the van der Waals S-atom radius sum of 3.60 Å (shortest intrastack distance 3.759 (1) Å).[11] One of the ethylene groups of the ET molecule is disordered. The corresponding "corrugated sheet" network of S–S interactions, through which electrical conduction likely occurs, and which lie principally along the *a* and *b* axes, is shown in Figure 1. The four shortest interstack interaction distances range from 3.574 (1) to 3.599 (1) Å. Preliminary X-ray investigations at 125 K reveal satellite reflections for all zones of diffraction vectors, indicating the presence of a complex modulated superstructure for at least the I_3^- anions. A full structural study at 125 K is presently under way.

While the previous workers[4] used four-probe resistivity measurements to identify ambient-pressure superconductivity in $(ET)_2I_3$, we have used RF penetration depth measurements,[12,13] performed as a function of temperature in a pumped helium cryostat containing either ^3He or ^4He. Temperatures were determined by vapor phase pressure thermometry. Measurements in superfluid ^4He showed the onset temperature for bulk superconductivity in the distorted-hexagon-shaped crystals to be 1.40 ± 0.02 K (see also ref 10). Separate measurements in pumped ^3He show, as illustrated in Figure 2, a broad transition that is not complete at the lowest temperature obtained, 0.44 K. Qualitatively, the RF frequency vs. temperature data are similar to those for slow-cooled $(TMTSF)_2ClO_4$, which we have also determined.[14] The onset temperature in the $(ET)_2I_3$ salt is slightly lower than that reported earlier from four-probe resistivity measurements. This difference is consistent with a broad transition width, which allows a low-resistance filament to be detected resistively before the superconductivity in the bulk of the sample can be detected inductively. Details of the RF penetration depth measurements of the superconducting transition temperature and critical magnetic field are given elsewhere.[14] Finally, a number of new $(ET)_x(I_yBr_z)$ derivatives are presently being characterized which are ambient-pressure superconductors. The transition temperatures, measured by RF penetration depth, range from 2.3 K to, in one sample, 4.2 K.

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Registry No. $(ET)_2I_3$, 89061-06-3; ET, 66946-48-3; $(n\text{-}Bu_4N)I_3$, 13311-45-0.

Supplementary Material Available: Table of final positional parameters and anisotropic temperature factors at 298 K (1 page). Ordering information is given on any current masthead page.

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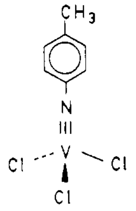
Preparation, Chemistry, and ^{51}V NMR Spectroscopy of (*p*-Tolylimido)vanadium(V) Complexes

Sir:

Despite the current interest in transition-metal organoimido species, there are only a few well-characterized vanadium(V) organoimido complexes.[1] Moreover, there has been virtually no chemistry reported for these compounds since the majority of them are thermally unstable and often decompose to yield polymeric materials. We now report our preparation, characterization, and preliminary chemical investigations of (*p*-tolylimido)vanadium trichloride, $V(Ntol)Cl_3$ (**1**), a readily prepared, thermally stable species that provides a convenient entry into vanadium(v) organoimido chemistry.[2]



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In a typical preparation, a solution of *p*-tolyl isocyanate (60 mmol) in octane (10 mL) was added, under an N_2 atmosphere, to a solution of $VOCl_3$ (40 mmol) in octane (50 mL) and refluxed for 3 h, resulting in copious evolution of CO_2 and forming a dark green solution.[3] After removal of solvent and drying at 110 °C in vacuo overnight, the dark residue was sublimed at 130 °C (10^{-4} torr) onto a water-cooled probe to yield 9.1 g (87%) of **1** as large, glistening purple-black crystals.[4] The mass spectrum of **1** (determined at 35 °C) reveals only the expected mononuclear isotopomers to be present. While all of the complexes described herein possess excellent thermal stability, they all are exceedingly moisture sensitive; their solutions acquire an intense violet color immediately upon exposure.

$V(Ntol)Cl_3$, with a formal 12-electron configuration, behaves as a Lewis acid and readily forms addition complexes with donor ligands. Thus, dissolution of **1** in THF, followed by slow admission of hexane, affords orange crystalline $V(Ntol)Cl_3(THF)$.[5] The reaction of **1** with PPh_3 in CH_2Cl_2 similarly yields $V(Ntol)Cl_3(PPh_3)$ as khaki-colored microcrystals.[6] The isolation of these monoadducts is surprising, given the electron deficiency of **1** and in view of the chemistry

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(2) A related species, $V(NC_6H_5)Cl_3$, was reported by Slawisch[1c] to be polymeric. $V(NC_6H_5)Cl_3$ has also been mentioned by Bradley and co-workers,[1f] but no details were given and the compound was apparently contaminated with phenyl isocyanate.

