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Differing Reactivities of (trimpsi)M(CO)$_2$(NO) Complexes [M = V, Nb, Ta; trimpsi = ^{t}BuSi(CH$_2$PMe$_2$)$_3$] with Halogens and Halogen Sources

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Treatment of (trimpsi)V(CO)$_2$(NO) (trimpsi = ^{t}BuSi(CH$_2$PMe$_2$)$_3$) with 1 equiv of PhICl$_2$ or C$_2$Cl$_6$ or 2 equiv of AgCl affords (trimpsi)V(NO)Cl$_2$ (**1**) in moderate yields. Likewise, (trimpsi)V(NO)Br$_2$ (**2**) and (trimpsi)V(NO)I$_2$ (**3**) are formed by the reactions of (trimpsi)V(CO)$_2$(NO) with Br$_2$ and I$_2$, respectively. The complexes (trimpsi)M(NO)I$_2$(PMe$_3$) (M = Nb, **4**; Ta, **5**) can be isolated in moderate to low yields when the (trimpsi)M(CO)$_2$(NO) compounds are sequentially treated with 1 equiv of I$_2$ and excess PMe$_3$. The reaction of (trimpsi)V(CO)$_2$(NO) with 2 equiv of ClNO forms **1** in low yield, but the reactions of (trimpsi)M(CO)$_2$(NO) (M = Nb, Ta) with 1 equiv of ClNO generate (trimpsi)M(NO)$_2$Cl (M = Nb, **6**; Ta, **7**). Complexes **6** and **7** are thermally unstable and decompose quickly at room temperature; consequently, they have been characterized solely by IR and ^{31}P{^{1}H} NMR spectroscopies. All other new complexes have been fully characterized by standard methods, and the solid-state molecular structures of **1**·3CH$_2$Cl$_2$, **4**·(3/4)CH$_2$Cl$_2$, and **5**·THF have been established by single-crystal X-ray diffraction analyses. A convenient method of generating Cl^{15}NO has also been developed during the course of these investigations.

Introduction

Ongoing research in our laboratories is focused on the derivatives of Cp′M(CO)$_2$NO (Cp′ = Cp, Cp*; M = Mo, W), specifically the 16e bis(alkyl) species Cp′M(NO)R$_2$ for which a substantial chemistry has been developed.[1,2] Cp′M(NO)R$_2$-type complexes are synthesized from the corresponding dichloro precursors, Cp′M(NO)Cl$_2$, which are made by treating Cp′M(CO)$_2$NO with PCl$_5$.[3] The isolation of the isoelectronic (trimpsi)M(NO)X$_2$ complexes (trimpsi = ^{t}BuSi(CH$_2$PMe$_2$)$_3$; M = V, Nb, Ta; X = Cl, Br, I), synthesized in similar fashion from the known 18e precursors (trimpsi)M(CO)$_2$(NO),[4] would be of considerable interest given the current paucity of group 5 nitrosyl complexes. Only two niobium nitrosyls and three tantalum nitrosyls are currently known, namely (trimpsi)M(CO)$_2$(NO),[5] [M(CNAr)$_4$(NO)$_2$]$^+$ (Ar = 2,6-Me$_2$C$_6$H$_3$),[6] and Ta(NO)(CNAr)$_5$,[7] and all are {M(NO)}^{6}-type species.[8] Vanadium nitrosyls are almost as rare.[9,10] The most common class of vanadium nitrosyls involves {V(NO)}^{6}-type complexes, examples of which include V(L)$_x$(CO)$_{5-x}$(NO)- and [V(L)$_4$(NO)$_2$]$^+$-type compounds (L = neutral Lewis base).[11–20] A few {V(NO)}^{4}-

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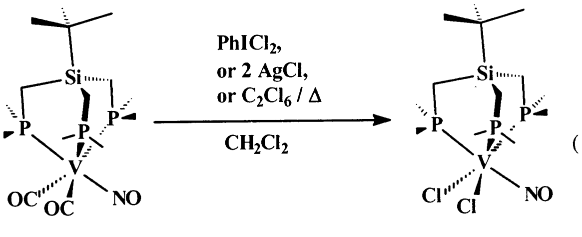
type complexes, such as $[V(CN)_5(NO)]^{3-}$,[21-23] $[V(CN)_6(NO)]^{4-}$,[24-26] and $[V(NO)(N(CH_2CH_2O)_3)]^-$,[27,28] are also known.

This contribution describes the reactivity of (trimpsi)M(CO)$_2$(NO) complexes with halogens, such as Br_2 and I_2, and halogen sources, such as PCl_5 and iodobenzene dichloride ($PhICl_2$). The reactions of the (trimpsi)M(CO)$_2$(NO) species with nitrosyl chloride (ClNO) are also outlined. These transformations are of interest since ClNO is well-known in inorganic chemistry as both a chlorinating and a nitrosylating agent.[10] For instance, ClNO reacts with CpM(CO)$_2$(NO) (M = Cr, Mo, W) to form CpM(NO)$_2$Cl complexes in high yields.[29] In contrast, treatment of $Mn_2(CO)_{10}$ with excess ClNO produces $Mn(CO)_5Cl$ as the only isolable product.[30] Also, Tp*Mo(CO)$_2$(NO) reacts with excess ClNO to form Tp*Mo(NO)Cl$_2$ via the dinitrosyl intermediate, Tp*Mo(NO)$_2$Cl.[31]

Results and Discussion

Formation of (trimpsi)V(NO)X$_2$ (X = Cl, Br, I). Solutions of (trimpsi)V(CO)$_2$(NO) in CH_2Cl_2 react with 1 equiv of $PhICl_2$[32] at −78 °C to generate yellow solutions of (trimpsi)V(NO)Cl$_2$ (**1**) with the concomitant evolution of CO (eq 1). Crystallization of the reaction residue from CH_2Cl_2 affords **1** as a yellow crystalline material in 60% yield. In the solid state, **1** is stable in air for several hours and exhibits a ν(NO) at 1601 cm^{-1} (Nujol), a frequency higher than that of (trimpsi)V(CO)$_2$(NO) (1543 cm^{-1}, Nujol).[4] The room-temperature $^{31}P\{^1H\}$ NMR and ^1H NMR spectra of **1** are consistent with the proposed formulation and the expected C_S molecular symmetry. For instance, the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 consists of two broad singlets at −24.5 ppm (1P) and −0.1 ppm (2P). In the ^1H NMR spectrum of **1** the expected three methyl environments of the trimpsi ligand are evinced by virtual triplets at 1.68 and 1.89 ppm and a doublet at 1.03 ppm. Each of these signals appears as a singlet in the $^1H\{^{31}P\}$ NMR spectrum.



(1)

1

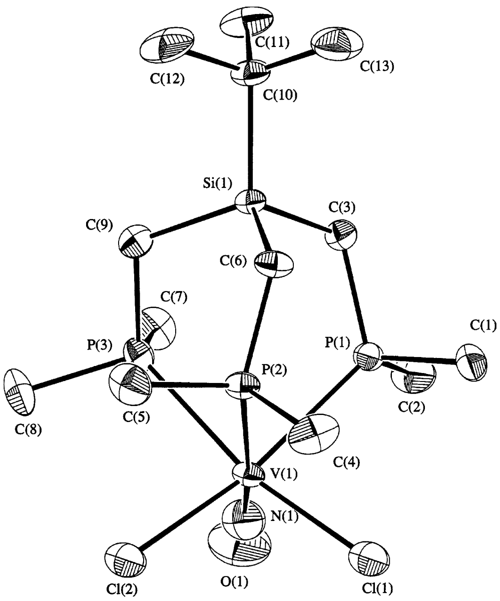


Figure 1. ORTEP diagram of (trimpsi)V(NO)Cl$_2$ (**1**) with thermal ellipsoids at the 50% probability level.

