Imido-Bridged Homo- and Heterobimetallic Complexes

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S *Supporting Information*

ABSTRACT: Transamination reactions of primary amines with group 4 and 5 amido precursors $M(NMe_2)_4$ have been studied to prepare homo- and heterobimetallic complexes $[(Me_2N)_2M^1(\mu\text{-}NR^1)(\mu\text{-}NR^2)M^2(NMe_2)_2(NHMe_2)_x]$ ($x = 0, 1$) with two identical or distinct bridging imido ligands.

Transition-metal imido complexes have been actively studied in the past 2−3 decades, in great part because of their ability to promote a variety of transformations in which the imido ligand is directly involved in the reactivity or may act as a spectator ligand.[1,2] The imido ligand is particularly suitable for stabilization of transition metals in their highest oxidation states because of their ability to participate in extensive ligand-to-metal π donation.[3] Furthermore, the imido group presents the advantage of possessing an organic substituent, through which the steric and electronic properties of the complexes may be influenced in order to tune its (stoichiometric or catalytic) reactivity.

We have previously described the one-pot synthesis [from $M(NMe_2)_4$, RNH_2, and Me_3SiCl], coordination chemistry, and catalytic applications of titanium(IV) and vanadium(IV) imido complexes of the general formula $M(=NR)Cl_2(NHMe_2)_2$ (M = Ti, V).[2f,4] During these studies, we were confronted with the mechanism of formation of the imido group.[5] The initial step in the formation of such species from $M(NMe_2)_4$ precursors involves a transamination reaction with a primary amine, and in some cases, imido-bridged dimeric complexes $\{M(\mu\text{-}NR)(NMe_2)_2\}_2$ have been isolated (Scheme 1), although their involvement as intermediates in the reaction described above is not ascertained.[4a,5] Although imido-bridged group 4 metal complexes have been known for almost 50 years by the pioneer work of Bradley and Torrible[6] and subsequent studies by Nugent et al.,[7] they are currently less studied than terminal imido analogues (and they were often obtained while seeking complexes with a terminal imido function).[8] We are currently exploring potential extensions of such dimeric complexes toward more complex structures. In this report, we describe an investigation that has led to insight into the synthesis of unprecedented *homo-* and *hetero*bimetallic complexes with two *identical* or *distinct* bridging imido ligands.[9] Herein we report our initial efforts toward this goal.

$Ti(NMe_2)_4$ (2 equiv) reacts readily with 1 equiv of the substituted aniline $2,6\text{-}^iPr_2C_6H_3NH_2$ ($Ar^{iPr_2}NH_2$) followed by 1 equiv of alkylamine 1-adamantanamine ($AdaNH_2$), at room temperature in toluene, to yield the corresponding homobimetallic complex **1**. **1** crystallizes from the solution as red large

Scheme 1. Formation of Imido-Bridged Group 4 Complexes

$$2\ M(NMe_2)_4 + 2\ RNH_2 \xrightarrow{-4\ NHMe_2} \{M(\mu\text{-}NR)(NMe_2)_2\}_2$$

Scheme 2. Synthesis of Homo- and Heterobimetallic Imido Dimers
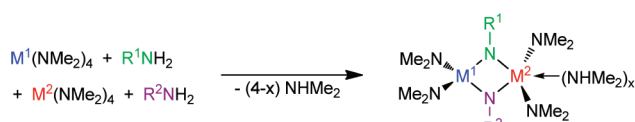
	M^1	M^2	R^1	R^2	x	yield (%)
1	Ti	Ti	Ar^{iPr_2}	Ada	0	66
2	V	V	Ar^{iPr_2}	Ada	0	10
3	Ti	Zr	Ar^{iPr_2}	Ar^{iPr_2}	1	65
4	Ti	Hf	Ar^{iPr_2}	Ar^{iPr_2}	1	63
5	Ti	Zr	Ar^{iPr_2}	Ada	1	44

crystals in reasonable yield (Scheme 2). In a similar fashion, the vanadium analogue precursor $V(NMe_2)_4$ affords a mixture of complexes.[10] Nevertheless, after suitable workup, the expected parent compound **2** was obtained as dark-red crystals albeit in very low yield. Both **1** and **2** were characterized to be the dimers $\{M_2(\mu\text{-}NAr^{iPr_2})(\mu\text{-}NAda)(NMe_2)_4\}$ (M = Ti, V); this formulation follows from spectroscopic data (see below) and elemental analysis and has been confirmed unequivocally through crystal structure determinations.

