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THE NATURE OF THE BRIDGING NITRIDO LIGAND. SYNTHESIS AND REACTIVITY OF HETEROBIMETALLIC NITRIDO-BRIDGED COMPOUNDS*

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Abstract—Heterobimetallic nitrido-bridged compounds $(R_3SiO)_3V{\equiv}N{-}M(CO)(PPh_3)_2$ (R = Me or Et and M = Ir or Rh) and $(Me_3SiO)_3V{\equiv}N{-}Rh(PPh_3)_3$ have been synthesized by condensation reactions between vanadium silylimido compounds, $V(NSiR_3)(OSiR_3)_3$, and group VIII metal fluorides, $MF(L)(PPh_3)_2$. Oxidative addition of small molecules (MeI, O_2, H_2) to the iridium(I) of $(R_3SiO)_3V{\equiv}N{-}Ir(CO)(PPh_3)_2$ occurs, producing iridium(III) compounds in which the $V{\equiv}N{-}Ir$ interaction is retained. In contrast, however, the nitrido linkages in $(Me_3SiO)_3V{\equiv}N{-}M(L)(PPh_3)_2$ are readily cleaved by silylating reagents ($ClSiMe_3$, $ClSiEt_3$, $HSiEt_3$), producing $V(NSiR_3)(OSiMe_3)_3$ and a group VIII metal chloride or hydride product. Comparison of the reactivity and spectroscopic data among the nitrido-bridged compounds and with related iridium(I) and rhodium(I) complexes suggests that the nitrido-bridged compounds are best viewed as adducts in which anionic $[(R_3SiO)_3V{\equiv}N{:}]^-$ acts as a simple two-electron donor to the 14-electron cationic $[M(L)(PPh)_2]^+$ fragment.

The nitride ion, N^{3-}, is a simple ligand that can be incorporated into a variety of environments in transition-metal compounds. It forms short, strong triple bonds to metals as a terminal ligand,[1–4] can bridge two or more centers in multimetallic or cluster compounds,[1–5] and acts as an interstitial atom in solid state metal nitrides.[6] Our interest in the nitride ion arises, in part, from our search for a bridging ligand to link transition-metal centers in new polymeric materials.[7] This has led us to prepare and study a series of dinuclear nitrido-bridged compounds as models for understanding the nature of the bridging nitrido ligand.[8–12] Our approach has involved the systematic study of the synthesis, reactivity, and spectroscopy of these species of which there are now several homobimetallic and heterobimetallic examples.

The diverse synthetic methods used to prepare the nitrido-bridged compounds reported in the literature[3] do not appear to be easily generalized to allow variation of the metal, its oxidation state, or its ligand environment. Consequently, our research has focused on developing a rational and versatile synthesis of M(N)M species using a condensation reaction between silylimido compounds and metal halides (eq. 1).[7–10]

$$L_nM(NSiR_3)+XM'L'_n \rightarrow L_nM(N)M'L'_n+XSiR_3 \qquad (1)$$

We report here the synthesis and study of a series of heterobimetallic nitrido-bridged compounds prepared by condensation reactions between vanadium(V) silylimidos and iridium(I) or rhodium(I) fluorides. We chose to begin our study of the condensation reaction (eq. 1) using the previously reported $V(NSiMe_3)(OSiMe_3)_3$,[13,14] because it can be prepared in good yield from readily available starting materials.[13–15] Similarly, the iridium(I) and rhodium(I) Vaska's fluoride derivatives that

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*Dedicated to Professor John E. Bercaw on the occasion of his 50th birthday.

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we have used are readily synthesized[16,17] and are rare examples of well-characterized fluoride complexes.[18] Furthermore, because compounds of the type $MX(L)(PPh_3)_2$ (M = Ir or Rh) have been extensively studied,[19] we have been able to use the information available in the literature to interpret the chemical and spectroscopic features of nitrido-bridged compounds derived from these starting materials.

RESULTS

Syntheses

Tris(trimethylsiloxy)trimethylsilylimidovanadium, $V(NSiMe_3)(OSiMe_3)_3$ (**1a**), reacts cleanly and quantitatively with square-planar group VIII metal fluoride compounds, $MF(L)(PPh_3)_2$, to yield the heterobimetallic nitrido-bridged compounds, $(Me_3SiO)_3V{\equiv}N{-}Ir(CO)(PPh_3)_2$ (**2a**), $(Me_3SiO)_3V{\equiv}N{-}Rh(CO)(PPh_3)_2$ (**3a**), and $(Me_3SiO)_3V{\equiv}N{-}Rh(PPh_3)_3$ (**4**), plus one equivalent of fluorotrimethylsilane (eq. 2).

1a, R = Me

1b, R = Et

2a, R = Me, M = Ir, L = CO
3a, R = Me, M = Rh, L = CO
4, R = Me, M = Rh, L = PPh₃
2b, R = Et, M = Ir, L = CO
3b, R = Et, M = Rh, L = CO

Analogous triethylsiloxy-substituted nitrido-bridged compounds, $(Et_3SiO)_3V{\equiv}N{-}M(CO)(PPh_3)_2$ (M = Ir, **2b**; Rh, **3b**), are prepared starting from $V(NSiEt_3)(OSiEt_3)_3$ (**1b**) (eq. 2). Compounds **2**–**4** range in color from bright yellow (**3**) through orange (**2**) to brick red (**4**). These compounds are soluble in aromatic solvents and tetrahydrofuran, forming solutions that are stable indefinitely at room temperature; soluble in chlorocarbons and acetonitrile, but undergoing slow decomposition in these solvents at room temperature; and sparingly soluble in pentane from which they can be recrystallized.

The vanadium trialkylsilylimido starting materials (**1**) are readily synthesized by the reaction of ammonium metavanadate with two equivalents of the hexaalkyldisilazane[13] in the presence of a small amount of N,N-dimethylacetamide,[15] which facilitates trialkylsilyl transfer (eq. 3).

$$NH_4VO_3 + 2\,NH(SiR_3)_2 \xrightarrow{MeC(O)NMe_2} V(NSiR_3)(OSiR_3)_3 + 2\,NH_3 \quad (3)$$

$$\mathbf{1a}, R = Me$$

$$\mathbf{1b}, R = Et$$

Compound **1a** is isolated as a yellow crystalline solid; **1b** is a green waxy solid. The vanadium oxo compounds, $V(O)(OSiR_3)_3$[20] (R = Me, Et), are isolated as byproducts of reaction 3.

