Organoimido Ligands with Remote Functionality: A *p*-Pyridylimido Complex of Vanadium(V) and its Use as a Metalloligand

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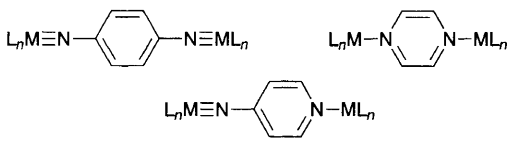
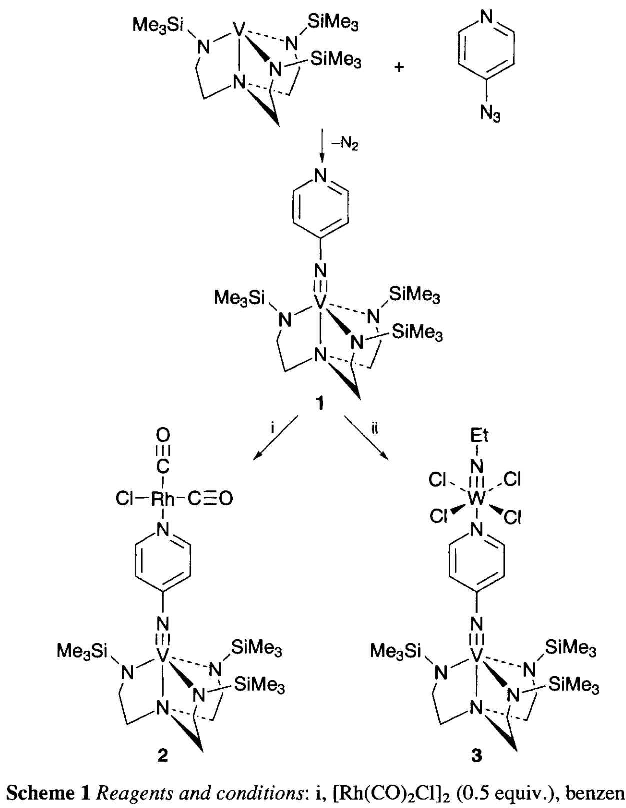
The exposed nitrogen atom of the *p*-pyridylimido ligand in the vanadium(V) species $[(N_3N)V{\equiv}N\text{-}C_5H_4N]$ **1** $\{N_3N = [(Me_3SiNCH_2CH_2)_3N]^{3-}\}$ provides a reactive site capable of complexing a second metal fragment, enabling the construction of new types of heterobimetallic complexes linked by a compact conjugated bridge.

We report here the preparation, structure and preliminary reactivity patterns of an organoimido vanadium(V) complex in which the organoimido substituent is a *p*-pyridyl group, namely $[(N_3N)V{\equiv}N\text{–}C_5H_4N]$ **1** $\{N_3N = [(Me_3SiNCH_2CH_2)_3N]^{3-}\}$. The *p*-pyridylimido ligand ($[N\text{-py}]^{2-}$) incorporates two disparate functionalities (a σ-donor/π-acceptor pyridyl nitrogen atom and a σ-donor/π-donor imido nitrogen atom) into a compact conjugated system and thus offers the potential for constructing a variety of new types of bimetallic complexes. The $[N\text{-py}]^{2-}$ ligand can be regarded as a hybrid derived from phenylenediimido(4−)[1–4] and pyrazine[5] 'parents' as illustrated schematically for their resultant complexes below. While our work was in progress, Hopkins *et al.*[6] reported the preparation and structures of related polymeric W^{VI} systems $[(RO)_3W{\equiv}C\text{-}py']_\infty$ featuring 3-pyridylalkylidyne and 4-lutidylalkylidyne ligands.



Reaction of $[(N_3N)V^{III}]$[7] with 4-azidopyridine in pentane solution at room temperature occurs rapidly to evolve N_2 and produce a garnet solution of **1** (Scheme 1). Crystals of **1** were obtained as red–black blocks from pentane at −35 °C;† the recovered yield was 27%, caused at least in part by the extreme solubility of **1**. The ^{51}V NMR spectrum of **1** consists of a partially resolved 1:1:1 triplet ($^1J_{^{14}N\text{–}^{51}V}$ = 89 Hz) at δ −146.5. This chemical shift value is similar to that reported for the analogous *p*-tolylimido system $[(N_3N)V{\equiv}N\text{-}C_6H_4Me]$ (δ −159),[7] and the magnitude of the vanadium–nitrogen spin coupling observed within **1** likewise accords with the range (92–112 Hz) previously reported for various alkyl- and arylimido vanadium(V) systems.[8] The N_5-coordination sphere of **1** is very effective at stabilizing the $d^0\text{-}V^V$ centre: cyclic voltammetry (MeCN; $[Bu_4N]PF_6$ supporting electrolyte; glassy carbon working electrode; 298 K; 100 mV s^{-1}) reveals an essentially irreversible reduction wave at −1.93 V (*vs.* Ag/Ag^+).

