20 mL). The orange solution was filtered through a plug of Celite (3 × 1 cm) supported on a medium-porosity frit, and the plug was subsequently washed with CH_2Cl_2 (2 × 10 mL). The combined orange filtrates were taken to dryness in vacuo, and the remaining solid was dissolved in THF (20 mL). This solution was concentrated in vacuo until incipient crystallization, at which point the mixture was cooled to −30 °C overnight. This cooling resulted in the deposition of **5** as an orange powder (0.736 g, 50% yield). Anal. Calcd for $C_{17}H_{44}ClNOP_3Si_2V\cdot C_8H_{16}O_2$: C, 45.62; H, 9.19; N, 2.13. Found: C, 45.42; H, 9.33; N, 2.17. IR (Nujol mull): ν(NO) 1550 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.03 (s, SiMe$_3$), 0.51 (dd, J_{HH} = 15.0 Hz, J_{PH} = 9.0 Hz, CH), 0.72−0.85 (m, 4 CH), 0.87 (s, CMe$_3$), 0.99 (br t, J_{HH} = 14.8 Hz, J_{PH} = 12.0 Hz, CH), 1.21 (d, J_{PH} = 4.8 Hz, PMe), 1.29 (d, J_{PH} = 5.3 Hz, PMe), 1.41 (d, J_{PH} = 7.2 Hz, PMe), 1.56 (d, J_{PH} = 6.4 Hz, PMe), 1.59 (d, J_{PH} = 7.1 Hz, PMe), 1.69 (d, J_{PH} = 7.5 Hz, PMe), 2.56 (m, Me$_3$SiC*H*), 3.27 (m, Me$_3$SiC*H*). ^{1}H{^{31}P} NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.03 (s, SiMe$_3$), 0.51 (d, J_{HH} = 14.9 Hz, CH), 0.72 (d, J_{HH} = 5.0 Hz, CH), 0.75 (d, J_{HH} = 4.5 Hz, CH), 0.81 (s, CH), 0.84 (s, CH), 0.87 (s, CMe$_3$), 0.99 (d, J_{HH} = 14.8 Hz, CH), 1.21 (s, PMe), 1.29 (s, PMe), 1.41 (s, PMe), 1.56 (s, PMe), 1.59 (s, PMe), 1.69 (s, PMe), 2.56 (d, J_{HH} = 10.0 Hz, Me$_3$SiC*H*), 3.27 (d, J_{HH} = 10.0 Hz, Me$_3$SiC*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 1.7 (s, SiMe$_3$), 7.8 (d, J_{CP} = 6.5 Hz, CH), 8.2 (d, J_{CP} = 6.5 Hz, CH), 9.1 (br s, CH), 15.0−15.4 (br m, 2 PMe), 15.6 (dd, J_{CP} = 6.0, 2.9 Hz, PMe), 16.2 (q, J_{CP} = 5.5 Hz, *C*Me$_3$), 16.5 (dd, J_{CP} = 11.3, 6.3 Hz, PMe), 22.4 (dd, J_{CP} = 15.4, 6.8 Hz, PMe), 22.6 (dd, J_{CP} = 18.6, 7.3 Hz, PMe), 24.9 (s, C*Me*$_3$), 72.9 (br s, Me$_3$SiC*H*$_2$). ^{1}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 25 °C): δ −22.7 (br s, 1P), −4.8 (br s, 2P). MS (LSIMS, thioglycerol matrix; *m*/*z*): 498 [$P^+ - CH_3$].