The metal fluorides were prepared by the reaction of tris(dimethylamino)sulfonium difluorotrimethylsiliconate, $[(Me_2N)_3S](F_2SiMe_3)$ (TASF),[21] with the corresponding metal chlorides[22] in tetrahydrofuran and are isolated as yellow crystalline solids in good yields. The identity of the fluoride reagent used to synthesize $MF(L)(PPh_3)_2$ is important in determining the ease of the condensation reactions shown in eq. 2. For example, when $IrF(CO)(PPh_3)_2$ is prepared with TASF as the source of the fluoride, its reaction with **1a** is extremely fast, requiring only minutes at room temperature in benzene. In contrast, when $IrF(CO)(PPh_3)_2$ is prepared using AgF, reaction with **1a** in benzene is significantly slower, requiring up to several days to reach completion at room temperature.[23]

The iridium nitrido-bridged compound **2a** is also formed in good yield by the reaction of **1a** with an iridium methoxide, $Ir(OMe)(CO)(PPh_3)_2$,[24] releasing the silyl ether $MeOSiMe_3$. Similarly, the rhodium derivative **3a** is generated in high yield by the reaction of **1a** with a rhodium acetate, $Rh(O_2CMe)(CO)(PPh_3)_2$,[25] producing $MeCOOSiMe_3$. In contrast, no reaction is observed between **1a** and $MCl(CO)(PPh_3)_2$ (M = Ir or Rh), even upon heating for several weeks at 70°C.

Characterization

Multinuclear NMR spectroscopy has proven extremely useful in the characterization of **2**–**4**. ^1H

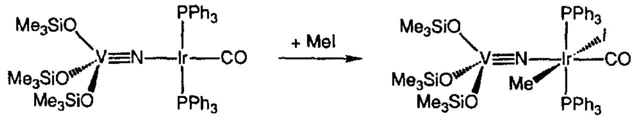
NMR spectra show a single singlet for the three trimethylsiloxy ligands of **2a**, **3a**, and **4** and one set of ethyl resonances for the triethylsiloxy ligands of **2b** and **3b**; typical ^{1}H NMR resonances are observed for the aryl substituents on the triphenylphosphine ligands. The $^{31}P\{^{1}H\}$ NMR spectra for **2**–**3** show one signal between δ 21 and 26 for the two equivalent phosphine ligands *cis* to the tris(trimethylsiloxy)vanadium nitrido group. For **4**, two resonances are observed at δ 25 and 39 in a 2 : 1 ratio for the inequivalent phosphines *cis* and *trans* to the tris(trimethylsiloxy)vanadium nitrido group, respectively. The ^{51}V NMR chemical shifts for **2**–**3** fall in an extremely narrow range $\delta -317$ to -329, whereas **4** appears at $\delta - 163$. Note additionally that the ^{51}V NMR resonances are broad ($\nu_{1/2} = 1400$–2400 Hz) due, in part, to the low symmetry (C_s) of **2**–**4**;[26] unresolved coupling to the ^{14}N nucleus may also contribute to the line width.

The infrared spectra of **2**–**4** are dominated by bands characteristic of the trialkylsiloxy[27] and triphenylphosphine ligands. Additionally, a band near 1095 cm^{-1} in each compound is assigned to $\nu_{V\equiv N}$. In general, metal–nitrogen stretches for terminal nitrido compounds are found in the 950–1135 cm^{-1} range, with 970–1033 cm^{-1} reported for V≡N.[28] The observation of $\nu_{V\equiv N}$ in **2**–**4** at the high end of these ranges is consistent with previous reports that coordination of Lewis acids to triply-bonded metallonitrides shifts the metal–nitrogen stretches to higher frequencies.[29] An intense carbon–oxygen stretching mode is observed in the 1960–1983 cm^{-1} range for **2**–**3** with ν_{CO} for the rhodium compounds at slightly higher frequency than for the iridium compounds, as generally observed in the square-planar $MX(CO)(PPh_3)_2$ system.

The electronic spectra of **2a** and **2b** show four bands in the visible region with energies and intensities that, on comparison to the spectra of **1a** and **1b** (single absorption) and $IrF(CO)(PPh_3)_2$ (three well-defined bands), are consistent with a simple sum of the two chromophores.

Reactivity

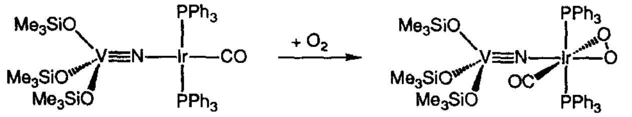
Compound **2a** undergoes oxidative addition reactions with polar and nonpolar reagents at its iridium(I) center to afford vanadium(V)/iridium(III) compounds in which the V≡N—Ir interaction is retained. Methyl iodide reacts with **2a** quantitatively over several days to yield $(Me_3SiO)_3V\equiv N—Ir(Me)(I)(CO)(PPh_3)_2$ (**5**) (eq. 4). Compound **5** has been characterized by NMR and IR spectroscopy. The infrared spectrum of **5** shows a shift of ν_{CO} to higher frequency as expected upon oxidation of iridium(I) to iridium(III). Note that the band for $\nu_{V\equiv N}$ in **5** is at almost the same frequency as in **2a**. Compound **5** displays a single singlet in its $^{31}P\{^{1}H\}$ NMR spectrum and one set of triphenylphosphine resonances and a triplet ($J_{PH} = 5$ Hz) for the methyl group in its ^{1}H NMR spectrum, indicating equivalent and *trans* phosphine ligands at its octahedral iridium(III) center. Of the three possible isomers with *trans* phosphine ligands we favor the one with a *trans* disposition of the methyl and iodide ligands by analogy to the geometry of methyl iodide oxidative addition products derived from $IrCl(CO)(PPh_3)_2$.[30] Surprisingly, the ^{51}V NMR resonance for **5** ($\delta -311$) is near the same narrow chemical shift range observed for **2**–**3**.