The molecular structure of **1** is shown in Fig. 1.‡ The short V–N(1) bond length [1.693(7) Å] and nearly linear V–N(1)–C(6) bond angle [173.0(5)°] are consistent with the presence of a formal V≡N-py triple bond. The three equatorial vanadium–amido bond lengths are statistically identical at 1.897(6) Å, while the axial V–N(2) amine bond length of 2.364(7) Å is substantially longer than those in related V^V structures[9] and suggests a very weak dative interaction. As seen in the space-filling representation of Fig. 2, the imido nitrogen atom is buried within the $[N_3N]$ ligand cavity, but the pyridyl nitrogen atom of **1** is exposed and thus available as a potential donor atom. This potential is verified by the reaction of **1** with $[Rh(CO)_2Cl]_2$ (0.5



Scheme 1 *Reagents and conditions*: i, $[Rh(CO)_2Cl]_2$ (0.5 equiv.), benzene, room temp; ii, $[(EtN)WCl_4]_2$, (0.5 equiv.), benzene, room temp.

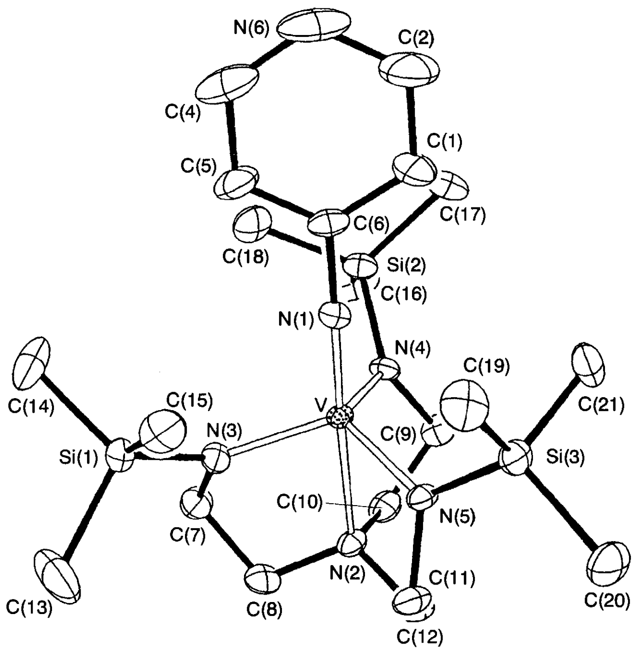


Fig. 1 ORTEP representation of the non-hydrogen atoms of **1** showing the atomic numbering scheme. Selected bond distances (Å) and angles (°): V–N(1) 1.693(7), V–N(2) 2.364(7), V–N(3) 1.895(6), V–N(4) 1.897(5), V–N(5) 1.898(6), V–N(1)–C(6) 173.0(5), V–N(3)–Si(1) 129.8(4), V–N(4)–Si(2) 126.1(3), V–N(5)–Si(3) 123.9(3), N(1)–V–N(2) 177.3(2), N(1)–V–N(3) 104.0(3), N(1)–V–N(4) 100.5(3), N(1)–V–N(5) 102.5(3).

equiv.) to afford the vanadium(V)–rhodium(I) bimetallic species **2** (*Scheme 1*).§

The IR spectrum of **2** (Nujol mull) displays ν(CO) bands at 2105(s), 2025(sh), and 2000(s) cm^{-1}. A comparison of these values to those of $[Rh(CO)_2Cl(py)]$[10] [2075(s), 2060(m), 2010(vs), 1980(m)] suggests that **1** is a somewhat better π-acceptor than pyridine. The ^{51}V NMR resonance of **2** appears at δ −106.7, *ca.* 40 ppm downfield of that for **1**. In the ^1H NMR spectrum of **2**, the resonances for the *p*-pyridylimido and the $[N_3N]$ ligand portions are both shifted upfield with respect to their positions in the spectrum of **1**.

Preliminary results indicate that **1** can bind at high valent metal centres also: reaction of **1** with the d^0-W^{VI} organoimido system $[Et\text{-}N{\equiv}WCl_4]_2$[11] affords a black crystalline adduct **3** (Scheme 1), with δ(^{51}V) −101.3. In contrast to the spectral changes observed upon formation of **2**, the ^1H NMR spectrum of **3** reveals downfield shifts for the resonances of the ethylimido and pyridylimido ligands as compared to those of the free precursors.¶

Given the broad development of organoimido systems and the variety of preparative routes available,[12] we expect that a rich chemistry will develop employing pyridylimido and related remotely functionalized imido systems, but the inherent difunctionality of any pyridylimido delivery reagent can introduce synthetic obstacles. For example, reaction of $[WCl_2(PMePh_2)_4]$ with the *p*-pyridyl phosphinimine reagent $Ph_3P{=}Npy$ affords only the adduct $[WCl_2(PMePh_2)_3(Ph_3P{=}Npy)]$, and not the W^{IV} pyridylimido system, in contrast to the corresponding reaction using $MePh_2P{=}NTol$.[13] Further investigations of **1** and other pyridylimido systems are under way.

