is such that the nitrido ligand is electron-rich relative to the ground state. An explanation based on stabilization of a charge-separated excited state by a dielectric continuum can be rejected, since the static dielectric constant (D_s) does not correlate with E_{em}.

Since the quantum yield of emission of *trans*-[NRe-$(Me_2PCH_2CH_2PMe_2)_2Cl]^+$ is generally <0.004 for the solvents in question, the excited-state lifetime is controlled by radiationless decay processes. Although quantitative data are not yet available, it is clear from the absorption spectral changes which accompany prolonged irradiation that a photochemical reaction channel competes with radiative decay. The decrease in lifetime as the excited-state energy increases may be due to more effective thermal population of a higher lying reactive state. This may prove an important point in the eventual understanding of the photochemistry of metal-multiple-bonded complexes.

Preliminary cyclic voltammetry studies show that *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^+$ possesses a quasireversible ($i_{pa}/i_{pc} = 0.30$) oxidation at +1.5 V (SCE, $CH_3CN/0.1$ M tetra-*n*-butylammonium hexafluorophosphate, 100 mV/s sweep rate) that is coupled to the formation of a product at $E_p = 1.0$ V and a large multielectron irreversible reduction at $E_p = -1.9$ V. These data allow a rough estimate of the one-electron redox potentials of the excited state to be made. For the *trans*-NRe-$(Et_2PCH_2CH32PEt_2)_2Cl^{+,*/0}$ couple this is +0.4 V, while for *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^{2+/+,*}$ this is -0.8 V. Our future studies are focused on the exploration of these excited-state redox properties, the implied atom transfer properties, and the understanding of the relationship of the photochemical pathway to these.

Registry No. *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^+$, 136838-66-9; *trans*-$NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+$, 136838-67-0; *trans*-NRe-$(Me_2PCH_2CH_2PMe_2)_2Br^+$, 136838-68-1; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; H_2O, 7732-18-5.

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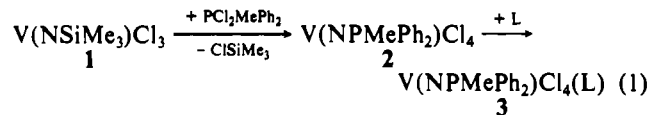   **B. Patrick Sullivan***

Reactions at Metal-Bound Nitrogen Atoms. Synthesis and Structure of V(NPMePh₂)Cl₄(NCMe)·MeCN

We have been exploring the synthesis and chemistry of complexes with silyl-substituted imido ligands in order to use the nitrogen–silicon bond as a reactive site for formation of nitride-bridged transition-metal compounds and materials.[1-3] In order to understand in a general sense the range of reactivity available to silylimido derivatives, their chemistry with a variety of reagents capable of attacking the silylimido ligand is being examined. We report here reactions of $V(NSiMe_3)Cl_3^{1a,4}$ (1) with PCl_2MePh_2 and Cl_2 which result in unusual transformations of the silylimido ligand into phosphiniminato and chloroimido ligands, respectively.

Addition of 1 equiv of PCl_2MePh_2 to **1** in dichloromethane results in rapid elimination of 1 equiv of $ClSiMe_3$ and quantitative formation of a vanadium(V) phosphiniminato compound, V-$(NPMePh_2)Cl_4$ (**2**) (eq 1). The ^1H NMR spectrum of **2** shows

$$V(NSiMe_3)Cl_3 \xrightarrow[- ClSiMe_3]{+ PCl_2MePh_2} V(NPMePh_2)Cl_4 \xrightarrow{+ L}$$
$$\textbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{2}$$
$$V(NPMePh_2)Cl_4(L) \quad (1)$$
$$\textbf{3}$$

a doublet for the phosphiniminato methyl protons with a chemical shift (δ 2.88) and a proton–phosphorus coupling constant ($J = 12$ Hz) in the range we have found to be characteristic of methyl groups attached to the phosphorus(V) of phosphiniminato ligands.[5] The ^{31}P NMR chemical shift for **2** (δ 58) is likewise in the region expected,[5] although this signal is unusually broad ($\nu_{1/2} = 600$ Hz) as the result of unresolved coupling of the phosphorus to nitrogen and vanadium.[6] Compound **2** is isolated from cold dichloromethane in 75% yield as an air-sensitive maroon crystalline solvate, $V(NPMePh_2)Cl_4·^1/_2CH_2Cl_2$. The IR spectrum of this solid exhibits a strong absorption at 1120 cm⁻¹ assigned to the asymmetric VNP vibration and characteristic of phosphiniminato complexes.[7] The solid-state structure of **2** is not known, but by analogy to the related niobium and tantalum phosphiniminato complexes, $[Nb(NPPh_3)Cl_4]_2·CH_2Cl_2^8$ and $[Ta(NPPh_3)Cl_4]_2,^9$ we expect that **2** is a chloro-bridged dimer.

