



Review

Titanium and vanadium imido-bridged complexes

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Contents

1. Introduction and overview	77
2. Synthetic methodologies that result in the formation of bridging M–NR bond	77
2.1. Cleavage of a nitrogen- α -substituent single bond	77
2.1.1. N–H bond cleavage in amines or amides	77
2.1.2. N–Si bond cleavage in silylamines or silylamides	77
2.2. From metal–imido species	82
2.2.1. By dimerization of terminal imides	82
2.2.2. Ligand substitution from existing imido (bridged or linear) precursor	82
2.2.3. By reduction of higher-valent imido precursors	82
2.2.4. By transimination	82
2.3. Oxidation of low-valent precursors	82
2.4. Miscellaneous or unclassified reactions	84
3. Survey of Ti- and V-imido-bridged complexes	84
3.1. Ti-imido-bridged complexes	84
3.1.1. Amido complexes	84
3.1.2. Alkoxy complexes	85
3.1.3. Alkyl complexes	85
3.1.4. Chloro complexes	85
3.1.5. Cyclopentadienyl complexes	86
3.1.6. Complexes supported by miscellaneous ligands	87
3.2. V-imido-bridged complexes	87
3.2.1. Amido complexes	87
3.2.2. Alkyl complexes	88
3.2.3. Alkoxy and chloro complexes	88
3.2.4. Cyclopentadienyl complexes	88
4. Structural properties	89
4.1. Bis-imido bridged complexes	89
4.2. Mono-imido bridged complexes	92
4.3. Tris-capped imido complexes	92
5. Applications	92
5.1. Uses as precursors to other complexes and reactivity	92
5.1.1. Uses as precursors to other complexes	92
5.1.2. Reactivity	93
5.2. Catalytic properties	94
5.3. Electrochemical studies	94
5.4. As source of materials	95
6. Conclusions	95
Acknowledgements	95
References	95

Abbreviations: Ad, 1-adamantyl substituent; Ar*, 2,6- i -Pr₂-C₆H₃ substituent; Bz, benzyl; Cp, cyclopentadienyl (η^5 -C₅H₅⁻); Cp*, pentamethylcyclopentadienyl (η^5 -C₅Me₅⁻); COT, cyclooctatetraenyl; MAO, methylaluminoxane; Mes, mesityl; Mw, molecular weight; Neophyl, PhCMe₂CH₂; py, pyridine; THF, tetrahydrofuran.

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ABSTRACT

This review summarizes the syntheses, structures, reactivity, and applications of titanium- and vanadium-complexes bearing a bridging imido group reported until September 2014. The incorporation of this functional group has evolved from ‘fortuitous approaches’ to designed syntheses of molecules of higher diversity and greater complexity. The review begins with an introduction and a general and brief description of the bridging imido motifs, followed by a discussion of the more common synthetic approaches used to generate such Ti and V compounds. The main focus of the review is the survey of the imido-bridged complexes of Ti and V with an emphasis on their synthesis and reactivity, and with a particular attention to the recent research conducted in the author’s group at the Laboratoire de Chimie de Coordination (LCC), as this review is part of a thematic issue ‘Perspective in coordination chemistry on the occasion of the 40th anniversary of the LCC-CNRS’.

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1. Introduction and overview

The synthesis, structures, bonding, and reactivity of transition metal imido complexes continue to attract considerable interest, driven by their capacity to promote a variety of transformations in which the imido ligand is directly involved in the reactivity or may act as a spectator ligand [1–8]. The imido ligand (formally RN^{2-}) is particularly suitable for the stabilization of transition metal in their highest oxidation states because of its ability to participate in extensive ligand-to-metal π -donation. Furthermore, the steric and electronic properties of the imido complexes may be tuned (in order to impact their stoichiometric or catalytic reactivity) by easy changes in the organic substituent composing the imido group.

Although imido-bridged titanium complexes have been known since 1963 by the pioneer work of Bradley [9], and were first structurally characterized in 1974 [10] (and 1983 for V [11]), they are currently less studied than terminal imido analogs, and historically they were often obtained by accident: indeed, initially, many μ -NR complexes were unintentionally prepared from primary amines RNH_2 , in a first attempt to synthesize the desired corresponding amido (M-NHR) or terminal imido (M=NR) functions (*vide infra*).