Figure 1 shows the molecular structure of **1**. It clearly demonstrates the compound to be the dimer formulated as $\{Ti_2(\mu\text{-}NAr^{iPr_2})(\mu\text{-}NAda)(NMe_2)_4\}$ with two *distinct* imido ligands bridging two $(Me_2N)_2Ti$ moieties. The coordination geometry of both titanium centers is distorted tetrahedral (although Ti2 may be regarded as five-coordinated; see below). The Ti_2N_2 core displays a considerable asymmetry in one of its Ti−N−Ti bridges (namely, $\mu\text{-}NAr^{iPr_2}$), both in the Ti−N distances [Ti1−N1 = 1.8611(16) Å; Ti2−N1 = 2.0410(17) Å] and in the distortion, which brings the arylimido C_{ipso} to within the η^2-bonding distance of Ti2. The $\mu\text{-}[\eta^1\text{-}(N):\eta^2(N,C)]$-bonding mode exhibited by the μ-arylimido ligand includes the following structural features: (i) The Ti2−C1 distance is 2.6443(19) Å. (ii) The shorter $Ti\text{-}N_{imido}$
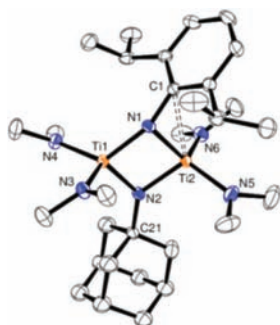
Figure 1. Thermal ellipsoid plot of **1** with partial atom labeling. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms bonded to carbon atoms are omitted.
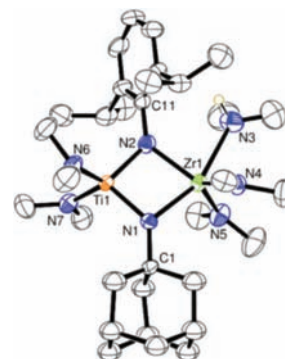

Figure 2. Thermal ellipsoid plot of **5** with partial atom labeling. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms bonded to carbon atoms are omitted. Hydrogen atoms bonded to nitrogen atoms are drawn as spheres of arbitrary radius.

distance of 1.8611(16) Å is longer by ca. 0.15 Å than that in terminal imido complexes.[3,4b] (iii) The nearly linear Ti1−N1−C1 bond angle of 159.37(14)° leads to an acute Ti2−N1−C1 of 98.42(11)° and contrasts with the more symmetric Ti−N_{Ada}−Ti bridge, where Ti−N−C angles are 131.40(12)° and 133.15(13)° associated with Ti−N_{Ada} bond distances of 1.9554(16) and 1.8978(16) Å, respectively for Ti1 and Ti2. Although unusual, this type of μ-$[\eta^1(N):\eta^2(N,C)]$-bonding mode for a μ-arylimido ligand is not unprecedented.[11] The Ti_2N_2 core is almost planar (torsion angle Ti1−N1−Ti2−N2 = 0.43°) and is characterized by a short Ti···Ti distance of 2.8096(5) Å common in imido dimers.[4b,7a−7c] The angles formed by bridging nitrogen atoms with two titanium atoms [Ti1−N1−Ti2 = 91.99(7)°; Ti1−N2−Ti2 = 93.62(7)°] deviate significantly from that expected for an sp^2 nitrogen atom. The $(Me_2N)_2Ti$ moiety is normal, with the expected Ti−N bond distances and angles [Ti−N_{amido} ranging from 1.810 to 1.926 Å].

The molecular structure of **2** is given in SI. The complex is a dimer with two imido ligands bridging two $(Me_2N)_2V$ moieties with tetrahedrally coordinated vanadium centers. The V−N_{imido} bond distances are in the range of those found in related arylimido dimers [V1−N1 = 1.907(8) Å; V2−N1 = 1.832(8) Å; V1−N2 = 1.809(9) Å; V2−N2 = 1.872(9) Å].[1j,4a] The main difference observed in the structure of **2** versus **1** is a more symmetric arrangement of the bridging arylimido ligand. Because titanium and vanadium have almost identical ionic radii, the symmetry in **2** cannot be explained by steric factors but should result from electronic differences due to less Lewis acidic V d^1 centers (vs Ti d^0 centers). The V_2N_2 core is planar (torsion angle 0.4°) with a short V···V distance of 2.4967(9) Å. Such a short distance has been found in other dinuclear complexes of vanadium and may be indicative of a V−V bond.[12] For comparison, it is almost identical with one of the shortest distances found in related arylimido dimers $\{V(\mu\text{-}NAr)(NMe_2)_2\}_2$.[1j,4a]

Complexes **1** and **2** could subsequently be characterized by ^1H and ^{13}C NMR spectroscopy, IR, elemental analysis, and the absence of a magnetic moment for **2**. The structural features (strong dissymmetry) observed in the solid state for **1** have not been revealed in solution. In fact, the ^1H and ^{13}C NMR spectra at room temperature show respectively a single resonance for the −NMe_2 protons (a singlet at 3.23 ppm) and carbons (at 45.6 ppm), suggesting equivalency of the four −NMe_2 ligands at this temperature. The symmetry in solution is also apparent in the NMR spectrum of diamagnetic complex **2**. This diamagnetism indicates a strong electronic coupling between the two metal d^1

centers, either through the nitrogen atoms of the imido bridges or as a result of the short V−V distance (see above). Moreover, the sharpness of the peaks of the well-resolved ^1H NMR spectrum of **2** indicates that the dinuclear structure is retained in a C_6D_6 solution.