Coordinating solvents readily add to **2**, producing adducts $V(NPMePh_2)Cl_4(L)$, where L = MeCN (**3a**), THF (**3b**), or pyridine (**3c**) (eq 1). Compound **3a** crystallizes from acetonitrile as a monosolvate, $V(NPMePh_2)Cl_4(NCMe)·MeCN$, for which the solid-state structure has been determined by X-ray diffraction.[10] There are two independent six-coordinate molecules of **3a** per asymmetric unit (Figure 1). Their V–N(phosphiniminato) distances, V(1)–N(1) = 1.653 (3) Å and V(2)–N(3) = 1.656 (3) Å, are the same within experimental error and in the range of V–N distances reported for vanadium(V) imido compounds.[11a] The short V–N(phosphiniminato) distances suggest substantial vanadium–nitrogen π-bonding, consistent with a triple bond. Distortions from idealized octahedral geometry further support this idea: the cis chlorides are bent away from the phosphiniminato ligand and the elongated V–N(acetonitrile) distances suggest a significant trans influence.[11b] The N–P distances, N(1)–P(1) = 1.660 (3) Å and N(3)–P(2) = 1.667 (3) Å, are typical of those observed for phosphiniminato ligands,[5,7] midway between the values quoted for N–P single and double bonds.[12] This is usually interpreted as indicating phosphorus–nitrogen π-bonding;[7] however, the shortened N–P distances can also be rationalized as arising from the sp hybridization of the nitrogen atoms.[13] The VNP angles differ somewhat between the two independent molecules of **3a** (V(1)–N(1)–P(1) = 171.8 (2)° and V(2)–N–

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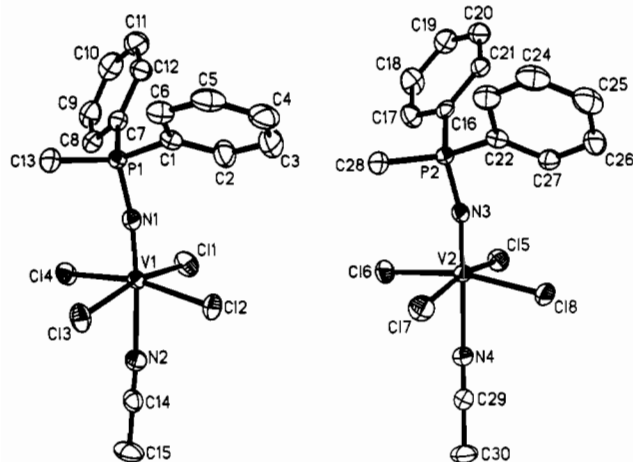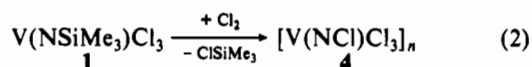
Figure 1. ORTEP drawings of the two crystallographically independent molecules of **3a** in the structure of $V(NPMePh_2)Cl_4(NCMe)\cdot MeCN$ with 50% thermal ellipsoids for non-hydrogen atoms. Selected bond distances (Å) and angles (deg) not mentioned in text: $V(1)-N(2)$, 2.221 (3); $V(1)-Cl(1)$, 2.285 (1); $V(1)-Cl(2)$, 2.277 (1); $V(1)-Cl(3)$, 2.327 (1); $V(1)-Cl(4)$, 2.305 (1); $V(2)-N(4)$, 2.263 (3); $V(2)-Cl(5)$, 2.293 (1); $V(2)-Cl(6)$, 2.295 (1); $V(2)-Cl(7)$, 2.317 (1); $V(2)-Cl(8)$, 2.319 (1); $N(1)-V(1)-N(2)$, 175.6 (1); $N(1)-V(1)-Cl(1)$, 98.4 (1); $N(1)-V(1)-Cl(2)$, 98.9 (1); $N(1)-V(1)-Cl(3)$, 94.3 (1); $N(1)-V(1)-Cl(4)$, 95.3 (1); $N(3)-V(2)-N(4)$, 176.5 (1); $N(3)-V(2)-Cl(5)$, 98.6 (1); $N(3)-V(2)-Cl(6)$, 95.8 (1); $N(3)-V(2)-Cl(7)$, 94.0 (1); $N(3)-V(2)-Cl(8)$, 97.0 (1).

$(3)-P(2) = 164.9$ $(2)°)$; however, there are no accompanying changes in the V–N(phosphiniminato) and N–P distances. This observation suggests that the small deviations of the VNP angles from 180° arise from crystal packing forces rather than variations in the V–N and N–P bonding. Overall, the structural data for **3a** indicate that the vanadium phosphiniminato linkage in this compound is best viewed as having a vanadium–nitrogen triple bond and a nitrogen–phosphorus single bond, $(MeCN)Cl_4V\equiv N-PMePh_2$.