In an attempt to improve the yield of **1**, three other chlorinating reagents were tried, namely AgCl,[33] hexachloroethane (C_2Cl_6),[34] and PCl_5.[3] Treatment of (trimpsi)V(CO)$_2$(NO) with excess AgCl at room temperature leads to the formation of **1** in 51% isolated yield and the concomitant deposition of silver metal. The use of AgCl is particularly convenient since excess AgCl can be added with no apparent deleterious effects. Refluxing a CH_2Cl_2 solution of (trimpsi)V(CO)$_2$(NO) and 1 equiv of C_2Cl_6 for 4 h gives **1** in 37% yield after crystallization from CH_2Cl_2. Finally, the reaction between (trimpsi)V(CO)$_2$(NO) and 1 equiv of PCl_5 in CH_2Cl_2 at −78 °C leads to evolution of a gas and the formation of an insoluble white precipitate. This precipitate shows no bands in its IR spectrum attributable to a nitrosyl ligand and proves to be intractable. Regrettably, none of these routes provides **1** in higher yields than does the synthesis using $PhICl_2$ as the chlorinating agent.

Crystals of **1**·3CH$_2$Cl$_2$ suitable for X-ray diffraction analysis can be grown from a saturated CH_2Cl_2 solution. The solid-state molecular structure of **1** is shown in Figure 1, and its pertinent bond lengths and bond angles are collected in Table 1. Somewhat surprisingly, **1**, formally a 16e complex, remains monomeric in the solid state rather than associating through chloride bridges. Unfortunately, the nitrosyl ligand is disordered between the three coordination sites not occupied by phosphines. Furthermore, the nitrosyl ligand is distributed unevenly between the three sites, the relative occupancies being 0.68, 0.21, and 0.11. This type of structural disorder is relatively common in metal−nitrosyl complexes,[35] and it precludes accurate determination of the V−N and N−O bond distances and the V−N−O bond angle.

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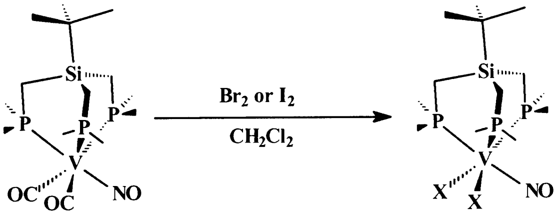
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for (trimpsi)V(NO)Cl_2 (**1**)[a]

	Bond Lengths		
V(1)−Cl(1)	2.316(2)	V(1)−N(1)	1.690(8)
V(1)−Cl(2)	2.356(1)	V(1)−N(2)	1.55(2)
V(1)−Cl(3)	2.343(7)	V(1)−N(3)	1.58(2)
V(1)−P(1)	2.542(1)	N(1)−O(1)	1.20(1)
V(1)−P(2)	2.578(1)	N(2)−O(2)	1.21(5)
V(1)−P(3)	2.528(1)	N(3)−O(3)	1.21(3)
	Bond Angles		
Cl(1)−V(1)−P(1)	86.00(6)	P(1)−V(1)−P(2)	84.99(3)
Cl(1)−V(1)−P(2)	89.42(6)	P(1)−V(1)−P(3)	83.23(4)
Cl(1)−V(1)−P(3)	168.45(6)	P(1)−V(1)−N(1)	93.0(2)
Cl(2)−V(1)−P(1)	168.99(5)	P(1)−V(1)−N(2)	170.8(1)
Cl(2)−V(1)−P(2)	85.50(4)	P(1)−V(1)−N(3)	90.2(7)
Cl(2)−V(1)−P(3)	90.50(5)	P(2)−V(1)−P(3)	85.50(4)
Cl(3)−V(1)−P(1)	88.8(1)	P(2)−V(1)−N(1)	171.7(3)
Cl(3)−V(1)−P(2)	170.1(2)	P(2)−V(1)−N(2)	86(1)
Cl(3)−V(1)−P(3)	86.2(2)	P(2)−V(1)−N(3)	93.5(7)
P(3)−V(1)−N(1)	86.2(3)	V(1)−N(1)−O(1)	173.7(7)
P(3)−V(1)−N(2)	96.6(1)	V(1)−N(2)−O(2)	136(3)
P(3)−V(1)−N(3)	173.4(7)	V(1)−N(3)−O(3)	159(2)

[a] The NO and Cl ligands are mutually disordered.

The average V−P distance of 2.55 Å in **1** is slightly longer than the average V−P bond length extant in (trimpsi)V$(CO)_2$(NO) (2.47 Å).[4]

Reaction of 1 equiv of Br_2 with (trimpsi)V$(CO)_2$(NO) in CH_2Cl_2 at −78 °C results in a color change from red to yellow as (trimpsi)V(NO)Br_2 (**2**) is formed (eq 2). Complex **2** can be isolated in 82% yield by crystallization from CH_2Cl_2/pentane (2:1) and exhibits a ν(NO) at 1589 cm^{-1} (Nujol), very close to that observed for **1**. Indeed, the spectroscopic properties of **2** are practically identical to those exhibited by **1**.



(2)

X = Br, **2**
X = I, **3**

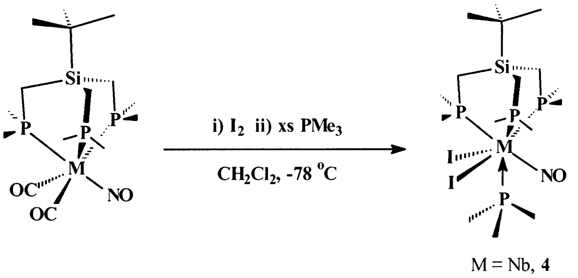
Yellow crystals of **2** can be grown from $CHCl_3$ and have been subjected to an X-ray diffraction analysis, but again severe positional disorder is evident in the solid-state molecular structure. In this instance the greater electron density of the bromide ligands effectively masks the positions of the N and O atoms of the nitrosyl ligand, thereby making it impossible to extract any meaningful metrical parameters. Nevertheless, the X-ray crystallographic analysis does confirm the anticipated atom connectivity.

Finally, reaction of 1 equiv of I_2 with (trimpsi)V$(CO)_2$(NO) in CH_2Cl_2 at −78 °C results in a color change from red to purple as (trimpsi)V(NO)I_2 (**3**) is formed (eq 2). Crystallization from THF/hexanes (3:1) provides **3**·THF as an analytically pure purple powder. This material exhibits an IR spectrum having a single ν(NO) at 1607 cm^{-1} (Nujol) and ^1H and $^{31}P\{^1H\}$ NMR spectra resembling those of **1** and **2**.

Several attempts to form the congeneric difluoro complex, (trimpsi)V(NO)F_2, were unsuccessful. For instance, oxidation of (trimpsi)V$(CO)_2$(NO) with 2 equiv of AgF or 1 equiv of AgF_2 afforded no tractable products. The attempted metathesis of (trimpsi)V(NO)Cl_2 with NaF or AgF also failed to provide an isolable nitrosyl complex.

Formation of (trimpsi)M(NO)I_2(PMe_3) (M = Nb, Ta). The reaction of (trimpsi)Nb$(CO)_2$(NO) with I_2 in CH_2Cl_2 at −78 °C results in the formation of a pale orange solution and a pale yellow precipitate. No absorptions attributable to a nitrosyl ligand are evident in the IR spectra of the precipitate or the solution. Attempts to ascertain the identity of any of the products formed have proven to be fruitless. Similar results have been obtained for the reaction between (trimpsi)Ta$(CO)_2$(NO) and I_2. The use of other oxidants such as Br_2, PCl_5, and $PhICl_2$ has also yielded unidentifiable materials.

Given the stability of (trimpsi)V(NO)X_2 (X = Cl, Br, I), it is not unreasonable to assume that (trimpsi)M(NO)X_2 (M = Nb, Ta) species may well be generated during the reactions of (trimpsi)M$(CO)_2$(NO) with halogens but that they subsequently decompose. Consistent with this view is the following observation. When (trimpsi)Nb$(CO)_2$(NO) is allowed to react with 1 equiv of I_2 at −78 °C for approximately 20 s and excess PMe_3 is then added via syringe, a clear yellow solution forms. Crystallization of the reaction residue from THF/hexanes affords (trimpsi)Nb(NO)I_2(PMe_3) (**4**) as a yellow powder in 64% yield (eq 3). The related (trimpsi)Ta(NO)I_2(PMe_3) (**5**) can be isolated in an identical manner in 10% yield. Complexes **4** and **5** exhibit extremely low ν(NO) values of 1467 and 1450 cm^{-1} (KBr), respectively, in their IR spectra.[36] To our knowledge, these represent the lowest recorded values for a terminal nitrosyl ligand and document the very strong M→NO back-bonding present in these early-metal nitrosyl complexes. The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 at room temperature consists of three broad singlets at −10.1 ppm (2P), −14.7 ppm (1P), and −45.7 ppm (1P). The ^1H NMR spectrum of **4** in CD_2Cl_2 contains the signals anticipated for the trimpsi ligand in a C_S symmetric environment along with a doublet attributable to the PMe_3 ligand. Complex **5** decomposes quickly in CD_2Cl_2, but in THF-d_8 at room temperature it exhibits a ^1H NMR



(3)

M = Nb, **4**
M = Ta, **5**

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[36] The ν(NO) value for **5**-^{15}N is 1399 cm^{-1} (KBr).