(4)

2a **5**

Dioxygen adds to the iridium center of **2a** to produce $(Me_3SiO)_3V\equiv N—Ir(O_2)(CO)(PPh_3)_2$ (**6**)

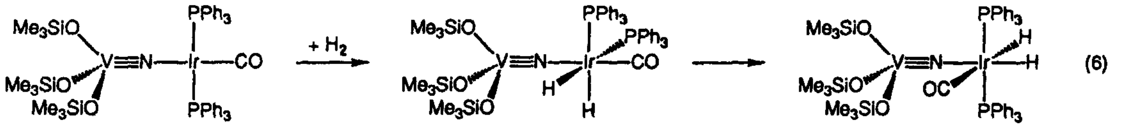


(5)

2a **6**

(eq. 5). *Cis* addition of the reagent is required based on the oxygen–oxygen single bond in the product and the NMR spectra of **6** indicate equivalent phosphine ligands. Therefore, the phosphines must be either *trans* to each other or each *trans* to an oxygen atom. Of these two possibilities, we favor the isomer with *trans* phosphine ligands by analogy to the previously reported dioxygen adducts derived from $IrCl(CO)(PPh_3)_2$.[30]

The oxidative addition of dihydrogen to **2a** initially yields one isomer of $(Me_3SiO)_3V{\equiv}N{-}Ir(H)_2(CO)(PPh_3)_2$ (**7a**) which then converts to a second isomer (**7b**) over a few hours at room temperature (eq. 6).



2a **7a** **7b** (6)

Note that the formation of different kinetic and thermodynamic isomers has been observed in the oxidative addition of H_2 to related iridium(I) compounds.[31]

The ^1H and selectively decoupled ^{31}P NMR spectra of **7a** indicate that this isomer has equivalent phosphine ligands in an AA′XX′ coupling pattern with two hydrides that are observed as a single high-field multiplet. There are two possible isomers for **7** with both the phosphine and hydride ligands equivalent: *cis,cis* and *trans,trans*. The former, in which each hydride is *trans* to a phosphine ligand, is consistent with the AA′XX′ coupling pattern observed.[32] The NMR spectra of **7b** indicate that it has equivalent phosphine ligands coupled to two inequivalent hydrides that appear as two high-field triplets of doublets. Only one isomer of **7** with equivalent phosphine ligands and inequivalent hydrides is possible: **7b** with *trans* phosphine ligands and *cis* hydrides, analogous to the product derived from oxidative addition of dihydrogen to $IrCl(CO)(PPh_3)_2$.[30] Again, the ^{51}V NMR signal for **7b** ($\delta -301$) is very close to the narrow chemical shift range observed for **2**–**3** and **5**.

In contrast to the clean oxidative addition chemistry observed for the iridium system, the rhodium(I) compounds **3a** and **4** do not yield analogous vanadium(V)/rhodium(III) species. Compound **3a** does not react with dihydrogen at room temperature over a period of two weeks, comparable to the lack of reactivity of $RhCl(CO)(PPh_3)_2$ with dihydrogen.[33a] In contrast, reactions between **3a** and methyl iodide, **4** and methyl iodide, and **4** and dihydrogen result in decomposition of the nitrido-bridged compounds, with **1a**, $V(O)(OSiMe_3)_3$, and hexamethyldisiloxane as major products identified by NMR spectroscopy. Our observation of complex reactivity of **3a** and **4** with small molecules is not inconsistent with the reactions of $RhX(CO)(PR_3)_2$ with methyl iodide[33b] and of $RhX(PPh_3)_3$ with methyl iodide[33c] and dihydrogen[33d] which yield products which vary with X and R and which are not always straightforward.

Although **2a** adds dihydrogen to produce vanadium(V)/iridium(III) nitrido-bridged compounds (**7**), triethylsilane reacts with **2a** to cleave the nitrogen–iridium bond forming tris (trimethylsiloxy)triethylsilylimidovanadium, $V(NSiEt_3)(OSiMe_3)_3$ (**1c**), and the known iridium(III) compound $IrH_2(SiEt_3)(CO)(PPh_3)_2$[34] (eq. 7).

$$\underset{\mathbf{2a}}{(Me_3SiO)_3V{\equiv}N{-}Ir(CO)(PPh_3)_2} + HSiEt_3 \rightarrow \underset{\mathbf{1c}}{V(NSiEt_3)(OSiMe_3)_3} + IrH_2(SiEt_3)(CO)(PPh_3)_2 \quad (7)$$

This is analogous to the reaction of $IrCl(CO)(PPh_3)_2$ with $HSiEt_3$, albeit at elevated temperatures, producing chlorotriethylsilane and $IrH_2(SiEt_3)(CO)(PPh_3)_2$.[34]

The silicon–chlorine bonds of chlorotrialkylsilanes also cleanly cleave the nitrogen–iridium or –rhodium bonds of the nitrido-bridged compounds. Chlorotrimethylsilane reacts readily with **2a**, **3a**, and **4** to produce **1a** and the corresponding group VIII metal chloride in high yields (eq. 8).

Similarly, chlorotriethylsilane reacts with **2a** over a period of a day to produce the iridium chloride and **1c** (eq. 8); this provides a means for synthesizing this mixed trialkylsiloxy/silylimido vanadium compound.

Several other reagents cleave the iridium–nitrogen bond of **2a**, however, they also attack the vanadium center, decomposing the tris(tri-

$$(Me_3SiO)_3V{\equiv}N{-}M(L)(PPh_3)_2 + ClSiR_3 \rightarrow V(NSiR_3)(OSiMe_3)_3 + MCl(L)(PPh_3)_2. \quad (8)$$

2a, M = Ir, L = CO	R = Me	**1a**
	R = Et	**1c**
3a, M = Rh, L = CO	R = Me	**1a**
4, M = Rh, L = PPh_3	R = Me	**1a**

methylsiloxy)vanadium nitrido group (cf. the decomposition of **3a** and **4** described above). For example, **2a** reacts with HCl to produce **1a**, $V(O)(OSiMe_3)_3$, and $IrCl(CO)(PPh_3)_2$. Likewise, **2a** reacts with H_2O or MeOH initially producing $V(O)(OSiMe_3)_3$, and ultimately producing a silyl ether, $Me_3SiOSiMe_3$ or $MeOSiMe_3$, respectively, as well as other decomposition products.

The square-planar group VIII metal fluorides, $MF(CO)(PPh_3)_2$, are reported to have ionic character in polar solvents (eq. 9),[35] and stable bis(triphenylphosphine)carbonyliridium cations, $[Ir(L)(CO)(PPh_3)_2]^+$ are readily prepared (eq. 9).[35,36]

$$IrX(CO)(PPh_3)_2 + L \rightleftarrows [Ir(L)(CO)(PPh_3)_2]^+ + X^- \quad (9)$$

The solution conductivity of **2a** suggests that this nitrido-bridged compound has comparable ionic character, undergoing equilibrium dissociation in tetrahydrofuran (eq. 10).