Preparation of (trimpsi)V(NO)(CH$_2$SiMe$_3$)Br (6). THF (30 mL) was vacuum-transferred onto an intimate mixture of (trimpsi)V(NO)Br$_2$ (0.615 g, 1.1 mmol) and Mg(CH$_2$SiMe$_3$)$_2$·*x*(dioxane) (0.168 g, 1.2 mmol of $CH_2SiMe_3^-$) at −196 °C. The reaction mixture was warmed slowly to room temperature while being vigorously stirred for 2 h. The final orange suspension was taken to dryness in vacuo, and the remaining orange powder was dissolved in CH_2Cl_2 (30 mL). The orange solution was filtered through a plug of Celite (3 × 1 cm) supported on a medium-porosity frit, and the plug was subsequently washed with CH_2Cl_2 (2 × 10 mL). The volume of the combined orange filtrates was reduced in vacuo until a solid began to precipitate, and the mixture was then cooled to −30 °C overnight to induce the deposition of **6** as orange crystals. These crystals (0.104 g) were collected by filtration and dried in vacuo. The supernatant solution was taken to dryness in vacuo, the remaining orange powder was dissolved in THF (5 mL), and the resulting solution was cooled to −30 °C overnight. These operations resulted in the deposition of additional orange crystals (0.302 g). The total yield of **6** was 0.406 g (48%). Anal. Calcd for $C_{17}H_{44}BrNOP_3Si_2V$: C, 36.56; H, 7.94; N, 2.51. Found: C, 36.60; H, 7.82; N, 2.56. IR (Nujol mull): ν(NO) 1555 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.07 (s, SiMe$_3$), 0.56 (dd, J_{PH} = 7.3 Hz, J_{HH} = 14.8 Hz, CH), 0.71−0.85 (m, 4 CH), 0.88 (s, CMe$_3$), 0.99 (m, CH), 1.24 (d, J_{PH} = 4.9 Hz, PMe), 1.40 (d, J_{PH} = 5.4 Hz, PMe), 1.42 (d, J_{PH} = 7.7 Hz, PMe), 1.55 (d, J_{PH} = 6.6 Hz, PMe), 1.58 (d, J_{PH} = 7.4 Hz, PMe), 1.72 (d, J_{PH} = 7.6 Hz, PMe), 2.26 (m, Me$_3$SiC*H*), 3.13 (m, Me$_3$SiC*H*). ^{1}H{^{31}P} NMR (C_6D_6, 500 MHz, 25 °C): δ −0.06 (d, J_{HH} = 14.7 Hz, CH), 0.13−0.32 (m, 5 CH), 0.57 (s, SiMe$_3$), 0.73 (s, CMe$_3$), 0.93 (s, PMe), 1.00 (s, PMe), 1.17 (s, PMe), 1.26 (s, PMe), 1.43 (s, PMe), 1.54 (s, PMe), 2.61 (d, J_{HH} = 10.0 Hz, Me$_3$SiC*H*), 3.32 (d, J_{HH} = 10.0 Hz, Me$_3$SiC*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 2.7 (s, SiMe$_3$), 8.7 (d, J_{CP} = 8.3 Hz, CH), 8.9 (d, J_{CP} = 5.0 Hz, CH), 10.0 (br s, CH), 15.7 (dd, J_{CP} = 16.9, 5.1 Hz, PMe), 16.0−16.4 (br m, 2 PMe), 17.0 (q, J_{CP} = 5.0 Hz, *C*Me$_3$), 18.7 (dd, J_{CP} = 12.5, 5.0 Hz, PMe), 23.6 (dd, J_{CP} = 20.0, 6.5 Hz, PMe), 25.0 (dd, J_{CP} = 14.8, 6.4 Hz, PMe), 24.9 (s, C*Me*$_3$), 77.9 (br s, Me$_3$SiC*H*$_2$). ^{1}P{^{1}H} NMR (C_6D_6, 202 MHz, 25 °C): δ −24.9 (br s, 1P), −7.7 (br s, 1P), −5.4 (br s, 1P). MS (LSIMS, thioglycerol matrix; *m*/*z*): 559 [P^+].