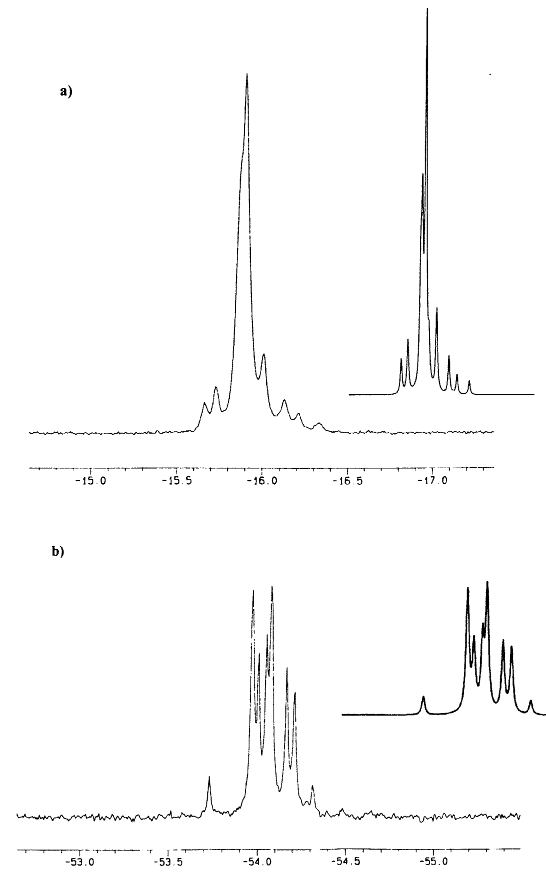


Figure 2. (a) The AB$_2$ portion of the AB$_2$X pattern exhibited by **5** in its ^{31}P{^{1}H} NMR spectrum. (b) The X portion of the AB$_2$X pattern exhibited by **5**. Simulated spectra are shown as insets.

spectrum similar to **4**. The ^{31}P{^{1}H} NMR spectrum of **5** consists of an AB$_2$X pattern with two multiplets evident at −15.9 ppm (3P) and −54.0 ppm (1P) (Figure 2). The signal at −15.9 ppm is the sum of A and B, most likely the two equivalent ^{31}P nuclei of the trimpsi ligand and the ^{31}P nucleus of the PMe$_3$ ligand, while the signal at −54.0 is due to the third ^{31}P nucleus of the trimpsi ligand. The spectrum can be simulated by fixing the peak separation of A and B to 39.1 Hz and by setting J_{AB} to 17.1 Hz, J_{AX} to 34.3 Hz, and J_{BX} to −39.6 Hz.

X-ray quality crystals of **4**·(3/4)CH$_2$Cl$_2$ can be obtained from a saturated CH$_2$Cl$_2$ solution, and they have been analyzed crystallographically. There are two independent molecules in the asymmetric unit; the solid-state molecular structure of one of these is shown in Figure 3. Selected bond lengths and bond angles are collected in Tables 2 and 3, respectively. The geometry around niobium is best described as monocapped distorted octahedron in which the nitrosyl ligand occupies the capping position while P(1), P(2), and P(4) define the capped face of the octahedron and P(3), I(1), and I(2) define the opposite face. Consistent with the IR spectrum which indicates considerable Nb→NO π-back-bonding, the Nb(1)−N(1) bond is quite short [1.836(4) Å] while the N(1)−O(1) bond is long [1.239(5) Å]. These values are much different than those found for (trimpsi)Nb(CO)$_2$(NO),[4] but they are comparable to those of Ta(CNAr)$_5$(NO), which exhibits a Ta−N distance of 1.897(12) Å and an N−O distance of 1.214(14) Å.[7]

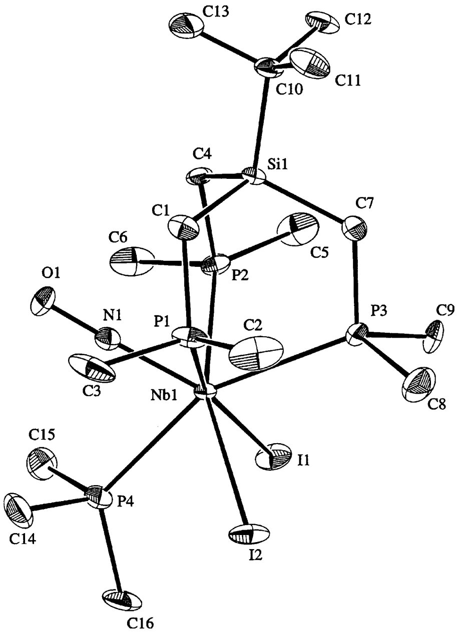


Figure 3. ORTEP diagram of (trimpsi)Nb(NO)I$_2$(PMe$_3$) (**4**) with thermal ellipsoids at the 50% probability level.

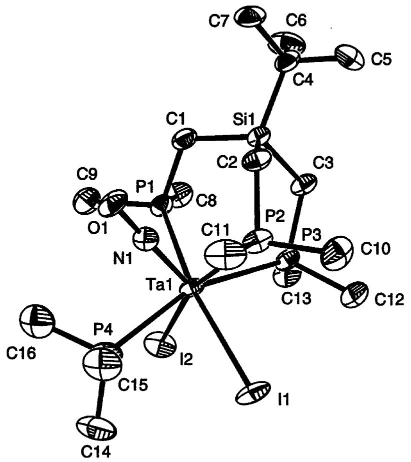


Figure 4. ORTEP diagram of (trimpsi)Ta(NO)I$_2$(PMe$_3$) (**5**) with thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) for (trimpsi)Nb(NO)I$_2$(PMe$_3$) (**4**)[a] and (trimpsi)Ta(NO)I$_2$(PMe$_3$) (**5**)

4		**5**	
Nb(1)−I(1)	2.9818(5)	Ta(1)−I(1)	2.9407(5)
Nb(1)−I(2)	2.9808(5)	Ta(1)−I(2)	2.9552(6)
Nb(1)−P(1)	2.610(1)	Ta(1)−P(1)	2.582(2)
Nb(1)−P(2)	2.610(1)	Ta(1)−P(2)	2.593(2)
Nb(1)−P(3)	2.727(1)	Ta(1)−P(3)	2.711(2)
Nb(1)−P(4)	2.597(1)	Ta(1)−P(4)	2.600(2)
Nb(1)−N(1)	1.836(4)	Ta(1)−N(1)	1.824(5)
N(1)−O(1)	1.239(5)	N(1)−O(1)	1.264(7)

[a] For one of the independent molecules in the asymmetric unit.