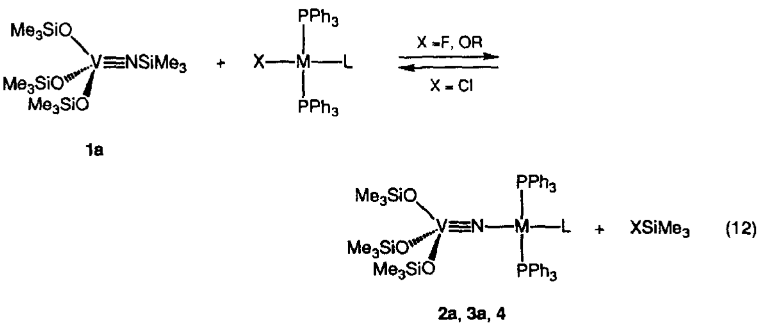
$$\underset{\mathbf{2a}}{(Me_3SiO)_3V{\equiv}N{-}Ir(CO)(PPh_3)_2} + THF \rightleftarrows [V(N)(OSiMe_3)_3]^- + [Ir(THF)(CO)(PPh_3)_2]^+ \quad (10)$$

Conductivity measurements on THF solutions of **2a** are very similar to those of the iridium fluoride in THF solutions of comparable concentrations. In contrast, **1a** has no measurable conductivity in THF, indicating that the ionic species responsible for the conductivity of **2a** do not arise from the trimethylsiloxy ligands. The equilibrium in eq. 10 appears to lie significantly to the left as **2a** is found to be a weak electrolyte.[37] The ionic species in eq. 10 have not been detected spectroscopically in solutions of **2a**, nor has it been possible to synthesize the vanadium nitrido anion $[V(N)(OSiMe_3)_3]^-$, independently;[38] therefore, we have not been able to determine the equilibrium constant for eq. 10. However, further support for the lability of the N—M bond is provided by the observation of exchange of the group VIII metal centers between **2a**/**3a** and $MF(CO)(PPh_3)$ (eq. 11)

$$\underset{\mathbf{2a}}{(Me_3SiO)_3V{\equiv}N{-}Ir(CO)(PPh_3)_2} + RhF(CO)(PPh_3)_2 \rightleftarrows \underset{\mathbf{3a}}{(Me_3SiO)_3V{\equiv}N{-}Rh(CO)(PPh_3)_2} + IrF(CO)(PPh_3)_2. \quad (11)$$

DISCUSSION

Reactions between vanadium trialkylsilylimidos (**1**) and iridium(I) or rhodium(I) fluoride, methoxide or acetate compounds result in high-yield formation of heterobimetallic nitrido-bridged compounds **2**–**4** (eq. 2). These represent further successful examples of our use of the condensation



of metal silylimido compounds and metal halides to generate M(N)M species (eq. 1).[7–10]

The identity of the X group in $MX(L)(PPh_3)_2$ is important in determining whether formation of nitrido-bridged compounds occurs, as demonstrated for **2a, 3a** and **4** (eq. 12). For X = F, OMe, or OAc the reaction proceeds to the right, whereas for X = Cl, condensation does not occur. Instead, chlorotrialkylsilanes cleave the N—Ir/Rh bond, the reverse of the condensation reaction. These observations indicate that although the pathway for condensation is accessible for the $MX(L)(PPh_3)_2$ compounds we have examined, the thermodynamic preference for reactants or products is determined by the identity of X. In particular, formation of a strong Si—X bond in the $XSiMe_3$ byproduct is important to provide sufficient driving force for the forward reaction as demonstrated by the production of nitrido-bridged compounds by the reactions of **1** with group VIII metal fluorides and methoxides or acetates, but not chlorides.[39]

We formulate **2–4** as containing tetrahedral vanadium(V) linked to square-planar iridium(I) or rhodium(I) by a linear asymmetric $V\equiv N—M$ linkage. This is expected because the d^0 vanadium(V) has a high propensity to form triple bonds to nitrogen in nitrido and imido compounds[40] and because there are no empty *d*-orbitals of π-symmetry available on the d^8 metal centers for π-bonding with the nitrido ligand. Our formulation of **2–4** is supported by the chemistry and spectroscopy of these compounds, which show strong parallels to tetrahedral vanadium(V) silylimido compounds and square-planar iridium(I) or rhodium(I) analogs, and by the crystallographic characterization of a related vanadium(V)/platinum(II) nitrido-bridged complex, $(Me_3SiO)_3V\equiv N—Pt(Me)(PEt_3)_2$.[8]

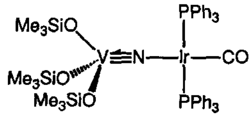
Formation of nitrido-bridged compounds by the condensation reaction (eq. 1) results in the formal replacement of a covalent N—Si bond with a covalent N—M bond, as we have previously discussed.[8] This suggests that the heterobimetallic nitrido-bridged compounds formed by this reaction might be better described as metalloimido compounds (**A**) than as dative nitrido adducts (**B**).

$M\overset{-}{\equiv}N—M'$ $\quad$ $M\equiv N{:}\!\rightarrow M'$

A $\quad$ **B**

The formalism is clear cut for $(Me_3SiO)_3V\equiv N—Pt(Me)(PEt_3)_2$[8] and $(Me_3SiO)_3V\equiv N—Re(CO)_2(PPh_3)_3$,[9] which behave as robust metallonitrides (**A**), and for $(Et_2PhP)_3Cl_2Re\equiv N:\rightarrow PtCl_2(PEt_3)$[29] and $(Me_2PhP)_3Cl_2Re\equiv N:\rightarrow MoCl_4(NCMe)$,[41] which are labile adducts involving dative coordination of terminal nitrido compounds to coordinatively unsaturated metal centers (**B**). However, for **2–4** the distinction is less straightforward.

Although **2a** is formed by a condensation reaction, its solution conductivity and ability to exchange metal centers (eq. 12) suggest formulation as a vanadium nitrido anion coordinated to an iridium cation as in **D**.



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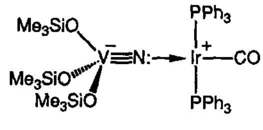

D

This is comparable to the description of Vaska's compound, $IrCl(CO)(PPh_3)_2$, and many of its analogs that possess polar Ir—X bonds and that undergo a variety of chemistry consistent with dissociation of X^-.[35,36] The analogy between Vaska's compound and **2a** is further supported by their parallel reactions with small molecules (MeI, O_2, H_2, $HSiEt_3$).