To go one step further in seeking heterobimetallic compounds linked by μ-imido bridges, we reacted $Ti(NMe_2)_4$ with 2 equiv of $Ar^{iPr_2}NH_2$, followed by 1 equiv of $Zr(NMe_2)_4$. After 12 h of stirring, removal of the volatiles, and washing with pentane, orange **3** was obtained with good yields. Spectroscopic as well as X-ray diffraction studies indicate this compound to be the dinuclear complex $\{(Me_2N)_2Ti(\mu\text{-}NAr^{iPr_2})_2Zr(NMe_2)_2(NHMe_2)\}$. In particular, the ^1H NMR spectrum exhibits signals (a doublet at 1.73 ppm) attributable to one $NHMe_2$ ligand, in addition to signals corresponding to two equivalent μ-NAr^{iPr2} and two types of −NMe_2. In addition to NMR spectroscopic data, single-crystal X-ray diffraction studies[13] confirm the proposed connectivity: the $NHMe_2$ ligand is attached to a pentacoordinated zirconium center (see also below for the structure of **5**), while the geometry around the titanium center is tetrahedral.

Following reaction conditions similar to those described for **3**, the heterobimetallic titanium/hafnium dimer **4** could be prepared as well.[14] As in **3**, only one of the metal centers of **4** is coordinated to a $NHMe_2$ ligand, the hafnium center, while the titanium center is tetrahedrally coordinated.[15]

Finally, in order to combine within the same molecule two different metals and two different bridging imido ligands, we sequentially treated a solution of $Ti(NMe_2)_4$ with 1 equiv of $Zr(NMe_2)_4$, 1 equiv of $Ar^{iPr_2}NH_2$, and 1 equiv of $AdaNH_2$. After suitable workup, a yellow solid was obtained and was characterized by ^1H NMR spectroscopy as being the expected heterobimetallic complex **5** in which the two different metals are indeed held together by two distinct μ-imido groups. This formula was subsequently confirmed by X-ray crystallography, following isolation of suitable crystals from pentane. The thermal ellipsoid plot is presented in Figure 2. The two *distinct* imido ligands are bridging $(Me_2N)_2Ti$ and $Zr(NMe_2)_2(NHMe_2)$ moieties. The coordination geometry of titanium is distorted tetrahedral, while that of zirconium is strongly distorted trigonal bipyramidal ($\tau = 0.57$)[16] because of coordination of one dimethylamine [Zr−N_{NHMe_2} = 2.411(5) Å]. The TiN_2Zr core is almost planar (torsion angle = 0.75°) and is characterized by a Ti···Zr distance of 3.0023(11) Å, two Ti−N_{imido} bond

distances of 1.844(4) and 1.922(5) Å, and two $Zr-N_{imido}$ bond distances of 2.139(4) and 2.109(4) Å.

In summary, the present work has established, for the first time, the propensity of group 4 and 5 amido precursors toward the formation of unique dimer complexes with two distinct bridging μ-imido ligands, as well as heterobimetallic species bridged by μ-imido ligands. It is important to note that the selective isolation of such dimeric complexes (with either two different imido ligands and/or two different metals) may be regarded as unexpected considering the difficulties to obtain homobimetallic complexes in a pure form, in particular with very sterically demanding 2,6-diisopropylarylimido ligand.[5] These results point out a number of new avenues to explore in the synthesis of homo- and heterodinuclear complexes.[9] Studies are underway to probe the scope of such reactions and their applications, as well as to investigate in more detail the reasons for the selective formation of such species.[17]

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Complete X-ray crystallographic data in CIF format for compounds **1**, **2**, and **5** and synthetic details for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Conducting the reaction at 110 °C leads also to similar complex mixtures. These complexes were shown by multinuclear NMR spectroscopy to be the expected complex **2**, contaminated by $\{V(NMe_2)_2(\mu\text{-}NAr^{iPr_2})(\mu\text{-}NAda)V(NMe_2)(NHAr^{iPr_2})\}$, and small amounts of $\{V(\mu\text{-}NAda)(NMe_2)_2\}_2$.

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(13) See the SI.

(14) A zirconium/hafnium complex could be prepared as well; however, in this case, it is obtained as a mixture of two isomers.

(15) As shown by ^{1}H NMR spectroscopy with comparison with homobimetallic-related complexes $\{M(\mu\text{-}NAr^{iPr_2})(NMe_2)_2\}_2(NHMe_2)_x$ complexes (M = Ti, Zr, Hf). The crystal structure of **4** could not be fully resolved because of crystallographic problems (see ref 13).

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(17) In preliminary mechanistic studies, scrambling reactions between two homobimetallic complexes did not lead to the interchanged products (e.g., scrambling $\{Ti(\mu\text{-}NAr^{iPr_2})(NMe_2)_2\}_2$ with $\{Ti(\mu\text{-}NAda)-(NMe_2)_2\}_2$ caused no formation of **1** at room temperature). In agreement with this observation, we presume that R^1NH_2 and R^2NH_2 react with $M^1(NMe_2)_4$ to form transient $M^1(NMe_2)_2(NHR^1)(NHR^2)$, which then is able to act as a chelating metalladiamine and react with a further $M^2(NMe_2)_4$.

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