X-ray diffraction quality crystals of **5**·THF can be obtained from a saturated THF solution. The solid-state molecular structure of **5** is shown in Figure 4, and pertinent bond lengths and bond angles are collected in Tables 2 and 3, respectively. The tantalum complex exhibits the same

Table 3. Selected Bond Angles (deg) for (trimpsi)Nb(NO)I_2(PMe_3) (4)[a] and (trimpsi)Ta(NO)I_2(PMe_3) (**5**)

4		**5**	
I(1)−Nb(1)−I(2)	94.35(1)	I(1)−Ta(1)−I(2)	91.02(2)
I(1)−Nb(1)−P(1)	163.24(4)	I(1)−Ta(1)−P(1)	161.81(4)
I(1)−Nb(1)−P(2)	77.22(3)	I(1)−Ta(1)−P(2)	79.05(4)
I(1)−Nb(1)−P(3)	87.17(3)	I(1)−Ta(1)−P(3)	87.06(4)
I(1)−Nb(1)−P(4)	76.36(3)	I(1)−Ta(1)−P(4)	77.06(5)
I(1)−Nb(1)−N(1)	123.4(1)	I(1)−Ta(1)−N(1)	125.6(2)
I(2)−Nb(1)−P(1)	77.96(3)	I(2)−Ta(1)−P(1)	78.48(5)
I(2)−Nb(1)−P(2)	162.23(3)	I(2)−Ta(1)−P(2)	160.99(5)
I(2)−Nb(1)−P(3)	86.90(3)	I(2)−Ta(1)−P(3)	86.74(4)
I(2)−Nb(1)−P(4)	76.86(3)	I(2)−Ta(1)−P(4)	78.16(5)
I(2)−Nb(1)−N(1)	124.7(1)	I(2)−Ta(1)−N(1)	126.5(2)
P(1)−Nb(1)−P(2)	105.79(4)	P(1)−Ta(1)−P(2)	106.42(6)
P(1)−Nb(1)−P(3)	77.64(4)	P(1)−Ta(1)−P(3)	77.63(6)
P(1)−Nb(1)−P(4)	115.54(4)	P(1)−Ta(1)−P(4)	114.56(7)
P(1)−Nb(1)−N(1)	72.6(1)	P(1)−Ta(1)−N(1)	72.2(2)
P(2)−Nb(1)−P(3)	77.18(4)	P(2)−Ta(1)−P(3)	76.68(6)
P(2)−Nb(1)−P(4)	115.39(4)	P(2)−Ta(1)−P(4)	114.65(7)
P(2)−Nb(1)−N(1)	72.4(1)	P(2)−Ta(1)−N(1)	71.9(2)
P(3)−Nb(1)−P(4)	155.72(4)	P(3)−Ta(1)−P(4)	157.74(6)
P(3)−Nb(1)−N(1)	129.0(1)	P(3)−Ta(1)−N(1)	127.3(2)
P(4)−Nb(1)−N(1)	75.3(1)	P(4)−Ta(1)−N(1)	75.0(2)
Nb(1)−N(1)−O(1)	178.1(3)	Ta(1)−N(1)−O(1)	179.2(6)

[a] For one of the independent molecules in the asymmetric unit.

coordination geometry as the niobium congener. In this instance P(1), P(2), and P(4) define the capped face of the octahedron while I(1), I(2), and P(3) define the opposite face. The Ta−N distance is 1.824(5) Å and the N−O distance is 1.264(7) Å. Again, these values are quite different from those determined for (trimpsi)Ta$(CO)_2$(NO),[4] but are similar to those found in **4**. The average Ta−P distance of 2.62 Å is also similar to that extant in **4**.

The fact that 16e (trimpsi)V(NO)I_2 is thermally stable under ambient conditions but the niobium and tantalum congeners require stabilization as 18e species by coordination of phosphine may well reflect the ability of the heavier metals to more readily form seven-coordinate complexes. For instance, the nitrosyl ligand in the coordinatively unsaturated (trimpsi)M(NO)I_2 (M = Nb, Ta) species may be able to bend to an η^2-bonding mode which could result in cleavage of the N−O bond and subsequent complex decomposition.[37] Alternatively, the (trimpsi)M(NO)I_2 complexes could oligomerize via isonitrosyl bridges that then facilitate oxygen atom transfer and subsequent decomposition. Such a process has been invoked to account for the facile decomposition of 16e Cp*Mo$(Me)_2$(NO) at room temperature.[2] Whatever the actual decomposition pathway, it is clear that coordination of PMe_3 to the vacant coordination site in the (trimpsi)M(NO)I_2 complexes renders the compounds kinetically stable and permits their isolation.

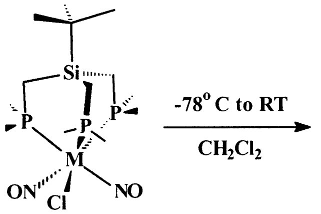
Synthesis of $Cl^{15}NO$. We have discovered that a convenient procedure for the generation of $Cl^{15}NO$ involves the metathesis reaction of [^{15}NO][BF_4] and [PPN][Cl] (PPN = $(Ph_3P)_2N$) (eq 4).

$$[NO][BF_4] + [PPN][Cl] \rightarrow ClNO + [PPN][BF_4] \quad (4)$$

To our knowledge no report of ClNO being generated in this fashion exists. When CH_2Cl_2 is added to an intimate mixture of [NO][BF_4] and [PPN][Cl], a yellow solution immediately results. Solution IR spectroscopy of this solution reveals the presence of a strong ν(NO) vibration at 1847 cm^{-1}, identical to that of authentic ClNO in CH_2Cl_2.[38] When [NO][BF_4] is replaced by [^{15}NO][BF_4], the IR spectrum that results has a ν(NO) peak at 1814 cm^{-1}, as expected for isotopic substitution of ^{14}N with ^{15}N. It may also be noted that another route for the formation of $Cl^{15}NO$ involves the reaction of [PPN][$^{15}NO_2$] with 2 equiv of Bu_3SiCl.[39]

Reactions of (trimpsi)M$(CO)_2$(NO) (M = V, Nb, Ta) with ClNO. Reaction of (trimpsi)V$(CO)_2$(NO) with 1 equiv of ClNO at −78 °C results in a color change from red to yellow and the evolution of a gas. Solution IR spectroscopy reveals the presence of the starting material and **1** (Scheme 1). Addition of a further equivalent of ClNO consumes the remaining (trimpsi)V$(CO)_2$(NO). When generated in this fashion, **1** can be isolated from the final reaction mixture in 33% yield. Two observations suggest that the transformation of (trimpsi)V$(CO)_2$(NO) to **1** does not proceed through a dinitrosyl intermediate. First, when only 1 equiv of ClNO is added to a solution of (trimpsi)V$(CO)_2$(NO), starting material is still present in solution as determined by IR spectroscopy. Second, when 2 equiv of $Cl^{15}NO$ is reacted with the vanadium carbonyl precursor, no evidence for the incorporation of a labeled nitrosyl ligand is provided by either IR spectroscopy or mass spectrometry. If (trimpsi)V(^{14}NO)(^{15}NO)Cl were an intermediate during the formation of **1**, then an equal distribution of (trimpsi)V(^{14}NO)Cl_2 and (trimpsi)V(^{15}NO)Cl_2 should result, assuming a negligible isotope effect. However, this distribution is not observed experimentally.

Reaction of (trimpsi)Nb$(CO)_2$(NO) with 1 equiv of ClNO at −78 °C results in a color change from maroon to olive green along with the evolution of CO (Scheme 1). An IR spectrum of the final solution reveals the presence of two strong absorptions at 1624 and 1529 cm^{-1} which are assigned as the ν(NO) vibrations of (trimpsi)Nb$(NO)_2$Cl (**6**). Upon warming the solution to room temperature, a striking color change from green to pale orange occurs along with the formation of a pale yellow precipitate (eq 5). An IR spectrum of the supernatant solution contains no features attributable to ν(NO) vibrations. The related (trimpsi)Ta$(CO)_2$(NO) reacts with ClNO in the same fashion at −78 °C to give an orange solution (Scheme 1). An IR spectrum of this solution reveals the presence of two strong absorptions at 1605 and 1515 cm^{-1} which are attributed to the ν(NO) vibrations of



(5)

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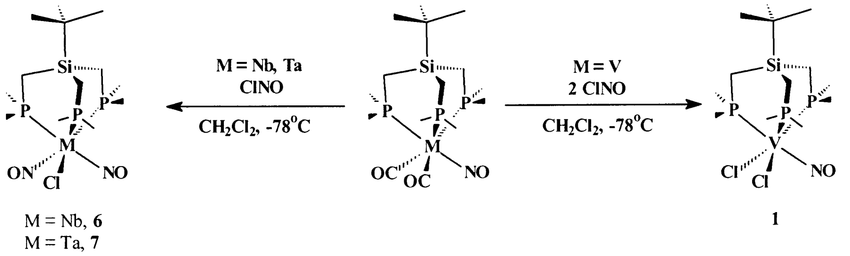
Scheme 1



(trimpsi)Ta(NO)$_2$Cl (**7**). No color change occurs upon warming of this solution, but a pale yellow precipitate is deposited (eq 5). Solution IR spectroscopy reveals a gradual diminution of the ν(NO) peaks, but at a much slower rate than that observed for **6**. Regrettably, all attempts to isolate **6** and **7** have so far been unsuccessful. However, analysis of the headspace above the two room-temperature solutions by GC/MS reveals the presence of N_2O (eq 5).