This review is concerned with the chemistry of Ti- and V-complexes containing bridging organoimido ligands (μ -NR) where R is an aryl, alkyl, silyl, stannyl, or sulfonyl group (Fig. 1). We will cover both dinuclear complexes in which the ligand bridges two metals and the few polynuclear derivatives in which the ligand bridges more metals. Several early examples of possible imido-bridged species, which have been claimed without supporting data but have not been substantiated or which may be suspect for other reasons, are not included (or are tagged as ‘poorly characterized’ in Tables 1 and 2). We will detail the main synthetic methodologies that have been used to introduce a μ -NR function (Section 2), and will survey the known Ti- and V-complexes with bridging imido ligands (Section 3).

The four known modes of bonding of the imido group are summarized below, and will be detailed in the section devoted to the structural properties (see Section 4). If we exclude terminal imido ligands, a number of Ti- and V-imido complexes fall in the doubly bridging category. In this category, most often the complexes are composed of two metals bridged by two μ -imido ligands

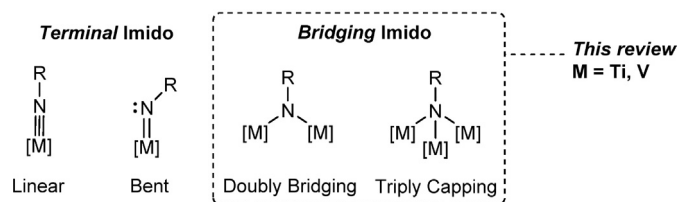


Fig. 1. Scope of the review.

(bis-imido bridged) and adopting a $\text{M}(\mu\text{-NR})_2\text{M}$ diamond core structure (somewhat similar to MO_2M). Rarely, single μ -imido $\text{M}(\mu\text{-NR})\text{M}$ or triple μ -imido $\text{M}(\mu\text{-NR})_3\text{M}$ units were encountered. The second category, triply bridging (or capping) coordination mode is only found in a very small number of complexes of these metals.

And finally, the main uses of these imido-bridged complexes of Ti and V (mainly as precursors to other imido species, reactivity, catalysis, and precursors to materials) will be explained in Section 5. The reactivity of bridging imido group $\text{M}-\mu\text{-NR}$ is lower than that of terminal imido bond $\text{M}=\text{NR}$ due to electronic and thermodynamic factors inherent to dimerization. Regarding electronic factors, the bonding electrons of the bridging imido ligands are more effectively utilized because of greater overlap with hybrid metal orbitals generated in the lower symmetry, but may also result from addition of one electron to the valence shell of each metal in the case of d^1-d^1 dimers (Ti^{III} or V^{IV} systems) in which a metal–metal bond is generally observed.

2. Synthetic methodologies that result in the formation of bridging M–NR bond

Several methods for introducing an imido function (either bridging or terminal) into a metal complex have been summarized [1,2,7,8] and only the most common preparations that have been effectively used to prepare imido-bridged Ti or V complexes are briefly outlined here with selected examples, and in particular examples of synthetic routes that seem to have some degree of generality.

2.1. Cleavage of a nitrogen- α -substituent single bond

2.1.1. N–H bond cleavage in amines or amides

Perhaps one of the most common and convenient utilized route for preparing Ti- and V-imido-bridged compounds is by dehydrohalogenation, deprotonation, and α -hydrogen abstraction or elimination from amines or amides by reaction with a metal chloride, amide, or alkyl precursor (Scheme 1). Due to their commercial and ready availability, and with a broad diversity (wide choice), amines have among the most practical value, and some of the reported methods are rather general in producing imido compounds [12,13] (*cf.* Tables 1 and 2 and text *vide infra*).

2.1.2. N–Si bond cleavage in silylamines or silylamides

Several μ -imido complexes have been prepared by trimethylsilyl chloride (or fluoride) elimination that exploits the stronger strength of Si–Cl bond when silylamines (or silylamides) are reacted with metal chloride precursors [10,14–16] (Scheme 2).

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