(3) For other examples of the use of isocyanates in the preparation of organoimido complexes see, e.g.: (a) Kolomnikov, I. S.; Koreshkov, Y. C.; Lobeeva, T. S.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432. (b) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J. *Ibid.* **1981**, 103. (c) Pederson, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

(4) Anal. Calcd for $C_7H_7NCl_3V$: C, 32.04; H, 2.69; N, 5.34. Found: C, 32.25; H, 2.91; N, 5.62. ^1H NMR ($CDCl_3$, 25 °C): δ 7.33 (q, 4 H, J_{AB} = 7.8 Hz, $C_6H_4CH_3$), 2.53 (s, 3 H, $C_6H_4CH_3$).

(5) Anal. Calcd for $C_{11}H_{15}NOCl_3V$: C, 39.49; H, 4.52; N, 4.19. Found: C, 39.48; H, 4.63; N, 4.15. ^1H NMR ($CDCl_3$, 25 °C): δ 7.42 (q, 4 H, J_{AB} = 8.3 Hz, $C_6H_4CH_3$), 4.34 (t, 4 H, $\overline{OCH_2(CH_2)_2C}H_2$), 2.55 (s, 3 H, $C_6H_4CH_3$), 2.06 (quintet, 4 H, $\overline{OCH_2(CH_2)_2C}H_2$).

(6) Anal. Calcd for $C_{25}H_{22}NPCl_3V$: C, 57.22; H, 4.23; N, 2.67. Found: C, 57.43; H, 4.46; N, 2.69. ^1H NMR ($CDCl_3$, 25 °C): δ 7.65–7.38 (m, 15 H, $P(C_6H_5)_3$), 7.13 (q, 4 H, J_{AB} = 8.2 Hz, $C_6H_4CH_3$), 2.47 (s, 3 H, $C_6H_4CH_3$).

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Table I. ^{51}V Chemical Shifts in Vanadium(V) Imido Species[a]

complex	chem shift, ppm	$\Delta\nu_{1/2}$, Hz
$V(Ntol)Cl_3$	305	500
$V(Ntol)Cl_3(THF)$	374	1900
$V(Ntol)Cl_3(PPh_3)$	392	700
$V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$	−171	500
$V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$	−472	390
$V(Ntol)(O\text{-}t\text{-}Bu)_3$	−654[b]	90
$V(Ntol)(\eta^5\text{-}C_5H_5)Cl_2$	−240	790

[a] Chemical shifts relative to external $VOCl_3/CDCl_3$ (75% v/v). Positive values denote downfield shifts. All spectra were determined as $CDCl_3$ solutions at 105.2 MHz at 25 °C. (b) This signal is a triplet with $^1J_{^{14}N-^{51}V} = 111$ Hz.

displayed by the isoelectronic $VOCl_3$ species that typically forms diadducts of the form $VOCl_3{\cdot}2L$.[7]

Preliminary studies have revealed that the chloride ligands in **1** are prone to substitution under mild conditions. Thus, the room-temperature reaction of **1** with 1, 2, or 3 equiv of potassium *tert*-butoxide in THF affords the imido alkoxides $V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$[8], $V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$,[9] and $V(Ntol)(O\text{-}t\text{-}Bu)_3$[10] as purple, orange, and yellow crystals, respectively. The reaction of **1** with NaC_5H_5 in THF yields $(\eta^5\text{-}C_5H_5)V(Ntol)Cl_2$,[11] a rare[12] example of an organometallic derivative of vanadium(V).

We have also examined the ^{51}V NMR spectra of **1** and its derivatives (Table I). Until now, the only ^{51}V chemical shift data reported for vanadium(V) complexes has concerned oxo species.[13] Inspection of the data in Table I reveals that the substitution of the *p*-tolylimido group for an oxo ligand has a dramatic effect on both the ^{51}V chemical shift and the line widths of the resonances (cf. the data for **1** with δ 305 and $\Delta\nu_{1/2} = 500$ Hz vs. $VOCl_3$ with δ 0 and $\Delta\nu_{1/2} = 23$ Hz). The downfield chemical shifts observed for **1** and its Lewis base adducts are unusual in ^{51}V NMR spectroscopy; the only other species known to resonate in this region is $VOBr_3$. In ^{51}V NMR studies of VOX_3 species (X = F, Cl, Br), it has been established that V(V) is one of the few nuclei to display an inverse halogen dependence, i.e., $\delta(OVBr_3) < \delta(OVCl_3) < \delta(OVF_3)$. This ordering has been interpreted in terms of decreasing paramagnetic contributions to the nuclear shielding constant.[13d] The intense colors of **1** and its derivatives (which, in these d^0 complexes, must arise from charge transfer) connote the presence of low-lying electronic excited states, thus implying a large paramagnetic component in their nuclear shieldings. We attribute the relatively large line widths observed for the present complexes to enhanced quadrupolar broadening ($Q(^{51}V) = 0.3$ b) as a result of the lowering of symmetry (assumed to be C_s) imposed by the *p*-tolylimido group. Except in the case of $V(Ntol)(O\text{-}t\text{-}Bu)_3$, the line widths observed are sufficiently large so as to obscure $^{51}V-^{14}N$ coupling, which has been reported to be 95 Hz in the compound $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$.[1d,14]

