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Synthesis and Crystal Structure of Unprecedented Phosphine Adducts of d^1-Aryl Imido–Vanadium(IV) Complexes

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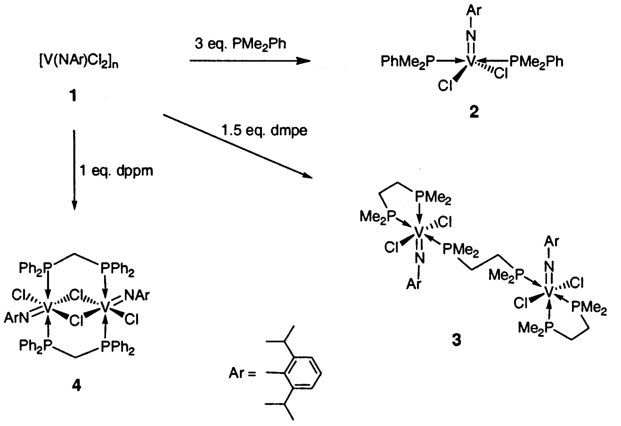
The reaction of the imido precursor $[V(NAr)Cl_2]_n$ (**1**) (Ar = 2,6-i-$Pr_2C_6H_3$) with 3 equiv of PMe_2Ph yields the monomeric complex $[V(=NAr)Cl_2(PMe_2Ph)_2]$ (**2**). Reacting **1** with 1.5 equiv of dmpe or 1 equiv of dppm affords the dimeric complexes $[V(=NAr)Cl_2(dmpe)]_2(\mu$-$P,P'$-dmpe) (**3**) and $[V(=NAr)Cl_2(dppm)]_2$ (**4**), respectively. Complexes **2**–**4** have been fully characterized by spectroscopic methods, magnetism studies, and X-ray crystallography.

Oxo and imido ligands are particularly suitable for the stabilization of transition metals in their high oxidation states because of their ability to participate in extensive ligand-to-metal π donation.[1] Transition metal imido complexes have been a focus of considerable activity over the past two decades;[1,2] the imido ligand has the advantage that it contains an organic substituent through which the steric and electronic properties of the complex may be influenced. The use of imido ligands in vanadium(V) chemistry is well documented,[3−5] and in some cases rare alkylvanadium(V) complexes have been obtained.[6,7] Although imido-bridged vanadium(IV) dimers are known, they often were accidentally prepared from the reactions of vanadium(V) precursors with alkylating agents.[8] Moreover, terminal imido vanadium(IV) complexes are still rare.[4,9,10]

Scheme 1. Synthesis of Aryl Imido−Vanadium(IV) Phosphine Adducts



As part of an ongoing study of vanadium complexes with various supporting ligand environments,[11−14] we recently described the synthesis and molecular structure of the new terminal imido complex $[V(=NAr)Cl_2(NHMe_2)_2]$ (Ar = 2,6-i-$Pr_2C_6H_3$),[10a] one of the very few Cp-free vanadium(IV) terminal imido compounds that have been structurally characterized,[4,9,10] and we embarked on the coordination chemistry of these new compounds toward neutral N-donor ligands (pyridine, bipyridine, tmeda).[10b] In addition, early transition metal species in their high oxidation states containing phosphine ligands are uncommon,[15] and consequently

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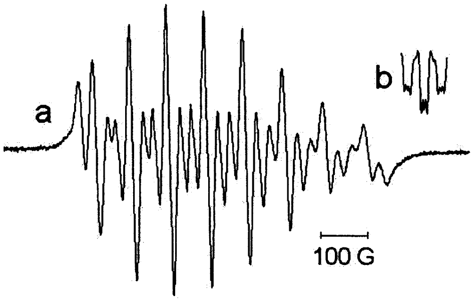

Figure 1. EPR (X band) of a dichloromethane solution of **2** at room temperature: (a) first-derivative spectrum; (b) a part of the second-derivative spectrum showing the superhyperfine coupling of the unpaired electron of the vanadium atom with the nitrogen atom (^{14}N nucleus, $I = 1$) of the imido group.

information on vanadium(IV) phosphine adducts are still scarce; as a typical example, a common feature of all reactions of VCl_4 with phosphines is reduction of vanadium from V(IV) to V(III).[16] This prompted us to investigate the chemical reactivity of our d^1 vanadium imido compounds versus monophosphines and bidentate diphosphines to determine whether the imido group may help to stabilize a V(IV) compound having a V−P bond. Here we present the synthesis, molecular structure, and EPR spectroscopy of the first recorded examples of phosphine imidovanadium(IV) complexes.