Preparation of (trimpsi)V(NO)(CH$_2$CMe$_3$)Cl (7). THF (10 mL) was vacuum-transferred onto an intimate mixture of (trimpsi)V(NO)Cl$_2$ (0.20 g, 0.43 mmol) and Mg(CH$_2$CMe$_3$)$_2$·*x*(dioxane) (0.065 g, 0.41 mmol of $CH_2CMe_3^-$) at −196 °C. The reaction mixture was warmed slowly to room temperature while being vigorously stirred for 2 h. The final orange solution was taken to dryness in vacuo, and the remaining powder was dissolved in CH_2Cl_2 (10 mL). The orange solution was filtered through a plug of Celite (3 × 1 cm) supported on a medium-porosity frit, and the plug was subsequently washed with CH_2Cl_2 (10 mL). The solvent was removed from the combined CH_2Cl_2 filtrates in vacuo, and the contents of the flask were dissolved in THF (3 mL). Hexanes (5 mL) were added, and the resulting solution was cooled to −30 °C overnight to induce the deposition of **7** as a deep red powder (0.065 g, 30% yield). Recrystallization of this powder from THF/hexanes provided the analytically pure material. Anal. Calcd for $C_{18}H_{44}ClNOP_3SiV$: C, 43.42; H, 8.91; N, 2.81. Found: C, 43.82; H, 8.63; N, 2.61. IR (Nujol mull): ν(NO) 1530 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.46 (m, C*H*CMe$_3$), 0.54 (dd, J_{HH} = 15.4, J_{HP} = 8.2 Hz, CH), 0.71 (dd, J_{HH} = 15.0, J_{HP} = 8.2 Hz, CH), 0.85 (m, CH), 0.88 (s, SiCMe$_3$), 0.92 (m, CH), 1.02 (m, 2CH), 1.19 (d, J_{PH} = 5.0 Hz, PMe), 1.26 (s, CMe$_3$), 1.33 (d, J_{PH} = 5.5 Hz, PMe), 1.48 (d, J_{PH} = 6.4 Hz, PMe), 1.52 (d, J_{PH} = 7.2 Hz, PMe), 1.58 (d, J_{PH} = 7.1 Hz, PMe), 1.66 (d, J_{PH} = 7.9 Hz, PMe), 3.73 (m, C*H*CMe$_3$, partially covered by residual THF). ^{1}H{^{31}P} NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.46 (d, J_{HH} = 11.6 Hz, C*H*CMe$_3$), 0.53 (d, J_{HH} = 14.8 Hz, CH), 0.85 (d, J_{HH} = 14.5 Hz, CH), 0.89 (s, SiCMe$_3$), 0.92 (d, CH), 1.19 (s, PMe), 1.24 (s, CMe$_3$), 1.33 (s, PMe), 1.49 (s, PMe), 1.52 (s, PMe), 1.58 (s, PMe), 1.67 (s, PMe), 3.73 (d, C*H*CMe$_3$, partially covered by residual THF). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 8.5 (m, 2CH$_2$P), 11.5 (m, CH$_2$P), 15.0 (dd, J_{PC} = 18.1, 5.4 Hz, PMe), 15.7 (dd, J_{PC} = 6.5, 3.8 Hz, PMe), 16.7−17.2 (m, 2PMe and Si*C*Me$_3$), 22.3 (dd, J_{PC} = 13.6, 6.9 Hz, PMe), 24.0 (dd, J_{PC} = 17.6, 8.5 Hz, PMe), 25.7 (s, SiC*Me*$_3$), 34.5 (s, C*Me*$_3$), 39.1 (d, J_{PC} = 12.8 Hz, CH$_2$*C*Me$_3$), 109.7 (br s, *C*H$_2$CMe$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 25 °C): δ −2.9 (br s, 1P), −5.3 (br s, 1P), −23.6 (br s, 1P). MS (LSIMS, 3-NBA matrix; *m*/*z*): 426 [$P^+ - CH_2CMe_3$].