Comparison of the spectroscopic characteristics of **2–4** with those of related $MX(L)(PPh_3)_2$ complexes provides an opportunity to assess the effect of the tris(trimethylsiloxy)vanadium nitrido group on the group VIII metal center. The CO stretching frequencies for **2–3** provide such information. Within the series of $MX(CO)(PPh_3)_2$ compounds, ν_{CO}[42] increases in the order $X^- = MeO^-$ (1928–1951 cm^{-1})[24,43] < $NHPh^-$ (1944 cm^{-1})[44] < F^- (1940–1957 cm^{-1})[35,43] < Cl^- (1949–1965 cm^{-1})[35,43] < $[(R_3SiO)_3V\equiv N{:}]^-$ (1960–1967 cm^{-1}) ≪ CN^- (1990 cm^{-1}).[35] Thus, the tris(trimethylsiloxy)vanadium nitrido group produces a more electron-poor metal center than methoxide, arylamide, fluoride, and chloride ligands, but a more electron-rich group VIII metal than cyanide, an excellent π-acceptor.

Electronic spectra can be used to assess the σ-donor and π-acceptor strengths of the X^- ligands in $IrX(CO)(PPh_3)_2$. The UV–vis spectra of $IrX(CO)(PPh_3)_2$ complexes show three bands in the visible region (300–800 nm), with the lowest energy band assigned as the $a_1(z^2)\rightarrow b_1\pi$ transition and found to correlate with the σ-donor and π-acceptor properties of the X^- ligand.[45] A red shift of this band is attributed to destabilization of the $a_1(z^2)$ orbital by a strong σ-donor and/or stabilization of the $b_1\pi$ orbital by a strong π-acceptor.[45] For $IrX(CO)(PPh_3)_2$ compounds the wavelength of this transition follows the trend X^- = < F^- (429 nm) < Cl^- (439 nm)[45] < $[(R_3SiO)_3V\equiv N{:}]^-$ (483 nm) < CN^- (490 cm^{-1}).[45] Again, the tris(trimethylsiloxy)vanadium nitrido group is intermediate between weak-field (poor σ-donor and/or good π-donor) and strong field (good σ-donor and/or good π-acceptor) ligands. Based on these data, we conclude that $[(R_3SiO)_3V{\equiv}N\!:]^-$ is a good σ-donor ligand[46] when coordinated to the iridium or rhodium centers in **2–4**.

In contrast to the variety of information that can be obtained from the perspective of the group VIII metal center in **2–7**, the $[(R_3SiO)_3V{\equiv}N\!:]^-$ fragment appears to be remarkably insensitive to the group attached to the nitrido ligand. ^{51}V NMR signals are typically very sensitive to the electronic environment of the vanadium center, spanning a range of almost 2000 ppm for vanadium imido compounds alone.[47] Thus it is surprising that the chemical shifts for **2, 3, 5** and **7** all fall within a narrow 30 ppm range. The vanadium in these nitrido-bridged compounds is apparently insensitive not only to the identity of the group VIII metal attached to the nitrido ligand (**2** *vs* **3**), but also to the oxidation state and coordination geometry of that metal (**2** *vs* **5** and **7**). The tris(triphenylphosphine)rhodium compound **4** is the only exception with its ^{51}V NMR chemical shift approximately 150 ppm downfield of the other nitrido-bridged compounds described here. Note that the relative insensitivity of the tris (trimethylsiloxy)vanadium nitrido group to the group VIII metal center attached to its nitrido ligand can be construed as further evidence for description of these nitrido-bridged compounds as containing a common anion $[(R_3SiO)_3V{\equiv}N\!:]^-$ coordinated to the group VIII metal center.

SUMMARY

Heterobimetallic nitrido-bridged compounds $(R_3SiO)_3V{\equiv}N{-}M(L)(PPh_3)_2$ have been synthesized by condensation reactions between vanadium silylimido compounds, $V(NSiR_3)(OSiR_3)_3$, and group VIII metal fluorides, $MF(L)(PPh_3)_2$. Comparison of the reactivity and spectroscopic data among the nitrido-bridged compounds and with related iridium(I) and rhodium(I) complexes suggests that the nitrido-bridged compounds are best viewed as adducts in which anionic $[(R_3SiO)_3V{\equiv}N\!:]^-$ acts as a simple two-electron donor to the 14-electron cationic $[M(L)(PPh)_2]^+$ fragment.

EXPERIMENTAL

General procedures

All reactions and manipulations were performed under standard anhydrous and anaerobic conditions using appropriately dried reagent-grade solvents and chemicals.[48] Hexamethyldisilazane and N,N-dimethylacetamide were purified by distillation (at 108–113°C under N_2 and at 55–60°C under 12 Torr vacuum, respectively). Hexaethyldisilazane was prepared by stirring crude triethylsilazane, made by the reaction of chlorotriethylsilane (100 g, 0.66 mol) with excess ammonia,[49] over dried activated 4Å molecular sieves for 2 days. The product was purified by trap-to-trap distillation at liquid nitrogen temperature to yield $NH(SiEt_3)_2$ (51.4 g, 63% based on starting chlorosilane) as a colorless oil in the non-volatile fraction (^1H NMR: 0.99 (t, $J = 8$, 18 H), 0.54 (q, $J = 8$, 12 H), NH not observed). Ammonium metavanadate was recrystallized from distilled water with 1–2% (by volume) of concentrated ammonium hydroxide added and was washed with diethyl ether and dried under vacuum prior to use. Tris(dimethylamino)sulfonium difluorotrimethylsiliconate,[21] $IrCl(CO)(PPh_3)_2$,[22a] $RhCl(CO)(PPh_3)_2$,[22b] $RhCl(PPh_3)_3$,[22c] and $Ir(OMe)(CO)(PPh_3)_2$[24] were prepared by literature procedures.

NMR spectra were recorded on Varian VXR300 and Bruker WM500 and AC200 spectrometers at ambient temperature in C_6D_6 solution. Chemical shifts are reported in ppm upfield relative to $\delta = 0$ for $SiMe_4$ (^1H), external 85% H_3PO_4 (^{31}P), and external $V(O)Cl_3$ (^{51}V); coupling constants and peak half-widths are reported in Hz. Infrared spectra were recorded using Perkin–Elmer 283 or 1600 spectrometers, and are reported in cm^{-1}. UV–vis spectra were recorded on a Hewlett–Packard 8450A spectrophotometer in the 200–800 nm range; absorbances are reported in nm with molar absorptivities in $mol^{-1}\,cm^{-1}$. Solution conductivities were measured using an Industrial Instruments RC-18 Conductivity Bridge. Solutions of known concentration (0.1–1.0 mM) were prepared using volumetric glassware and transferred to a glass conductivity cell with platinum electrodes (cell constant = 0.3626 cm^{-1}) that was placed in a constant temperature bath (*ca* 25°C) and allowed to stabilize for 4–6 h. Measurements were made in units of μmhos; representative data are given. Elemental analyses were carried out by Canadian Microanalytical Services, Ltd.