The interaction of early-metal complexes with NO frequently results in the formation of N_2O.[40,41] These reactions are often presumed to proceed via unobserved nitrosyl intermediates. In this instance, however, the nitrosyl intermediates are stable enough to be detected spectroscopically. The same transformation mediated by late transition metals also has precedents in the chemical literature.[42−45]

When (trimpsi)Nb(CO)$_2$(NO) is treated with 1 equiv of Cl^{15}NO in CH_2Cl_2 at −78 °C, an olive-green solution forms. Solution IR spectroscopy shows two ν(NO) bands at 1609 and 1511 cm^{-1}, thereby suggesting the formation of (trimpsi)Nb(^{14}NO)(^{15}NO)Cl. Similarly, (trimpsi)Ta(^{14}NO)(^{15}NO)Cl and (trimpsi)Ta(^{15}NO)$_2$Cl can be formed in an identical fashion from (trimpsi)Ta(CO)$_2$(NO) with corresponding ν(NO) values of 1590 and 1497 cm^{-1}, and 1572 and 1481 cm^{-1}, respectively.

The ^{31}P{^{1}H} NMR spectrum of **6** generated in situ at −45 °C in CD_2Cl_2 shows two broad singlets at −14.6 ppm (1P) and −31.5 ppm (2P), consistent with the proposed formulation. This spectrum is similar to that exhibited by **1** for which the resonance for the phosphine trans to the nitrosyl ligand occurs upfield from the resonance for the phosphine trans to the chloride. Upon warming, the resonances at −14.6 and −31.5 ppm quickly disappear as the complex decomposes. The room-temperature ^{31}P{^{1}H} NMR spectrum of **7** in CD_2Cl_2 consists of a triplet at −19.4 ppm (1P) and a doublet at −33.3 ppm (2P) with identical $^2J_{PP}$ coupling constants of 8.1 Hz. Again, over the course of several hours at room temperature these signals disappear. Finally, the ^{31}P{^{1}H} spectrum of **7**-$^{15}N_2$ at −20 °C in CD_2Cl_2 consists of a pseudoquintet at −19.4 ppm (1P) and a triplet of doublets at −33.3 ppm (2P) with $^2J_{PN}$ coupling constants of 8 and 13 Hz.

At first glance, the differing reactivities of the various (trimpsi)M(CO)$_2$(NO) complexes toward ClNO are a bit perplexing. Since ClNO is in equilibrium with Cl_2 and NO in solutions, our observations would seem to suggest that (trimpsi)V(CO)$_2$(NO) reacts more rapidly with the Cl_2 than with the ClNO present to form **1** as the principal product. Conversely, the niobium and tantalum congeners apparently react preferentially with ClNO to form **6** and **7**, respectively, as the main products. Even though we have previously observed similar chemistry with the isoelectronic Cp*M(CO)$_2$(NO) complexes of the group 6 elements,[29] substantiation of this hypothesis for the group 5 reactants requires additional experimental investigations.

Summary

The oxidation of (trimpsi)V(CO)$_2$(NO) with halogens and halogenating agents such as PhCl$_2$, Br$_2$, or I$_2$, at −78 °C affords the corresponding halo complexes (trimpsi)V(NO)X$_2$ (X = Cl, Br, I) in moderate yields. The oxidation of (trimpsi)M(CO)$_2$(NO) (M = Nb, Ta) with 1 equiv of I$_2$ at −78 °C, followed quickly by the addition of excess PMe$_3$, gives (trimpsi)M(NO)I$_2$(PMe$_3$) in moderate to low yields. The reaction of (trimpsi)V(CO)$_2$(NO) with 2 equiv of ClNO produces (trimpsi)V(NO)Cl$_2$, whereas the analogous reactions of (trimpsi)M(CO)$_2$(NO) (M = Nb, Ta) with 1 equiv of ClNO generate (trimpsi)M(NO)$_2$Cl species which are stable in solution only at low temperatures.

The availability of complexes **1**−**4** represents a unique opportunity to study the chemistry of the nitrosyl ligand when bound to an early transition metal. Specifically, the introduction of new ligands into the metals' coordination spheres via metathesis of the halide ligands of **1**−**4** may yield interesting chemistry. This avenue of investigation will be explored, and its results will be reported in due course. Unfortunately, the low yields of (trimpsi)Ta(NO)I$_2$(PMe$_3$) will limit the development of the corresponding tantalum system. Consequently, our future studies involving nitrosyl complexes of this metal will focus on improving the synthesis of the diiodo complex and on forming (trimpsi)Ta(NO)X$_2$(PMe$_3$) (X = Cl, Br), which may well be isolable in higher yields.

Experimental Section

General Methods. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or in an atmosphere of dinitrogen or argon. General procedures routinely employed in these laboratories have been described in detail previously.[46] Tetrahydrofuran was distilled

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from molten potassium, while dichloromethane, 1,2-dimethoxyethane (DME), and acetonitrile were distilled from calcium hydride. PMe_3 was dried over NaK prior to use, and CD_2Cl_2 was dried over activated 4 Å molecular sieves and degassed prior to use. CD_3CN was distilled from calcium hydride, and THF-d_8 was dried over a potassium mirror prior to use. [NO][BF_4] was purchased from Aldrich and was purified by sublimation under dynamic vacuum before use. The compounds (trimpsi)M$(CO)_2$(NO) (M = V, Nb, Ta),[4] [^{15}NO][BF_4],[47] Diazald-^{15}N,[2] and $PhICl_2$[48] were prepared by published procedures. All other reagents were used as received from commercial sources.

NMR spectra were recorded on Bruker AMX 500, AV 300, or AV 400 instruments. ^{1}H and ^{13}C spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^{1}H NMR) or the characteristic resonances of the solvent nuclei (^{13}C NMR). ^{31}P spectra are referenced to external 85% H_3PO_4. ^{31}P{^{1}H} NMR spectra were simulated using LAOCOON. Where appropriate, NMR spectral assignments were supported by conventional homonuclear and heteronuclear correlation spectroscopy experiments.

Headspace gas analysis was performed using a Carlo Erba Series 4160 gas chromatograph with a Supelco Mol Sieve 5A Plot column coupled to an Kratos MS80 mass spectrometer.

Preparation of Cl^{15}NO. To an intimate mixture of [^{15}NO][BF_4] (0.012 g, 0.10 mmol) and [PPN][Cl] (0.043 g, 0.08 mmol) was added CH_2Cl_2 (5 mL) via syringe. Over the course of 30 min the solution turned pale orange as Cl^{15}NO was formed. Unlabeled ClNO can be prepared similarly. Solutions generated in this fashion were usually cannulated directly into solutions of the starting material. The presence of [PPN][BF_4] in the reaction mixture did not seem to affect the course of the reaction, although if needed ClNO could be vacuum transferred into a new vessel.