The imido complex $[V(NAr)Cl_2]_n$ (**1**) (Ar = 2,6-i-$Pr_2C_6H_3$)[10b] was reacted with 3 equiv of PMe_2Ph in dichloromethane at room temperature for 3 days (Scheme 1). The initial red-purple color of the solution turned dark yellow. Removal of the volatiles under vacuum followed by washing the solid with pentane afforded an analytically pure sample of $[V({=}NAr)Cl_2(PMe_2Ph)_2]$ (**2**) in good yield (86%). Recently, a complex formulated as $[V(N\text{-}t\text{-}Bu)Cl_2(PEt_3)_2]$ was described,[4c] but no fully reliable characterization was available. The magnetic moment is consistent with a d^1 electronic configuration ($\mu_{eff} = 1.77\ \mu_B$) showing that the oxidation state +IV is maintained. The well-resolved electron paramagnetic resonance (EPR) spectrum of **2** at room temperature in dichloromethane solution (Figure 1) revealed a resonance at $g = 1.993$ with the characteristic octet pattern ($A_{iso}(^{51}V) = 83$ G) expected for the interaction of an unpaired electron of V^{IV} with the ^{51}V nucleus ($I = {}^7/_2$). Each of the eight vanadium lines is further split into a 1:2:1 triplet ($A_{iso}(^{31}P) = 30$ G); the hyperfine structure is attributed to two equivalent phosphorus nuclei of the phosphine ligands. In the second derivative spectrum, a superhyperfine coupling of the unpaired electron of the vanadium atom with the N imido group (^{14}N nucleus, $I = 1$) gives rise to a typical 1:1:1 triplet ($A_{iso}(^{14}N) = 5$ G).

Crystals of **2** suitable for a crystal structure determination were obtained from a cold (−20 °C) toluene−pentane solution of **2**. An ORTEP drawing of the molecule is shown in Figure 2 with important interatomic distances and angles. Complex **2** is best described as a distorted trigonal bipyramid with equatorial arylimido and chlorine atoms. The imido linkage exhibits a short vanadium−nitrogen distance of 1.663(6) Å and is almost linear [V1−N1−C1 = 175.5(5)°], which is consistent with the lone pair on nitrogen being donated to an acceptor orbital on vanadium. Hence the imido V−N bond can be considered as a triple bond. The two chlorine atoms are mutually cis with a Cl1−V−Cl2 angle of 129.03(9)° and mean V−Cl bonds of 2.311(3) Å. The two axial phosphine ligands are mutually trans [P1−V1−P2 = 165.50(8)°] with V−P distances of 2.517(2) Å (V−P1) and 2.489(2) Å (V−P2).

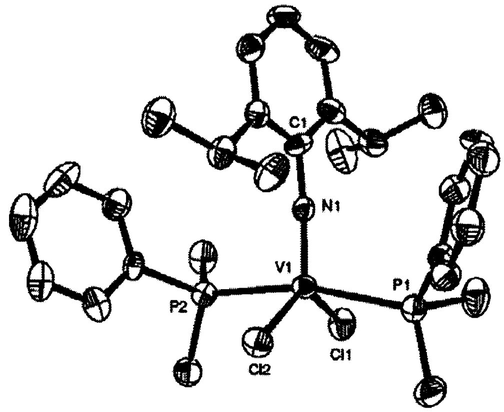

Figure 2. Molecular structure of **2**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−N1 1.663(6), V1−Cl1 2.318(2), V1−Cl2 2.303(2), V1−P1 2.517(2), V1−P2 2.489(2), N1−C1 1.391(9), Cl1−V1−Cl2 129.03(9), P1−V−P2 165.50(8), V1−N1−C1 175.5(5).