Further studies of the spectroscopy and reactivity of these and related species are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research at Kansas State University for support of this research. We thank Dr. W. A. Nugent and Dr. T. H. Tulip of E. I. du Pont de Nemours and Co., Inc., for helpful discussions. The WM-400 NMR spectrometer employed in this work was purchased with the assistance of an NSF instrumentation award.

Registry No. **1**, 90941-76-7; $V(Ntol)Cl_3(THF)$, 90941-80-3; $V(Ntol)Cl_3(PPh_3)$, 90941-81-4; $V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$, 90941-77-8; $V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$, 90941-78-9; $V(Ntol)(O\text{-}t\text{-}Bu)_3$, 90941-79-0; $V(Ntol)(\eta^5\text{-}C_5H_5)Cl_2$, 90941-82-5; $VOCl_3$, 7727-18-6; *p*-tolyl isocyanate, 622-58-2.

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(8) Anal. Calcd for $C_{11}H_{16}NOCl_2V$: C, 44.03; H, 5.37; N, 4.67. Found: C, 44.26; H, 5.33; N, 4.80. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.19 (q, 4 H, $J_{AB} = 8.2$ Hz, $C_6H_4CH_3$), 2.42 (s, 3 H, $C_6H_4CH_3$), 1.61 (s, 9 H, $OC(CH_3)_3$).

(9) Anal. Calcd for $C_{15}H_{25}NO_2ClV$: C, 53.34; H, 7.46; N, 4.15. Found: C, 53.29; H, 7.49; N, 4.59. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.11 (q, 4 H, $J_{AB} = 8.3$ Hz, $C_6H_4CH_3$), 2.36 (s, 3 H, $C_6H_4CH_3$), 1.50 (s, 18 H, $OC(CH_3)_3$.

(10) Anal. Calcd for $C_{19}H_{34}NO_3V$: C, 60.79; H, 9.13; N, 3.73. Found: C, 60.93; H, 9.05; N, 3.90. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.08 (q, 4 H, $J_{AB} = 8.3$ Hz, $C_6H_4CH_3$), 2.33 (s, 3 H, $C_6H_4CH_3$), 1.42 (s, 27 H, $OC(CH_3)_3$).

(11) This procedure yields $(\eta^5\text{-}C_5H_5)V(Ntol)Cl_2$ as black microcrystals. We have not yet succeeded in obtaining an analytical sample of this material, owing to the presence of a persistent impurity that appears at δ 1.26 (s) in the ^{1}H NMR spectrum. The intensity of this peak is ca. 5% of the C_5H_5 resonance. Alternative synthetic routes are being explored. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.13 (q, 4 H, $J_{AB} = 8.0$ Hz, $C_6H_4CH_3$), 6.58 (s, 5 H, C_5H_5), 2.44 (s, 3 H, $C_6H_4CH_3$).

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(14) Note, however, that the complex $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$ should possess C_{3v} symmetry and consequently a relatively narrow ^{51}V resonance, thus permitting the observation of coupling to ^{14}N.

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Characterization of a True Intermediate-Spin (Porphinato)iron(III) Complex

Sir:

Intermediate-spin (porphinato)iron(III) complexes have been accorded considerable interest. Their properties may be relevant to the behavior of certain biologically important heme-containing proteins,[1-4] and the physical chemistry of this infrequently encountered species is not well described.

At ambient temperatures, all of the intermediate-spin (tetraarylporphinato)iron complexes reported to date are accurately characterized as quantum-mechanical $S = {}^3/_2, {}^5/_2$ spin-state admixtures.[5-8] If one starts from a high-spin ferric configuration, the $S = {}^3/_2, {}^5/_2$ admixture is attained through weak axial ligation of the perchlorate ion. Porphyrin core contraction that accompanies an increased attraction between iron and the pyrrole nitrogens destabilizes the iron $d_{x^2-y^2}$ atomic orbital to the extent that partial demotion of the electron to

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