Vanadium silylimido compounds

$V(NSiMe_3)(OSiMe_3)_3$ (**1a**)[13–15]. This procedure represents our version of Chan's modification[15] of a literature method.[13] Yields can vary substantially (25–95%); a typical case is presented here.

A suspension of ammonium metavanadate (20.0 g, 0.171 mol) in hexamethyldisilazane (72 cm^3, 0.341 mol) with a small amount of N,N-dimethylacetamide (4 cm^3) added was heated at 130°C for 4 h resulting in a black mixture. After cooling to room temperature, the mixture was filtered to remove unreacted NH_4VO_3 (6.8 g), and the solid was washed with pentane until the washings were colorless. The filtrate and washings were combined and the volatiles removed under vacuum leaving a black residue. Initial purification of the product was accomplished by vacuum distillation from a flask heated to 100°C, through a short-path distillation head with its condenser maintained at 50°C, collecting yellow solid **1a** in a receiving flask at room temperature. Subsequent recrystallization from pentane at −100°C produced pure yellow crystalline **1a** (23.1 g, 50% based on reacted NH_4VO_3). ^1H NMR: 0.30 (s, 27 H), 0.17 (s, 9 H). ^{51}V NMR: −650 ($\nu_{1/2} = 220$). IR (Nujol) 1249, 1127, 992, 908, 845, 751, 689, 630. UV–vis (THF) 337 (2.5×10^3). Conductivity (THF) 0.00 (5.0×10^{-3} M).

$V(O)(OSiMe_3)_3$,[20] a byproduct of the reaction, was isolated as a yellow oil from early fractions of the distillation of **1a** and identified by comparison to an authentic sample. It goes from being a small byproduct (<5%) to a major product (>50%) as the reflux time for the reaction is increased. ^1H NMR: 0.27 (s, 27 H). ^{51}V NMR: −705 ($\nu_{1/2} = 10$).

$V(NSiEt_3)(OSiEt_3)_3$ (**1b**). A suspension of ammonium metavanadate (6.98 g, 59.7 mmol) in hexaethyldisilazane (28.1 g, 114 mmol) with N,N-dimethylacetamide (1 cm^3) added was heated to 120°C for 2 days resulting in a tan colored solution. The temperature was increased to 180°C for an additional 24 h. The resulting black oil was cooled to room temperature, dissolved in 30 cm^3 of pentane and filtered through glass wool. Removal of the pentane under reduced pressure produced a green–black liquid. Kugelrohr distillation of the product from a flask at 110–130°C to a receiving flask at room temperature allowed isolation of crude **1b** (7.20 g, 20%) as a green oil. Repeated Kugelrohr distillation produced pure **1b** as a green waxy solid. ^1H NMR: 1.14 (t, $J = 8$, 27 H), 1.10 (t, $J = 8$, 9 H), 0.80 (q, $J = 8$, 18 H), 0.69 (q, $J = 8$, 6 H). ^{51}V NMR: −630 (s, $\nu_{1/2} = 230$). IR (Nujol) 1412, 1236, 1118, 1017, 986, 966, 907, 739, 728. UV–vis (C_6H_6) 352 (1.0×10^3). Calc. for $C_{24}H_{60}NO_3Si_4V$: C, 50.22; H, 10.54; N, 2.44. Found: C, 50.25; H, 10.53; N, 2.27.

$V(O)(OSiEt_3)_3$,[20] a byproduct of the reaction, was isolated as a yellow oil from early fractions of the Kugelrohr distillation of **1b** and identified by NMR and IR spectroscopy and elemental analysis. ^1H NMR: 1.10 (t, $J = 8$, 27 H), 0.78 (q, $J = 8$, 18 H). ^{51}V NMR: −712 ($\nu_{1/2} = 15$). IR (neat) 1458, 1412, 1379, 1238, 1017, 898, 741, 729. Calc. for $C_{18}H_{45}O_4Si_3V$: C, 46.92; H, 9.84. Found: C, 47.40; H, 9.67.

$V(NSiEt_3)(OSiMe_3)_3$ (**1c**). Benzene (20 cm^3) was added to a mixture of solid **2a** (191 mg, 0.177 mmol) and liquid $ClSiEt_3$ (0.040 cm^3, 0.212 mmol) and the mixture was stirred at room temperature for 4 days. The solvent was removed under vacuum and pentane was added to produce a yellow solid, which was collected by filtration and identified as $IrCl(CO)(PPh_3)_2$, and a yellow solution from which the solvent was removed under vacuum to yield crude **1c** as a yellow oil. ^1H NMR: 1.08 (t, $J = 8$, 9 H), 0.67 (q, $J = 8$, 6 H), 0.31 (s, 27 H). ^{51}V NMR: −630 ($\nu_{1/2} = 210$).

Group VIII metal fluorides

Tetrahydrofuran (10 cm^3) was added to a mixture of solid $IrCl(CO)(PPh_3)_2$ (0.274 g, 0.351 mmol) and $[(Me_2N)_3S][F_2SiMe_3]$ (0.130 g, 0.472 mmol) resulting in a yellow solution and white precipitate, $[(Me_2N)_3S]Cl$. After stirring for 30 min at room temperature, the solution was filtered, the solvent removed from the filtrate under reduced pressure, and the resulting yellow powder recrystallized from chloroform yielding yellow crystalline $IrF(CO)(PPh_3)_2$[16] (0.188 g, 70%). UV–vis (C_6H_6) 334 (2.2×10^3), 379 (2.7×10^3), 428 (5.0×10^2); (THF) 334 (3.7×10^3), 379 (4.2×10^3), 430 (7.5×10^2). Conductivity (THF) 0.98 (5.4×10^{-3} M). By the same procedure, $RhCl(CO)(PPh_3)_2$ (0.333 g, 4.82 mmol) and $[(Me_2N)_3S][F_2SiMe_3]$ (0.211 g, 7.66 mmol) produced yellow crystalline $RhF(CO)(PPh_3)_2$[16] (0.297 g, 91%), and $RhCl(PPh_3)_3$ (0.151 g, 0.168 mmol) and $[(Me_2N)_3S][F_2SiMe_3]$ (0.072 g, 0.261 mmol) produced yellow crystalline $RhF(PPh_3)_3$[17] (0.124 g, 82%).