Preparation of (trimpsi)V(NO)(Me)Cl (8). THF (20 mL) was vacuum-transferred onto an intimate mixture of (trimpsi)V(NO)Cl$_2$ (0.160 g, 0.35 mmol) and MgMe$_2$·*x*(dioxane) (0.028 g, 0.36 mmol of Me^-) at −196 °C. The reaction mixture was stirred vigorously for 2 h while being warmed slowly to room temperature. The final yellow suspension was taken to dryness in vacuo, and the residue was dissolved in CH_2Cl_2 (15 mL). The yellow solution was filtered through a plug of Celite (3 × 1 cm) supported on a medium-porosity frit, and the plug was subsequently washed with CH_2Cl_2 (10 mL). The solvent was removed from the combined filtrates in vacuo, and the contents of the flask were dissolved in THF (5 mL). Hexanes (2 mL) were added, and the resulting solution was cooled to −30 °C overnight to induce the deposition of **8** as yellow needles (0.039 g, 25% yield). Recrystallization of these needles from THF/hexanes gave the analytically pure material. Anal. Calcd for $C_{14}H_{36}ClNOP_3SiV$: C, 38.06; H, 8.21; N, 3.17. Found: C, 37.84; H, 8.25; N, 3.34. IR (Nujol mull): ν(NO) 1543 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 0.55 (dd, $J_{PH} = 7.0$ Hz, $J_{HH} =$ 14.8 Hz, CH), 0.70 (dd, $J_{PH} = 7.9$ Hz, $J_{HH} = 14.8$ Hz, CH), 0.75−1.00 (m, 4 CH), 0.87 (s, $SiCMe_3$), 1.23 (d, $J_{PH} = 4.9$ Hz, PMe), 1.30 (d, $J_{PH} = 5.3$ Hz, PMe), 1.41 (d, $J_{PH} = 7.6$ Hz, PMe), 1.54 (d, $J_{PH} = 6.9$ Hz, PMe), 1.57 (d, $J_{PH} = 7.6$ Hz, PMe), 1.69 (d, $J_{PH} = 7.7$ Hz, PMe), 1.94 (d of t, $J_{PH} = 14.0$ Hz, $J_{PH} = 7.9$ Hz VMe). $^1H\{^{31}P\}$ NMR (C_6D_6, 300 MHz, 25 °C): δ 0.31 (d, $J_{HH} = 14.7$ Hz, CH), 0.45−0.74 (m, 5 CH), 0.80 (s, $SiCMe_3$), 1.08 (s, PMe), 1.20 (s, PMe), 1.22 (s, PMe), 1.44 (s, PMe), 1.52 (s, PMe), 1.64 (s, PMe), 2.13 (s, VMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 8.4 (dd, $J_{CP} = 14.7$, 4.7 Hz, CH_2), 8.6 (dd, $J_{CP} = 14.7$, 5.8 Hz, CH_2), 10.3 (m, CH_2), 15.7 (dd, $J_{CP} = 16.9$, 8.5 Hz, PMe), 15.6−15.8 (br m, 2 PMe), 16.3 (dd, $J_{CP} = 16.5$, 6.1 Hz, PMe), 17.1 (q, $J_{CP} = 5.6$ Hz, CMe_3), 17.2 (dd, $J_{CP} =$ 12.8, 5.4 Hz, PMe), 21.5 (dd, $J_{CP} = 13.4$, 7.5 Hz, PMe), 23.0 (dd, $J_{CP} = 22.5$, 7.0 Hz, PMe), 25.7 (s, $C\mathit{Me}_3$), 60.5 (br s, VMe). $^{31}P\{^1H\}$ NMR (CD_3CN, 202 MHz, 25 °C): δ −23.4 (br s, 1P), −4.4 (br s, 1P), −1.3 (br s, 1P). MS (EI, 300 °C; *m/z*): 426 [$P^+ - Me$].

X-ray Crystallography. Data collection for each structure was performed on a Rigaku/ADSC CCD diffractometer using graphite-monochromated Mo Kα radiation at −100 ± 1 °C.

Data for **1**·1.5C_6H_5Me were collected to a maximum 2θ value of 50.1° in 0.50° oscillations with 58.0 s exposures. The solid-state molecular structure was solved by direct methods[33] and expanded using Fourier techniques.[34] The material crystallized with 1.5 molecules of toluene in the asymmetric unit. One toluene was found to be disordered, but it was modeled successfully in two orientations using isotropic rigid groups. The major fragment, C30A−C36A, had a relative population of 0.59(1), while the minor fragment, C30B−C36B, had a relative population of 0.41(1). A second toluene residing on an inversion center was found, but it could not be modeled. PLATON[35] was used to correct the data for any electron density found in the void space around the inversion center. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 7314 observed reflections and 407 variable parameters.