Addition of 1.5 equiv of bis(dimethylphosphino)ethane (dmpe) to a dichloromethane solution of the imido compound **1**, followed by addition of pentane, causes the crystallization of dark yellow crystals of **3** (CH_2Cl_2 solvate). As revealed by an X-ray structure determination, **3** is a dimer of formula $[V({=}NAr)Cl_2(dmpe)]_2(\mu\text{-}P,P'\text{-}dmpe)$, containing one chelating dmpe ligand, two chlorine atoms, and one imido group per vanadium atom, plus an additional dmpe bridging the two vanadium(IV) centers. This is different from what has been observed on V(V) imido chemistry giving a 1:1 adduct.[17] The molecular structure is shown in Figure 3 with selected bond distances and angles. Each vanadium atom has a pseudo-octahedral geometry with a practically linear metal−imido moiety (V1−N1−C1 = 178.8(4)°; V−N1 = 1.691(5) Å) and a trans arrangement of the chloride ligands (mean V−Cl = 2.394(3) Å, Cl1−V1−Cl2 = 159.13(8)°). The chelating bidentate dmpe ligand (P1−V1−P2 = 78.62(7)°) is nonsymmetrically coordinated to the vanadium atom with a normal V1−P1 distance of 2.484(2) Å and an unusually larger V1−P2 bond length of 2.689(2) Å for the phosphorus atom trans to the imido group, reflecting the trans effect of the imido group that we have already observed in our octahedral imido−vanadium complexes.[10b] There is only one other group 5 imido complex containing a phosphine functionality occupying the trans position with respect to imido ligand.[17] The phosphorus atoms (P3) of the bridging

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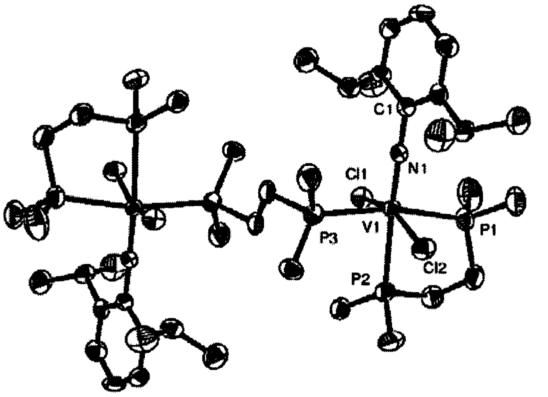

Figure 3. Molecular structure of **3**, showing 50% probability ellipsoids and partial atom-labeling schemes. Dichloromethane solvent and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−N1 1.691(5), V1−Cl1 2.400(2), V1−Cl2 2.387(2), V1−P1 2.484(2), V1−P2 2.689(2), 2.497(2), N1−C1 1.407(8), Cl1−V1−Cl2 159.13(8), P1−V−P2 78.62(7), V1−N1−C1 178.8(4), P1−V1−P3 168.54(8), P1−V1−N1 97.44(17).

dmpe ligand are in an equatorial position, trans to one phosphorus atom of the chelated dmpe (P1) with a normal V−P distance of 2.497(2) Å. The distance between two vanadium centers is 7.832 Å. The two V^{IV} centers are magnetically independent with a magnetic moment μ_{eff} of 1.83 μ_B at 298 K for the monomer unit.[18]