Preparation of (trimpsi)V(NO)Cl_2 (1). Method A. To a rapidly stirred solution of (trimpsi)V$(CO)_2$(NO) (2.12 g, 4.7 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added a solution of $PhICl_2$ (1.30 g, 4.7 mmol) in CH_2Cl_2 (20 mL) via a fine-bore cannula. The initially cherry-red solution became orange, and CO gas was evolved. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 18 h. The volume of the final solution was reduced to 10 mL under reduced pressure, and the flask was then cooled to −30 °C overnight. The large mass of yellow crystals of **1** (1.31 g, 60% yield) was collected by filtration and dried for several hours in vacuo. Anal. Calcd for $C_{13}H_{33}Cl_2NOP_3SiV$: C, 33.78; H, 7.20; N, 3.03. Found: C, 33.66; H, 7.04; N, 3.05. IR (Nujol): ν(NO) 1601 (s) cm^{-1}. NMR data: ^{1}H (CD_2Cl_2, 500 MHz, 25 °C) δ 0.42 (d, J_{PH} = 8.9 Hz, CH_2), 0.90 (s, CMe_3), 0.96 (m, 2 CH), 1.03 (d, J_{PH} = 6.3 Hz, PMe_2), 1.22 (m, 2 CH), 1.68 (vt, J_{PH} = 4.7 Hz, 2 PMe), 1.89 (vt, J_{PH} = 4.2 Hz, 2 PMe); ^{1}H{^{31}P} (CD_2Cl_2, 500 MHz, 25 °C) δ 0.42 (s, CH_2), 0.90 (s, CMe_3), 0.96 (d, J_{HH} = 14.7 Hz, 2 CH), 1.03 (s, PMe_2), 1.22 (d, J_{HH} = 14.7 Hz, 2 CH), 1.68 (s, 2 PMe), 1.89 (s, 2 PMe); ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz, 25 °C) δ 7.3 (d, J_{CP} = 6.3 Hz, CH_2), 8.9 (s, 2 CH_2), 15.7 (m, PMe_2), 17.1 (m, *C*Me_3), 23.7 (d, J_{CP} = 12.5 Hz, 2 PMe), 23.9 (d, J_{CP} = 12.5 Hz, 2 PMe), 25.6 (s, C*Me*$_3$); ^{31}P{^{1}H} (CD_2Cl_2, 202 MHz, 25 °C) δ −24.5 (br s, 1P), −0.1 (br s, 2P). MS (EI, 250 °C) *m*/*z*, 431 [P$^+$ − NO].

Method B. To a solution of (trimpsi)V$(CO)_2$(NO) (0.090 g, 0.20 mmol) in CH_2Cl_2 (20 mL) at −78 °C was added AgCl (0.113 g, 0.79 mmol) via a powder funnel. Upon warming of the mixture, gas evolution occurred, the color changed from cherry red to yellow, and a brown precipitate formed. The final mixture was filtered through Celite (2 cm × 2 cm) on a medium porosity frit. The volume of the filtrate was reduced to 5 mL in vacuo, and the flask was cooled to −30 °C overnight to induce the deposition of yellow crystals of **1** (0.047 g, 51% yield).

Method C. A red CH_2Cl_2 (20 mL) solution of (trimpsi)V$(CO)_2$(NO) (0.102 g, 0.23 mmol) and C_2Cl_6 (0.054 g, 0.23 mmol) was refluxed for 3 h to obtain a clear yellow solution. The volume of the solution was reduced to 5 mL in vacuo, and the flask was cooled to −30 °C overnight to induce the deposition of yellow crystals (0.036 g, 37% yield).

Method D. To a solution of (trimpsi)V$(CO)_2$(NO) (0.104 g, 0.23 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added ClNO (1.4 M CH_2Cl_2 solution, 0.35 mL, 0.49 mmol). Upon warming of the mixture, gas evolution occurred, the color changed from cherry red to yellow, and a small amount of a white precipitate formed. The mixture was filtered through Celite (2 cm × 2 cm) on a medium porosity frit. The volume of the filtrate was reduced to 5 mL in vacuo, and cooling of the flask to −30 °C overnight resulted in the deposition of yellow crystals of **1** (0.035 g, 33% yield).

Preparation of (trimpsi)V(NO)Br_2 (2). To a stirred solution of (trimpsi)V$(CO)_2$(NO) (0.90 g, 2.1 mmol) in CH_2Cl_2 (15 mL) at −78 °C was added a solution of Br_2 (5.5 mL, 0.43 M CH_2Cl_2 solution, 2.4 mmol) via a fine-bore cannula. The initially cherry-red solution became orange, and CO gas evolution occurred. The reaction mixture was warmed to room temperature and was stirred for an additional 20 min. The volume of the final solution was reduced to 10 mL in vacuo, and pentane (5 mL) was syringed into the solution. The flask was then cooled to −30 °C overnight to induce the formation of yellow crystals which were collected by filtration and dried under vacuum (0.92 g, 82% yield). These crystals were recrystallized from CH_2Cl_2/hexanes to obtain analytically pure **2**. Anal. Calcd for $C_{13}H_{33}Br_2NOP_3SiV$: C, 28.33; H, 6.03; N, 2.54. Found: C, 28.51; H, 5.96; N, 2.50. IR (Nujol): ν(NO) 1589 (s) cm^{-1}. NMR data: ^{1}H ($CDCl_3$, 500 MHz, 25 °C) δ 0.48 (d, J_{PH} = 8.8 Hz, CH_2), 0.90 (s, CMe_3), 0.98 (m, 2 CH), 1.19 (d, J_{PH} = 6.2 Hz, PMe_2), 1.21 (m, 2 CH), 1.75 (vt, J_{PH} = 4.4 Hz, 2 PMe), 1.86 (vt, J_{PH} = 4.0 Hz, 2 PMe); ^{1}H{^{31}P} ($CDCl_3$, 500 MHz, 25 °C) δ 0.48 (s, CH_2), 0.90 (s, CMe_3), 0.98 (d, J_{HH} = 14.7 Hz, 2 CH), 1.19 (s, PMe_2), 1.20 (d, J_{HH} = 14.7 Hz, 2 CH), 1.75 (s, 2 PMe), 1.86 (s, 2 PMe); ^{13}C{^{1}H} ($CDCl_3$, 125 MHz, 25 °C) δ 7.0 (d, J_{CP} = 6.4 Hz, CH_2), 8.5 (s, 2 CH_2), 15.8 (m, *C*Me_3), 17.2 (d, J_{CP} = 12.5 Hz, PMe_2), 25.6 (s, C*Me*$_3$), 26.2 (d, J_{CP} = 12.9 Hz, 2 PMe), 26.3 (d, J_{CP} = 12.9 Hz, 2 PMe); ^{31}P{^{1}H} ($CDCl_3$, 202 MHz, 25 °C) δ −26.1 (br s, 1P), −1.7 (br s, 2P). MS (EI, 300 °C) *m*/*z*, 521 [P$^+$ − NO].

Preparation of (trimpsi)V(NO)I_2 as Its THF solvate (3·THF). To a rapidly stirred solution of (trimpsi)V$(CO)_2$(NO) (0.144 g, 0.32 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added a solution of I_2 (5.0 mL, 0.06 M CH_2Cl_2 solution, 0.30 mmol) via a fine-bore cannula. The initially cherry-red solution became deep purple, and CO gas evolution occurred. The reaction mixture was warmed to room temperature and was stirred for an additional 30 min. The purple mixture was filtered through a plug of Celite (3 × 1 cm) supported on a medium porosity frit which was subsequently washed with CH_2Cl_2 (10 mL). Solvent was removed from the combined filtrates in vacuo, and the solid residue was taken into the glovebox. THF (5 mL) was pipetted onto the solid, and the resulting purple solution was filtered into a small vial through a plug of Celite (2 × 0.5 cm) supported by glass wool in a pipet. Hexanes (0.5 mL) were layered on top of the THF solution, and the vial was cooled to −35 °C overnight, whereupon a purple powder deposited (0.068 g, 29% yield). The powder was doubly

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recrystallized from THF/hexanes to obtain analytically pure **3**·THF. Anal. Calcd for $C_{13}H_{33}I_2NOP_3SiV \cdot C_4H_8O$: C, 28.47; H, 5.76; N, 1.95. Found: C, 28.43; H, 5.77; N, 1.92. IR (Nujol): ν(NO) 1607 (s) cm^{-1}. NMR data: ^1H (CD_2Cl_2, 500 MHz, 25 °C) δ 0.71 (d, $J_{PH} = 9.2$ Hz, CH_2), 0.93 (s, CMe_3), 1.02 (m, 2 CH), 1.20 (m, 2 CH), 1.45 (d, $J_{PH} = 6.2$ Hz, PMe_2), 1.74 (vt, $J_{PH} = 4.2$ Hz, 2 PMe), 1.78 (vt, $J_{PH} = 4.4$ Hz, 2 PMe); $^1H\{^{31}P\}$ (CD_2Cl_2, 500 MHz, 25 °C) δ 0.71 (s, CH_2), 0.93 (s, CMe_3), 1.02 (d, $J_{HH} = 14.5$ Hz, 2 CH), 1.20 (d, $J_{HH} = 14.6$ Hz, 2 CH), 1.45 (s, PMe_2), 1.74 (s, 2 PMe), 1.78 (s, 2 PMe); $^{13}C\{^1H\}$ (CD_3CN, 125 MHz, 25 °C) δ 6.4 (br s, CH_2), 7.4 (s, 2 CH_2), 15.8 (m, *C*Me$_3$), 20.5 (d, $J_{CP} = 12.5$ Hz, PMe_2), 25.7 (s, C*Me*$_3$), 29.8 (d, $J_{CP} = 12.5$ Hz, 2 PMe), 29.9 (d, $J_{CP} = 12.5$ Hz, 2 PMe); $^{31}P\{^1H\}$ (CD_2Cl_2, 202 MHz, 25 °C) δ −23.4 (br s, 1P), 1.0 (br s, 2P). MS (EI, 150 °C) *m*/*z*, 645 [P$^+$].