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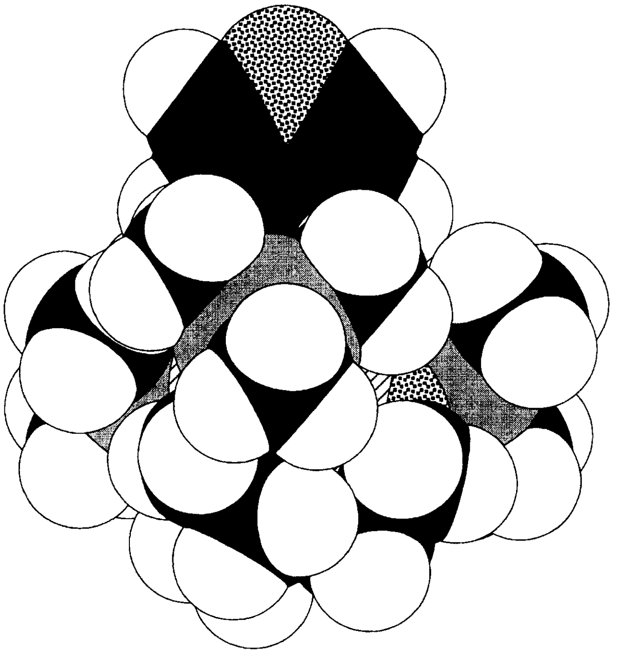

Fig. 2 Space-filling representation of **1**. Atoms are depicted as follows: ⊘ = V; ⊛ = N; ● = C; ◍ = Si; ○ = H.

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Footnotes

† *Selected data* for $C_{20}H_{43}N_6Si_3V$ **1**: Anal. Calcd. (Found) C 47.78 (47.07), H 8.62 (8.55), N 16.71 (16.50); ^1H NMR (C_6D_6, 296 K) δ 8.65 (d, 2H, C_5H_4N), 7.30 (d, 2H, C_5H_4N), 3.32 (t, 6H, CH_2), 2.38 (t, 6H, CH_2), 0.24 [s, 27H, $Si(CH_3)_3$]; ^{51}V NMR (C_6D_6, 300 K) δ −146.5 (1:1:1 triplet, $^1J_{^{14}N\text{-}^{51}V}$ 89 Hz).

‡ *Crystal data* (225 K) for $C_{20}H_{43}N_6Si_3V$, **1**: red–black blocks, orthorhombic, *Pna* 2_1, $a = 21.274(6)$, $b = 11.030(4)$, $c = 12.069(4)$ Å, $V = 2831.9(17)$ Å^3, $Z = 4$, μ(Mo-Kα) = 4.95 cm^{-1}; 3739 reflections (3406 independent) were collected ($4 \leq 2\theta \leq 55°$), of which 2376 with $F_o > 4\sigma(F_o)$ were used in refinement. Refinement in the centrosymmetric space group alternative *Pnma* was also explored and was abandoned when a chemically unreasonable structure resulted. All non-hydrogen atoms were refined with anisotropic displacement coefficients. H atoms were treated as idealized contributions. $R = 0.0549$ and $R_w = 0.0610$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Selected data* for $C_{22}H_{43}N_6O_2ClSi_3VRh$, **2**: Anal. Calcd. (Found) C 37.90 (37.52), H 6.22 (6.27), N 12.05 (12.10); ^1H NMR (C_6D_6, 296 K) δ 8.38 (d, 2H, C_5H_4N), 7.04 (d, 2H, C_5H_4N), 3.25 (t, 6H, CH_2), 2.33 (t, 6H, CH_2), 0.12 [s, 27H, $Si(CH_3)_3$]; ^{51}V NMR (C_6D_6, 300 K) δ −106.7.

¶ *Selected data* for **3**: ^1H NMR (C_6D_6, 296 K) δ 9.76 (d, 2H, C_5H_4N), 7.36 (d, 2H, C_5H_4N), 6.30 (q, 2H, CH_2CH_3), 3.30 (t, 6H, CH_2), 2.30 (t, 6H, CH_2), 1.06 (t, 3H, CH_2CH_3) 0.09 [m, 27H, $Si(CH_3)_3$]; ^{51}V NMR (C_6D_6, 300 K) δ −101.3.

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