The reaction of **1** with an excess of dry chlorine (2–4 equiv) in dichloromethane produces a known vanadium chloroimido compound[14] (**4**) and $ClSiMe_3$ (eq 2). This reaction proceeds very slowly at room temperature to produce a bright red solution. In CD_2Cl_2, the disappearance of the ^{51}V NMR signal for **1** (δ 14, $\nu_{1/2} = 185$ Hz) is accompanied by growth of a broad triplet (δ 268, t, $J_{VN} \approx 100$ Hz) assigned to **4**. The resolution of vanadium–nitrogen coupling in this species indicates that it is of relatively high symmetry,[15] suggesting that **4** is monomeric in solution. A yellow-orange solid eventually precipitates from the reaction mixture and is identified by IR spectroscopy as dimeric **4** on the basis of the comparison of its spectrum to that of the structurally characterized chloro-bridged dimer, $[V(NCl)Cl_3]_2$.[14a]

Overall, the vanadium(V) silylimido complex, $V(NSiMe_3)Cl_3$ (**1**), undergoes a variety of reactions at the metal-bound nitrogen atom. These are illustrated in Scheme I. Bridging and terminal vanadium nitrides are formed on reaction of **1** with coordinating nitrogen bases.[1] This is the self-condensation analogue of the formation of heterobimetallic nitride-bridged complexes by condensation between metal silylimido complexes and metal halides

$$V(NSiMe_3)Cl_3 \xrightarrow[-ClSiMe_3]{+ Cl_2} [V(NCl)Cl_3]_n \qquad (2)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{4}$$

Scheme I
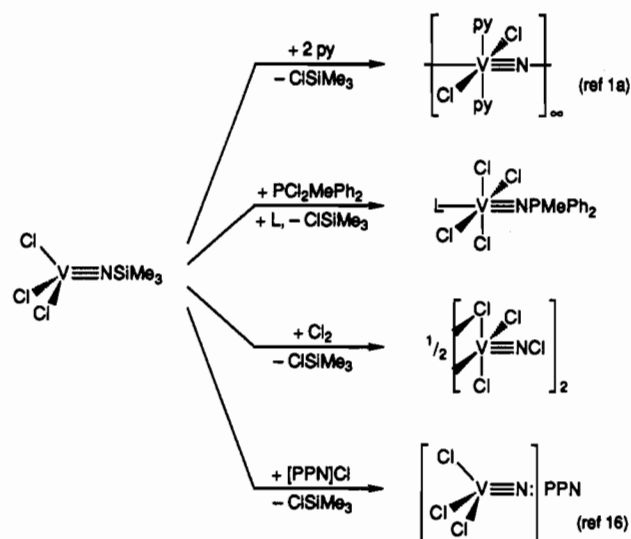
(eq 3).[2] Similarly, the formation of the vanadium phosphin-

$$L_nM\equiv NSiR_3 + X-M'L'_n \rightarrow L_nM\equiv N-M'L'_n + X-SiR_3 \qquad (3)$$

iminato compound (**2**) can be viewed as a main-group analogue of the condensation reaction in eq 3. Note, however, that PCl_2MePh_2 provides 2 equiv of chloride in its reaction with **1**, resulting in net loss of chlorotrimethylsilane and coordination of a chloride to the vanadium center. In contrast to the formation of a VNP linkage in eq 1, the reaction of **1** with [PPN]Cl ($[PPN]^+$ = $[Ph_3PNPPh_3]^+$) produces an anionic terminal nitrido complex, $[PPN][V(N)Cl_3]$,[16] and the reaction of **1** with $[PPh_4]Cl$ results in coordination of chloride to the vanadium center forming $[PPh_4][V(NSiMe_3)Cl_4]$.[4]

The formation of **4** from **1** plus Cl_2 involves an unusual direct conversion of a silylimido ligand into a chloroimido ligand. This may represent a good synthetic route to haloimido compounds, which are few in number and are generally prepared by methods involving hazardous reagents such as trihaloamines or halo azides. Note that in contrast to the other transformations in Scheme I, the formation of **4** plus $ClSiMe_3$ from **1** plus Cl_2 is not a simple metathesis reaction. Rather, this is an overall redox process in which two-electron oxidation of the multiply bonded nitrogen atom of the silylimido ligand occurs. Attack of chlorine at the silylimido nitrogen is the only reaction available because there are no metal d electrons present nor other oxidizable ligands.[5]

The silylimido ligand of **1** is a versatile site of reactivity producing bridging nitrido, phosphiniminato, chloroimido, or terminal nitrido ligands by the reactions in Scheme I. A common feature in this chemistry is loss of the trimethylsilyl group as $ClSiMe_3$. It can also be noted that the nitrogen atom from the silylimido ligand of **1** remains attached to the vanadium(V) center via a strong multiple bond in each of the products formed. The marked propensity of vanadium(V) to form triple bonds to nitrogen has been demonstrated.[1–4,16] This is likely an important factor which makes possible the varied chemistry observed at the silylimido ligand of $V(NSiMe_3)Cl_3$ (**1**).