Data for **5**·2C_4H_8O were collected to a maximum 2θ value of 50.5° in 0.50° oscillations with 50.0 s exposures. The solid-state molecular structure was solved by direct methods[33] and expanded using Fourier techniques.[34] The material crystallized with two molecules of THF in the asymmetric unit. One THF was disordered, and both its minor and major conformations were modeled and refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4281 observed reflections and 321 variable parameters.

Table 1. X-ray Crystallographic Data for Complexes 1·1.5C_6H_5Me and 5·2C_4H_8O

	1·1.5C_6H_5Me	**5**·2C_4H_8O
	Crystal Data	
empirical formula	$C_{39.5}H_{59}NO_5P_3SiV$	$C_{25}H_{60}ClNO_3P_3Si_2V$
cryst habit, color	needle, yellow	irregular, red-orange
cryst size (mm)	0.20 × 0.20 × 0.1	0.25 × 0.20 × 0.15
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
V (Å^3)	4462.4(5)	1801.2(4)
a (Å)[a]	9.4373(8))	9.4054(8)
b (Å)	17.004(1)	9.600(2)
c (Å)	27.820(3)	20.416(1)
α (deg)	90	83.455(4)
β (deg)	91.982(3)	85.320(4)
γ (deg)	90	80.216(8)
Z	4	2
formula wt	799.85	658.24
calcd density (Mg/m^3)	1.190	1.214
abs coeff (cm^{-1})	3.95	5.74
F_{000}	1700	708
radiation (λ (Å))	Mo Kα (0.710 69)	Mo Kα (0.710 69)
	Data Refinement	
final R indices[b]	R1 = 0.165, wR2 = 0.204	R1 = 0.101, wR2 = 0.210
goodness of fit on F^2 [c]	0.95	2.56
largest diff peak and hole (e Å^{-3})	0.70 and −0.45	0.68 and −0.71

[a] Cell dimensions based on the following: **1**·1.5C_6H_5Me, 7092 reflections, 6.4° < 2θ < 50.1°; **5**·2C_4H_8O, 5120 reflections, 6.0° ≤ 2θ ≤ 50.5°. [b] Number of observed reflections: **1**·1.5C_6H_5Me, 2480 ($I_o > 2\sigma I_o$); **5**·2C_4H_8O, 3117 ($I_o > 3\sigma I_o$). $R1 = \sum|(|F_o| - |F_c|)|/\sum|F_o|$; $wR2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum wF_o^4]^{1/2}$. For **1**·1.5$C_6H_5$Me $w = [\sigma^2(F_o^2) + (0.0485P)^2 + 109.80P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; for **5**·2$C_4H_8O$, $w = [\sigma^2 F_o^2\ ]^{-1}$. [c] $GOF = [\sum(w(F_o^2 - F_c^2)^2)/(\text{degrees of freedom})]^{1/2}$.

For both structure solutions and refinements neutral-atom scattering factors were taken from Cromer and Waber.[36] Anomalous dispersion effects were included in F_c;[37] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[38] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[39] All data sets were corrected for Lorentz and polarization effects. All calculations were performed using the CrystalClear software package of Rigaku/MSC[40] or SHELXL-97.[41] X-ray crystallographic data for both complexes are collected in Table 1, and full details of all crystallographic analyses are provided in the Supporting Information.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and postgraduate scholarships to T.W.H. P.L. is a Canada Council Killam Research Fellow.

Supporting Information Available: Text, tables and a figure giving details of the isolation and characterization of **9** and complete details of the three X-ray crystallographic studies as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034227P

---

(33) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(34) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(35) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(37) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781−782.

(38) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Kluwer Academic: Boston, 1992; Vol. C, pp 219−222.

(39) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*; Kluwer Academic: Boston, 1992; Vol. C, pp 200−206.

(40) CrystalClear, Version1.3.5b20; Molecular Structure Corp., The Woodlands, TX, 2002.

(41) Sheldrick, G. M. SHELXL97; University of Göttingen, Göttingen, Germany, 1997.