Preparation of (trimpsi)Nb(NO)I_2(PMe_3) (4). To a rapidly stirred solution of (trimpsi)Nb$(CO)_2$NO (0.205 g, 0.42 mmol) in CH_2Cl_2 (25 mL) at −78 °C was quickly added a solution of I_2 (0.106 g, 0.42 mmol) in CH_2Cl_2 (10 mL). The initially maroon solution became orange-brown, and CO gas was evolved. After 20 s, PMe_3 (0.3 mL, 2.9 mmol) was added via syringe, and the stirred solution was allowed to warm to room temperature. After being stirred for 30 min, the solvent was removed in vacuo, the remaining yellow-orange powder was dissolved in THF (10 mL), and the solution was filtered through a plug of Celite (2 × 2 cm). The Celite was rinsed with THF (5 mL), and the combined filtrates were concentrated under reduced pressure and were layered with hexanes (5 mL). The final mixture was cooled to −30 °C for 24 h, whereupon **4** deposited as an analytically pure orange powder (0.207 g, 64% yield) Anal. Calcd for $C_{16}H_{42}I_2NNbOP_4Si$: C, 25.18; H, 5.55; N, 1.84. Found: C, 25.11; H, 5.08; N, 1.91. IR (KBr): ν(NO) 1467 (s) cm^{-1}. NMR: ^1H (CD_2Cl_2, 500 MHz, 25 °C) δ 0.78 (d, $J_{PH} = 10.3$ Hz, CH_2), 0.85 (s overlapping m, CMe_3 and 2CH, 11H), 1.50 (vr t, 2PMe, 6H), 1.52 (vr t, 2PMe, 6H), 1.55 (d overlapping m, $J_{PH} = 9.0$ Hz, PMe_3 and 2CH, 11H), 1.90 (d, $J_{PH} = 7.0$ Hz, PMe_2, 6H); $^1H\{^{31}P\}$ (CD_2Cl_2, 500 MHz, 25 °C) δ 0.78 (s, CH_2), 0.85 (s overlapping d, CMe_3 and 2CH, 11H), 1.51 (s, 2PMe), 1.52 (s, 2PMe), 1.55 (s overlapping d, PMe_3 and 2CH, 11H), 1.90 (s, PMe_2); $^{31}P\{^1H\}$ (CD_2Cl_2, 202 MHz, 25 °C) δ −10.1 (br s, 2P), −14.7 (br s, 1P), −45.7 (br s, 1P); $^{13}C\{^1H\}$ (CD_2Cl_2, 125 MHz, 25 °C) δ 4.9 (br s, CH_2), 9.3 (d, $J_{PC} = 3.0$ Hz, 2CH_2), 16.4 (d, $J_{PC} = 26.2$ Hz, PMe_3), 19.0 (m, 2PMe), 20.4 (m, 2PMe), 26.5 (d of t, $J_{PC} = 14.8$ Hz, 3.8 Hz, PMe_2), 27.5 (s, C*Me*$_3$), signal for the quaternary carbon of the *tert*-butyl ligand was not found. MS (LSIMS, thioglycerol matrix, 150 °C) *m*/*z*, 687 [P$^+$ − PMe_3].

Preparation of (trimpsi)Ta(NO)I_2(PMe_3) (5). To a rapidly stirred solution of (trimpsi)Ta$(CO)_2$(NO) (0.211 g, 0.37 mmol) in CH_2Cl_2 (15 mL) at −78 °C was added a solution of I_2 (0.093 g, 0.37 mmol) dissolved in CH_2Cl_2 (15 mL). The initially maroon solution became orange-brown as CO gas was evolved. After 20 s, PMe_3 (0.2 mL, 1.9 mmol) was added via syringe, and the stirred mixture was allowed to warm to room temperature. After being stirred for 30 min, the solvent was removed in vacuo, and the remaining powder was dissolved in THF (2 mL) and the solution was filtered through a plug of Celite (0.5 cm × 2 cm). The orange filtrate was then layered with hexanes (2 mL). Storage of this mixture at −30 °C for 24 h resulted in the deposition of **5** as orange crystals (0.015 g) and a pale yellow powder. The powder remained suspended in the solution and could be separated from the crystalline product by decanting of the mother liquor. Recooling the decanted solution to −30 °C for several days provided a second crop of crystals (0.015 g) and additional yellow powder. Total yield: 0.030 g, 10%. Anal. Calcd for $C_{16}H_{42}I_2NTaOP_4Si$: C, 22.58; H, 4.97; N, 1.65. Found: C, 23.75; H, 5.01; N, 1.54. IR (KBr): ν(NO) 1450 (s) cm^{-1}. NMR: ^1H (THF-*d*$_8$, 500 MHz, 25 °C) δ 0.88 (s, CMe_3), 0.98 (d, $J_{PH} = 10.5$ Hz, CH_2), 1.04 (m, 2CH), 1.56 (br s overlapping d, 4PMe and PMe_3, 21H), 1.68 (m, 2CH), 1.99 (d, $J_{PH} = 7.0$ Hz, PMe_2, 6H); $^1H\{^{31}P\}$ (THF-*d*$_8$, 500 MHz, 25 °C) δ 0.88 (s, CMe_3), 0.98 (s, CH_2), 1.04 (d, $J_{HH} = 12.0$ Hz, 2CH), 1.56 (s, PMe_3), 1.57 (s, 4PMe), 1.68 (d, $J_{HH} = 13.7$ Hz, 2CH), 1.99 (s, PMe_2, 6H); $^{31}P\{^1H\}$ (THF-*d*$_8$, 202 MHz, 25 °C) δ −15.9 (m, 3P), −54.0 (m, 1P); $^{13}C\{1H\}$ (THF-*h*$_8$/C_6D_6, 125 MHz, −20 °C) δ 3.6 (br s, CH_2), 7.5 (br s, 2CH_2), 14.8 (br s, 2PMe), 15.5 (d, $J_{PC} = 20$ Hz, PMe_3), 17.4 (br s, 2PMe), 24.9 (s, C*Me*$_3$). Signal for one 2PMe resonance obscured by solvent peak at 15.8; signal for the quaternary carbon of the *tert*-butyl was not found. MS (EI, 150 °C) *m*/*z*, 776 [P$^+$ − PMe_3].

Preparation of (trimpsi)Nb$(NO)_2$Cl (6). To a rapidly stirred solution of (trimpsi)Nb$(CO)_2$(NO) (0.226 g, 0.46 mmol) in CH_2Cl_2 (10 mL) at −78 °C was quickly added a solution of ClNO (0.54 M CH_2Cl_2 solution, 0.85 mL, 0.46 mmol). Gas was evolved, the solution quickly turned deep green, and a green powder was deposited. The solution was separated from the powder by filter cannulation. The green powder was dried in vacuo. All manipulations of the powder were performed at temperatures below −30 °C. If the temperature was allowed to rise above 0 °C, the green powder quickly turned brown. Due to the thermally sensitive nature of this material, neither a combustion analysis nor a yield could be obtained. IR (CH_2Cl_2): ν(NO) 1624 (s), 1529 (s) cm^{-1}. NMR: $^{31}P\{^1H\}$ (CD_2Cl_2, 202 MHz, −45 °C) δ −14.6 (s, 1P), −31.5 (s, 2P). IR for (trimpsi)Nb(^{14}NO)(^{15}NO)Cl (in CH_2Cl_2): ν(NO) 1609 (s), 1511 (s) cm^{-1}.