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Articles

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Ni₂Cl₂[C(SiMe₃)(PMe₃)]₂, Containing a Very Short Ni–Ni Distance with Little Metal–Metal Bonding Character: Possible Synergy of Electronic and Steric Factors

Georges Trinquier,[†] Michèle Dartiguenave,[‡] Yves Dartiguenave,[‡] and Marc Bénard*,[§]

The electronic structure of the title compound, a recently characterized dimer of nickel(II), is investigated by means of extended Hückel calculations. In contradiction with early predictions based upon electron counting and structural considerations, the very short nickel–nickel distance (2.281 Å) does not appear to be the consequence of strong metal–metal bonding interactions. The origin of the rhombic conformation of the Ni₂C₂ metallacycle is then traced to the interactions that develop between the Ni₂Cl₂ fragment and the bridging ylide moieties, ensuring a tight nickel–carbon binding. Electronic effects alone do not seem to be sufficient to account for the very short Ni–Ni distance. H···H repulsive contacts that develop between the bulky substituents of the bridging ylides also tend to displace the equilibrium conformation toward shorter metal–metal distances. Ab initio calculations carried out on appropriate model systems indicate that the repulsive part of the H···H interaction energy could amount to 66 kJ·mol⁻¹ for the title complex at the equilibrium conformation and reach 125 kJ·mol⁻¹ in a hypothetical "square" conformation of the metallacycle corresponding to a Ni–Ni distance of 2.695 Å.

1. Introduction

The structure of a novel binuclear complex of nickel(II) with two symmetrically bridging ylide ligands has recently been reported.[1]   Ni₂Cl₂[C(SiMe₃)(PMe₃)]₂ (**1**) is a dimer with C_{2h} symmetry (Figure 1) characterized by an extremely short metal–metal bond length (2.281 Å), which is the shortest distance reported for binuclear Ni complexes. The angles in the Ni₂C₂ planar metallacycle are Ni–C–Ni = 73.5° and C–Ni–C = 106.5°. These structural characters were first interpreted as supporting the presence of a strong Ni–Ni bonding interaction. This appears to be in agreement with formal electron counting considerations that require a double metal–metal interaction in order to achieve a 16e environment around each nickel atom.[1]

We first carried out extended Hückel calculations on the model dimer Ni₂Cl₂[C(SiH₃)(PH₃)]₂ (**2**) in order to confirm the presence of the assumed metal–metal double bond. To our surprise, the calculations did not clearly corroborate the existence of a strong Ni–Ni bonding interaction. We therefore decided to carry out a more thorough investigation of the factors leading to such a short metal–metal bond. Most of the present work relies on extended Hückel (EH) calculations,[2] but a quantitative assessment of the steric effects was carried out through ab initio SCF calculations.

2. Computational Details

The orbital exponents and H_{ii}'s used for the EH calculations are listed in Table I.   The EH calculations on the model system **2** were carried

Table I. Extended Hückel Parameters

atom	orbital	H_{ii}, eV	ζ
Ni	4s	−6.86	2.10
	4p	−4.90	2.10
	3d	−12.99	5.49 (0.563 36)[a]
			2.00 (0.620 95)
C	2s	−21.40	1.625
	2p	−11.40	1.625
Si	3s	−17.30	1.383
	3p	−9.20	1.383
P	3s	−18.60	1.60
	3p	−14.00	1.60
Cl	3s	−30.00	2.033
	3p	−15.00	2.033
H	1s	−13.60	1.30

[a] Contraction coefficients used in the double-ζ expansion.

out using for the non-hydrogen skeleton the geometry corresponding to the X-ray structure of the real complex.[1] P–H distances of 1.42 Å and Si–H distances of 1.48 Å were then assumed, with C–Si–H and C–P–H angles of 109.47°. The metallacycle was then distorted from the experimental rhombus to a square shape corresponding to Ni–Ni and C···C distances of 2.695 Å. The Ni–C distances and all other geometrical parameters were kept constant. The molecule therefore retains the C_{2h} symmetry along the deformation path. Different sets of EH parameters had been used for Ni, Cl, and Si in preliminary calculations without

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