Nitrido-bridged compounds

(*Me*$_3$SiO)$_3$V(N)Ir(CO)(PPh$_3$)$_2$ (**2a**), *Procedure* 1. Benzene (20 cm^3) was added to a mixture of **1a** (0.109 g, 0.269 mmol) and $IrF(CO)(PPh_3)_2$ (0.200 g, 0.262 mmol). The resulting orange solution was stirred for 1 h at room temperature. The solvent and unreacted excess **1a** were removed under reduced pressure. The orange product was extracted with pentane and the extracts reduced in volume to produce orange crystals. This material was collected by filtration and dried under vacuum, yielding 0.234 g (83%) of orange crystalline **2a**. ^1H NMR: 8.02 (q, $J_{PH} \cong J_{HH} \cong 6$, 12 H), 7.18 (t, $J = 7$, 12 H), 7.08 (t, $J = 7$, 6 H), 0.10 (s, 27 H). $^{31}P\{^1H\}$ NMR: 22.9. ^{51}V NMR: −329 ($\nu_{1/2} = 1450$). IR (Nujol) 1960, 1434, 1430, 1238, 1092, 1024, 990, 924, 902, 836, 738, 688, 512. UV–vis (C_6H_6) 312 (2.5×10^3), 359

(1.0×10^3), 418 (8.7×10^2), 482 (4.0×10^2); (THF) 312 (1.1×10^3) 355 (4.3×10^3), 416 (3.2×10^3), 482 (1.3×10^3). Conductivity (THF) 0.40 ± 0.03 $(5.1\times10^{-3}$ M). Calc. for $C_{46}H_{57}IrNO_4P_2Si_3V$: C, 51.29; H, 5.33; N, 1.30. Found: C, 51.19; H, 5.58; N, 1.30.

Procedure 2. Benzene (10 cm^3) was added to a mixture of **1a** (0.184 g, 0.454 mmol) and Ir(OMe)(CO)$(PPh_3)_2$ (0.340 g, 0.438 mmol) at -78°C resulting in a yellow solution and yellow solid upon thawing. Stirring at room temperature for 2 days resulted in dissolution of the solids and formation of an orange solution. The product was isolated as in procedure 1, yielding orange crystalline **2a** (0.310 g, 66%).

$(Et_3SiO)_3V(N)Ir(CO)(PPh_3)_2$ (**2b**). Benzene (5 cm^3) was added to a mixture of **1b** (0.232 g, 0.404 mmol) and IrF(CO)$(PPh_3)_2$ (0.323 g, 0.423 mmol). Heating this mixture in a closed vessel at 70°C for 2 days resulted in a deep red solution. Solvent and volatiles were removed under reduced pressure, and the resulting red powder was recrystallized from pentane yielding orange **2b** (0.308 g, 63%). ^{1}H NMR: 7.99 (q, $J_{PH}\cong J_{HH}\cong 6$, 12 H), 7.18 (t, $J = 7$, 12 H), 7.08 (t, $J = 7$, 6 H), 1.07 (t, $J = 8$, 27 H), 0.58 (q, $J = 8$, 18 H). ^{31}P{^{1}H} NMR: 21.1 (s). ^{51}V NMR: -319 ($\nu_{1/2} = 1700$). IR (Nujol) 1967, 1958, 1096, 986, 922, 892, 721. UV–vis (C_6H_6) 319 (6.7×10^3), 356 (3.2×10^3), 412 (2.1×10^3), 484 (6.4×10^2). Calc. for $C_{55}H_{75}IrNO_4P_2Si_3V$: C, 54.89; H, 6.28; N, 1.16. Found: C, 54.90; H, 5.72; N, 1.16.

$(Me_3SiO)_3V(N)Rh(CO)(PPh_3)_2$ (**3a**). Using procedure 1 above, **1a** (0.356 g, 0.877 mmol) and RhF(CO)$(PPh_3)_2$ (0.560 g, 0.830 mmol) yielded bright yellow **3a** (0.738 g, 90%). ^{1}H NMR: 7.96 (q, $J_{PH}\cong J_{HH}\cong 6$, 12 H), 7.17 (t, $J = 7$, 12 H), 7.09 (t, $J = 7$, 6 H), 0.12 (s, 27 H). ^{31}P{^{1}H} NMR: 25.3 (d, $J_{RhP} = 138$). ^{51}V NMR: -326 ($\nu_{1/2} = 1400$). IR (Nujol) 1981, 1435, 1246, 1095, 969, 916, 897, 835, 746, 693. Calc. for $C_{46}H_{57}NO_4P_2RhSi_3V$: C, 55.92; H, 5.82; N, 1.42. Found: C, 56.31, H, 5.86, N 1.41.

$(Et_3SiO)_3V(N)Rh(CO)(PPh_3)_2$ (**3b**). Benzene (30 cm^3) was added to a mixture of **1b** (0.275 g, 0.479 mmol) and RhF(CO)$(PPh_3)_2$ (0.312 g, 0.463 mmol). Stirring this mixture for 2 days at room temperature produced a pale orange solution. Solvent was removed under reduced pressure, and the resulting yellow–orange solid was recrystallized from cold pentane producing bright yellow–orange **3b** (0.402 g, 78%). ^{1}H NMR: 7.97 (q, $J_{PH}\cong J_{HH}\cong 6$, 12 H), 7.18 (t, $J = 7$, 12 H), 7.10 (t, $J = 7$, 6 H), 1.08 (t, $J = 8$, 27 H), 0.60 (q, $J = 8$, 18 H). ^{31}P{^{1}H} NMR: 22.3 (d, $J_{RhP} = 137$). ^{51}V NMR: -317 ($\nu_{1/2} = 1800$). IR (Nujol) 1983, 1973, 1435, 1236, 1094, 990, 967, 925, 896, 739, 694. Calc. for $C_{55}H_{75}NO_4P_2RhSi_3V$: C, 59.29; H, 6.78; N, 1.26. Found: C, 59.29; H, 7.07; N, 1.36.