Preparation of (trimpsi)Ta$(NO)_2$Cl (7). To a rapidly stirred solution of (trimpsi)Ta$(CO)_2$(NO) (0.213 g, 0.37 mmol) in CH_2Cl_2 (10 mL) at −78 °C was quickly added a solution of ClNO (0.54 M CH_2Cl_2 solution, 0.90 mL, 0.47 mmol). Gas was evolved, and the solution quickly turned orange. Addition of pentane (10 mL) by syringe into the solution caused the deposition of an orange powder. The solution was separated from the powder by filter cannulation, and the powder was dried in vacuo. All manipulations of this powder (**7**) were performed at temperatures below −30 °C. IR (CH_2Cl_2): ν(NO) 1605 (s), 1515 (s) cm^{-1}. NMR: $^{31}P\{^1H\}$ (CD_2Cl_2, 202 MHz, 25 °C) δ −19.4 (t, $J = 8.1$ Hz, 1P), −33.3 (d, $J = 8.1$ Hz, 2P). IR for (trimpsi)Ta(^{14}NO)(^{15}NO)Cl (in CH_2Cl_2): ν(NO) 1590 (s), 1497 (s) cm^{-1}. IR for (trimpsi)Ta$(^{15}NO)_2$Cl (in CH_2Cl_2): ν(NO) 1572 (s), 1481 (s) cm^{-1}.

X-ray Crystallography. Data collection for each structure was carried out on a Rigaku/ADSC CCD diffractometer using graphite-monochromated Mo Kα radiation. Data collection for **1**·3CH_2Cl_2 and **4**·(3/4)CH_2Cl_2 was carried out at −100 ± 1 °C, while data collection for **5**·THF was done at −75 ± 1 °C.

Data for **1**·3CH_2Cl_2 were collected to a maximum 2θ value of 55.9° in 0.50° oscillations with 58.0 s exposures. The solid-state structure of **1**·3CH_2Cl_2 was solved by direct methods[49] and expanded using Fourier techniques.[50] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The material crystallizes with three molecules of CH_2Cl_2 in the asymmetric unit. The lone nitrosyl ligand appears to be disordered about three sites, with relative occupancies of 0.68, 0.21, and 0.11. The two chloride ligands are distributed over the same

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Table 4. X-ray Crystallographic Data for Complexes **1**·3CH$_2$Cl$_2$, **4**·(3/4)CH$_2$Cl$_2$, and **5**·THF

	1·3CH$_2$Cl$_2$	**4**·(3/4)CH$_2$Cl$_2$	**5**·THF
Crystal Data			
empirical formula	$C_{16}H_{39}Cl_8NOP_3SiV$	$C_{16.75}H_{43.5}Cl_{1.5}I_2NNbOP_4Si$	$C_{20}H_{50}I_2NO_2P_4SiTa$
crystal habit, color	irregular, orange	platelet, orange	platelet, orange
crystal size (mm)	0.30 × 0.20 × 0.12	0.20 × 0.20 × 0.05	0.25 × 0.10 × 0.04
crystal system	orthorhombic	triclinic	orthorhombic
space group	$Pna2_1$	$P\bar{1}$	Pbca
volume (Å^3)	3308.2(3)	3115.0(2)	6693.0(5)
a^a (Å)	18.2473(7)	14.2119(5)	14.9001(5)
b (Å)	9.263(1)	14.5235(6)	19.9581(8)
c (Å)	19.573(1)	15.5987(5)	22.507(2)
α (deg)	90	80.438(1)	90
β (deg)	90	78.926(1)	90
γ (deg)	90	89.433(2)	90
Z	4	4	8
fw (g/mol)	717.02	826.91	923.36
ρ_{calcd} (mg/m^3)	1.440	1.763	1.833
abs coeff (cm^{-1})	11.0	27.52	53.69
F_{000}	1472	1622	3568
radiation	Mo Kα, 0.710 69 Å	Mo Kα, 0.710 69 Å	Mo Kα, 0.710 69 Å
Data Refinement			
final R indices^b	$R_1 = 0.052$, wR$_2 = 0.111$	$R_1 = 0.055$, wR$_2 = 0.090$	$R_1 = 0.064$, wR$_2 = 0.085$
GOF on $F^{2\ c}$	1.15	1.07	0.75
largest diff peak and hole (e Å^{-3})	0.57 and −0.49	2.56 and −2.07	1.51 and −2.05

[a] Cell dimensions based on the following: **1**·3CH$_2$Cl$_2$, 13 912 reflections, 5.6° $\leq 2\theta \leq$ 55.9°; **4**·(3/4)CH$_2$Cl$_2$, 15 747 reflections, 5.6° $< 2\theta <$ 55.8°; **5**·THF, 5847 reflections, 5.5° $\leq 2\theta \leq$ 53.5°. [b] Number of observed reflections: **1**·3CH$_2$Cl$_2$, 5729 ($I_o > 2\sigma I_o$); **4**·(3/4)CH$_2$Cl$_2$, 8925 ($I_o > 3\sigma I_o$); **5**·THF, 3373 ($I_o > 3\sigma I_o$). R_1: **1**·3CH$_2$Cl$_2$, **4**·(3/4)CH$_2$Cl$_2$, and **5**·THF, $R_1 = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. wR$_2$: **1**·3CH$_2Cl_2$, wR$_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum wF_o^4]^{1/2}$; **4**·(3/4)CH$_2Cl_2$ and **5**·THF, wR$_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum wF_o^4]^{1/2}$. w: **1**·3CH$_2Cl_2$, $w = [\sigma^2 F_o]^{-1}$; **4**·(3/4)CH$_2$Cl$_2$ and **5**·THF, $w = [\sigma^2 F_o^2]^{-1}$. [c] GOF $= [\sum(w(F_o^2 - F_c^2|)^2)/$degrees of freedom$]^{1/2}$.

three sites with relative occupancies of 0.32, 0.79, and 0.89. Constraints were employed to make all V−Cl distances roughly equivalent. The same was done for all V−N and N−O distances. Lastly, the anisotropic displacement parameters for all three chloride ligands were made equivalent, as were the anisotropic displacement parameters of the disordered nitrosyl ligand. The final cycle of full-matrix least-squares refinement was based on 5823 observed reflections and 289 variable parameters.

Data for **4**·(3/4)CH$_2$Cl$_2$ were collected to a maximum 2θ value of 55.8° in 0.50° oscillations with 23.0 s exposures. The solid-state structure of **4**·(3/4)CH$_2$Cl$_2$ was solved by direct methods[49] and expanded using Fourier techniques.[50] The material crystallizes with two independent molecules in the asymmetric unit, in addition to 1.5 molecules of CH$_2$Cl$_2$. One CH$_2$Cl$_2$, disordered about an inversion center, was 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 12 717 observed reflections and 508 variable parameters.

For **5**·THF, the data were collected to a maximum 2θ value of 53.5° in 0.50° oscillations with 50.0 s exposures. The solid-state structure of **5**·THF was solved by heavy-atom Patterson methods[51] and expanded using Fourier techniques.[50] The material crystallizes with one disordered molecule of THF in the asymmetric unit. This THF molecule was modeled in two orientations and then left in fixed positions. Hydrogen atoms were not included on the carbons of the THF molecule. Other hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 6662 observed reflections and 235 variable parameters.

For all three structure solutions and refinements, neutral atom scattering factors were taken from Cromer and Waber.[52] Anomalous dispersion effects were included in F_{calc};[53] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[54] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[55] All data sets were corrected for Lorentz and polarization effects. All calculations were performed using the teXsan[56] crystallographic software package of Molecular Structure Corporation and/or SHELXL97.[57] X-ray crystallographic data for all five complexesare collected in Table 4, and full details of all crystallographic analyses are provided as Supporting Information.

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Supporting Information Available: Listings of crystallographic information, atomic coordinates and B_{eq} values, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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