In a last experiment, complex **1** was reacted with 1 equiv of bis(diphenylphosphino)methane (dppm) in dichloromethane at room temperature. Concentration of the solution under vacuum followed by slow addition of pentane caused the crystallization of yellow-brown crystals of complex **4**. As expected due to the ability of dppm to bridge dimeric complexes,[19] the structure was assigned as being the dimer compound $[V({=}NAr)Cl_2(\mu\text{-dppm})]_2$ on the basis of spectral and analytical data, and from an X-ray crystallographic structure determination. The atom-labeling scheme is defined in Figure 4 with selected bond distances and angles. The molecule of **4** is a slightly distorted edge-sharing bioctahedron that resides on a crystallographic inversion center. Each vanadium atom is coordinated to one imido group, one chlorine atom, two bridging chloride ligands, and two phosphorus atoms of the two bridging dppm ligands. The quasi-linear arylimido moiety (V1−N1−C1 = 175.6(3)°, V1−N1 = 1.685(3) Å) is almost in the same plane of the V_2Cl_2 core and the terminal chlorine atom. The terminal vanadium−chlorine bond is longer than the bridged ones (V1−Cl1 = 2.3396(14) Å compared to V1−Cl2 = 2.4128(14) Å and V1−Cl2′ = 2.5365(15) Å). The chelating dppm ligands are placed perpendicular to the plane of the V_2Cl_2 core with vanadium−phosphorus distances of 2.6068(15) Å (V1−P1) and 2.5452(15) Å (V1−P2). The length of the V···V′ vector, 3.807 Å, rules out any significant metal−metal bonding interaction.

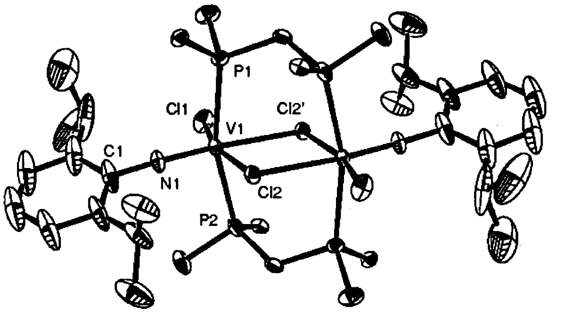

Figure 4. Part of the molecular structure of **4**, showing 50% probability ellipsoids and partial atom-labeling schemes. Dichloromethane solvent, part of the Ph carbon atoms on dppm ligands, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−N1 1.685(3), N1−C1 1.396(6), V1−Cl1 2.3396(14), V1−Cl2 2.4128(15), V1−Cl2′ 2.5365(15), V1−P1 2.6068(15), V1−P2 2.5452(15), V1−N1−C1 175.6(3), N1−V1−Cl2 100.13(14), Cl1−V1−Cl2 164.07(5), P1−V1−P2 163.80(5).

The magnetic susceptibility χ_M of **4** has been measured in the 2−300 K temperature range in a 1 T applied magnetic field. The effective moment μ_{eff} is 1.87 μ_B at 300 K for the monomer unit, in agreement with two independent d^1-vanadium(IV) species. μ_{eff} is practically constant from room temperature to 30 K and then decreases to a value of 0.13 μ_B at 2 K, reflecting a weak antiferromagnetic interaction ($J = -19.5$ cm^{-1}).[20]

In conclusion, we have shown that the first reported phosphine vanadium(IV) imido complexes are accessible without reduction at the metal center. Different structural organizations were observed according to the nature of the phosphine used. This feature demonstrated the great importance of the structural characterizations in this chemistry of paramagnetic vanadium(IV) compounds in which original and unexpected structures are often obtained. We firmly believe, as verified by other recent works on vanadium(IV) chemistry,[21] that significant advances could only be made if the structural characterization of the related paramagnetic complex is ascertained. Future studies will be directed toward alkylation of these promising phosphine adducts and their applications. The different geometries resulting from the particular phosphine that is used suggest that there will be structural diversity in the chemistry as well.

Supporting Information Available: Full details for experimental procedures and crystallographic data for compounds **2**−**4**, including ORTEP diagrams, tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) **3** is insoluble in most common organic solvents, except in dichloromethane, where it is, however, not stable very long, with precipitation of insoluble material (possibly following decoordination of one dmpe ligand or resulting from an equilibrium mixture in solution). As a result, interpretation of the EPR spectrum of this complex was not possible.

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(20) Complex **4** is insoluble in most common organic solvents, including THF, dichloromethane, and acetonitrile; therefore, recording its EPR spectrum in solution has not been possible.

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