$(Me_3SiO)_3V(N)Rh(PPh_3)_3$ (**4**). Using procedure 1 above, **1a** (0.330 g, 0.813 mmol) and RhF$(PPh_3)_3$ (0.600 g, 0.660 mmol) yielded brick red crystalline **4** (0.632 g, 78%). ^{1}H NMR: 7.70 (m, 12 H), 7.29 (t, $J_{PH}\cong J_{HH}\cong 9$, 6 H), 7.06 (m, 18 H), 6.88 (t, $J = 7$, 3 H), 6.71 (t, $J = 7$, 6 H), 0.22 (s, 27 H). ^{31}P{^{1}H} NMR: 38.7 (dt, $J_{RhP} = 157$, $J_{PP} = 39$), 25.2 (dd, $J_{RhP} = 156$, $J_{PP} = 39$). ^{51}V NMR: -163 ($\nu_{1/2} = 2400$). IR (Nujol) 1434, 1242, 1093, 1012, 988, 930, 916, 834, 742, 695. Calc. for $C_{63}H_{72}NO_3P_3RhSi_3V$: C, 61.91; H, 5.94; N, 1.15. Found: C, 61.59; H, 5.73; N, 0.77.

$(Me_3SiO)_3V(N)Ir(Me)(I)(CO)(PPh_3)_2$ (**5**). Excess methyl iodide was added by vacuum transfer to a benzene solution of **2a**. The initially orange solution turned yellow after stirring at room temperature for several days. The volume was reduced and pentane was added, resulting in the precipitation of yellow **5**. ^{1}H NMR: 8.24 (q, $J_{PH}\cong J_{HH}\cong 6$, 12 H), 7.16 (t, $J = 7$, 12 H), 7.01 (t, $J = 7$, 6 H), 1.52 (t, $J = 5$, 3 H), 0.22 (s, 27 H). ^{31}P{^{1}H} NMR: -12.7. ^{51}V NMR: -311 ($\nu_{1/2} = 1800$). IR (Nujol) 2038, 1243, 1091, 994, 922, 899, 837, 744, 693.

$(Me_3SiO)_3V(N)Ir(O_2)(CO)(PPh_3)_2$ (**6**). Reaction of excess dioxygen with **2a** in C_6D_6 in a sealed NMR tube for 1 day at room temperature produced a yellow solution containing **6** (>90%). ^{1}H NMR: 7.88 (q, $J_{PH}\cong J_{HH}\cong 7$, 12 H), 7.11 (m, 18H), 0.21 (s, 27 H). ^{31}P{^{1}H} NMR: 4.4.

$(Me_3SiO)_3V(N)Ir(H)_2(CO)(PPh_3)_2$ (**7**). Reaction of excess dihydrogen with **2a** in C_6D_6 in a sealed NMR tube was monitored. The initially orange solution turned yellow as the reaction proceeded. Formation of **7a** was observed immediately at room temperature reaching a maximum of roughly 25% of the V≡N—Ir compounds at this early stage of the reaction. Compound **7b** grows in more slowly, with a small amount detected in the initial spectra of the reaction mixture and with **7b** formed quantitatively after 2 days at room temperature. For **7a**: ^{1}H NMR: 7.57 (m, 12 H), 7.02 (m, 18 H), 0.34 (s, 27 H), -7.64 (AA′ m, 2 H). ^{31}P NMR: -0.9 (XX′ m). For **7b**: ^{1}H NMR: 7.92 (q, $J_{PH}\cong J_{HH}\cong 6$, 12 H), 7.17 (t, $J_{HH} = 7$, 12 H), 7.04 (t, $J_{HH} = 7$, 6 H), 0.26 (s, 27 H), -6.82 (td, $J_{PH} = 17$, $J_{HH} = 4$, 1 H), -21.95 (td, $J_{PH} = 17$, $J_{HH} = 4$, 1 H). ^{31}P NMR: 9.2 (t, $J_{PH} = 17$). ^{51}V NMR: -301 ($\nu_{1/2} = 1900$). IR (C_6D_6) $\nu_{CO} = 1994$.

Other reactions of the nitrido-bridged compounds

Reactions of **2a, 3a** and **4** with a slight excess of $ClSiMe_3$ were performed in C_6D_6 in sealed NMR tubes. Signals for **1a** and for MCl(L)$(PPh_3)_2$

(M = Ir, L = CO; M = Rh, L = CO, PPh_3; respectively) were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of **2a** and one equivalent of triethylsilane was performed in C_6D_6 in a sealed NMR tube. After 4 days at room temperature, conversion to **1c** and $IrH_2(SiEt_3)(CO)(PPh_3)_2$[34] [$^1H$ NMR: 7.47 (m, 6 H), 7.37 (m, 6 H), 6.90 (m, 18 H), 1.35 (t, $J = 8$, 9 H), 1.09 (q, $J = 8$, 6 H), −9.39 (ddd, $J_{PH} = 22$, 16, $J_{HH} = 4$, 1 H), −10.45 (ddd, $J_{PH} = 113$, 19, $J_{HH} = 4$, 1 H); ^{31}P NMR: 8.8 (dt, $J_{PH} = 106$, $J_{PH} \cong J_{PP} \cong 14$), 0.1 (q, $J_{PH} \cong J_{PH} \cong J_{PP} \cong 17$)] was complete.

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37. The concentration dependence of the specific conductance of **2a** is consistent with that of a weak electrolyte, and THF solutions of **2a** have measured conductivities about two orders of magnitude lower than those for comparable concentrations of NBu_4PF_6, a standard and weak nonaqueous electrolyte.
38. The anionic vanadium nitrido complex, $[V(N)(SiOMe_3)_3]^-$, has thus far eluded our efforts aimed at its preparation, although closely related anions [e.g. $[V(N)(O^tBu)_3]^-$] are readily prepared. K. A. Killeen, B. M. Schomber and N. M. Doherty, work in progress.
39. It is generally accepted that Si—X bond energies follow the order X = F > O > Cl > N, although reported bond dissociation energy values differ widely. Compare the general values of Si—F = 193 kcal mol^{-1}, Si—O = 127 kcal mol^{-1} and Si—Cl = 113 kcal mol^{-1} listed by Colvin [E. Colvin, *Silicon in Organic Synthesis*, Chapter 1. Butterworths, London (1981)] with the specific values of Si—F = 159 ± 5 kcal mol^{-1} in $FSiMe_3$, Si—O = 114 ± 2 kcal mol^{-1} in $MeOSiMe_3$ and Si—Cl = 113 ± 2 kcal mol^{-1} in $ClSiMe_3$ derived by Walsh [R. Walsh, *The Chemistry of Organic Silicon Compounds* (Edited by S. Patai and Z. Rappoport), Chapter 5. Wiley Interscience, New York (1989)].
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42. Reported values of ν_{CO} for any given $MX(CO)(PPh_3)_2$ compound vary dramatically. Nonetheless, based on the ν_{CO} values we have measured[43] and the data available in the literature, this trend appears to hold.
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