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Stabilisation of high oxidation-state niobium using 'electron-rich' bicyclic-guanidinates

Delia B. Soria [1], Joanna Grundy, Martyn P. Coles *, Peter B. Hitchcock

Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, UK

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Abstract

Synthetic procedures to high oxidation-state complexes of niobium incorporating the bicyclic guanidinate 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate, $[hpp]^-$, are described. The ligand source was either the *N*-trimethylsilylated guanidine or the lithium guanidinate and the reaction proceeded via elimination of trimethylsilylchloride or transmetallation from $NbCl_5$, respectively. A 1:1 ratio of reagents afforded the mono-ligand product, $Nb(hpp)Cl_4$ (**1**) and crystallisation from acetonitrile afforded the solvated species $Nb(hpp)Cl_4(MeCN)$ (**1a**), demonstrating the ability of the metal centre in **1** to bind small substrate molecules. A 2:1 ratio of lithium guanidinate to $NbCl_5$ resulted in formation of the seven-coordinate, bis-ligand compound, $Nb(hpp)_2Cl_3$ (**2**). These products represent the first examples of guanidinate compounds in which niobium is stable in the +5 oxidation-state, believed to result from enhanced electron donation caused by the bicyclic framework of the ligand. The molecular structures of **1**, **1a** and **2** are reported, presenting for the first time an opportunity to describe bonding parameters within compounds of this type.

Keywords: Niobium; Guanidinate; Crystal structure

1. Introduction

During the last 20 year the amidine and guanidine compounds, RC{NR′}{NHR′} (R = alkyl/aryl and amide, respectively), have been developed as versatile sources of nitrogen based ligands, with examples of coordination to different metals throughout the periodic table [1]. For the case of guanidine-based ligands, coordination has been observed in the neutral, monoanionic and dianionic form, subject to the number of substituents and 'protonation level' of the compound (e.g., trialkyl guanidines may be doubly deprotonated to afford dianions whilst it is not possible to form the corresponding species for the tetra-alkyl guanidines). Amongst the salient features which contribute to the widespread application of these ligands is the capacity to regulate both the steric and electronic environment at a metal centre by designing ligands with different combinations of nitrogen substituents. This is particularly notable in the chemistry of the guanidinate anion where the presence of a zwitterionic resonance (**A**, Scheme 1) will strongly affect the extent of electron-donation to the metal fragment.

In order to maximise the contribution of resonance structure **A** to the overall bonding, work in our laboratory has concentrated on the application of the bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, hppH, as a source of ligand (Scheme 2). Constraining the substituents of the tertiary amide in the same

* Corresponding author. Tel.: +1 273 877 339; fax: +1 273 677 196.
E-mail address: m.p.coles@sussex.ac.uk (M.P. Coles).
[1] Member of research Career of CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, on leave from CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, R. Argentina.

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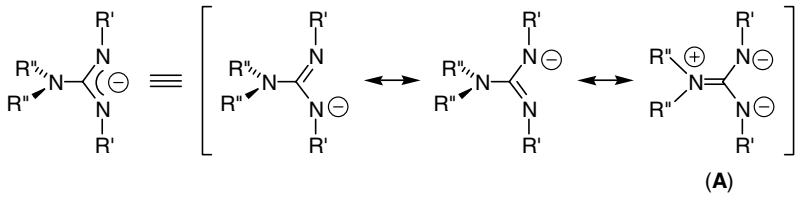
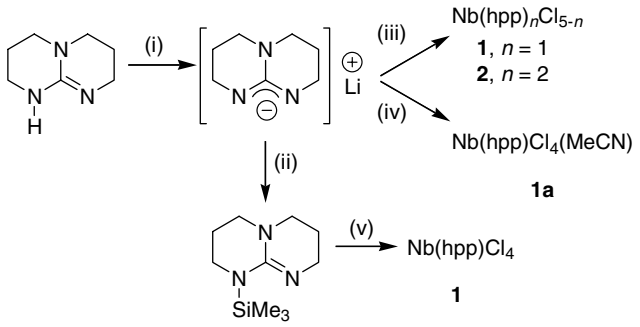


(A)

Scheme 1. Resonance structures of the guanidinate anion.



Scheme 2. (i) ^{n}BuLi, THF; (ii) $SiMe_3Cl$, THF; (iii) **1**, $NbCl_5$, toluene or **2**, 0.5 $NbCl_5$, toluene; (iv) $NbCl_5$, MeCN; (v) $NbCl_5$, CH_2Cl_2.

plane as the 'CN_2' amidine component in this molecule ensures a favourable alignment for overlap of the lone-pair with the empty p-orbital of the sp^2-hybridised carbon. Previous work by ourselves and others have shown that the $[hpp]^-$ anion chelates to a range of different main group and transition metals [2], including lithium [3], aluminium [4], tin [5], zinc [6], yttrium [7] and titanium [8,9]. Crystallographic data for a series of mono- and bis-ligand compounds of titanium has indicated notably shorter Ti–N distances in $[Ti(hpp)Cl_2(\mu\text{-}Cl)]_2$ and $Ti(hpp)_2Cl_2$ when compared to the corresponding benzamidinate [10] and acyclic guanidinate [11] compounds. These data are commensurate with an increased donation of π-electron density to the d^0-titanium centre, although it is noted that the reduced steric influence of the bicyclic framework may also play a role in the close ligand–metal interactions.

Previous studies by ourselves and others intended to extend the application of guanidinate ligands high oxidation state group 5 metals has, to date, met with limited success. For tantalum, both protonolysis [12] and salt metathesis [13] protocols have been explored as routes to compounds containing monoanionic guanidinates. A number of different product have been isolated in addition to the target molecules, including compounds with the *dianionic* ligand, $[(RN{=})C(NR)_2]^{2-}$ and those containing the imido group, $[NR]^{2-}$. In an earlier study in our laboratory we sought to utilise $[hpp]^-$ in the stabilisation of high oxidation-state tantalum complexes [14]. However, rather than forming the expected molecular species $Ta(hpp)_nCl_{5-n}$, the ionic species $[Ta(hpp)_4][TaCl_6]$ was isolated, containing the previously reported eight-coordinate cation, $[Ta(hpp)_4]^+$ [15]. A number of high-oxidation state niobium *amidinate* complexes have been reported in the literature [16]; however, this area has not been extended to include guanidinate species. The 2:1 reaction between the lithium salt of the guanidinate anion, $[(Me_3Si)_2NC\{NCy\}_2]^-$, and $NbCl_5$ resulted in the isolation and characterisation of the reduced Nb(IV) product, $Nb[(Me_3Si)_2NC\{NCy\}_2]_2Cl_2$ In this contribution we wish to report the successful application of the guanidinate anion $[hpp]^-$ to form high oxidation-state niobium chloride complexes.

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox operating at <1 ppm oxygen. Solvents were dried over the appropriate drying agent and degassed prior to use. The reagents hppH (Fluka), $NbCl_5$ (Aldrich), ^{n}BuLi (2.5 M in hexanes, Acros) and $SiMe_3Cl$ (Aldrich) were purchased from commercial sources and used as received. The compound $hppSiMe_3$ was synthesised according to the literature procedures and was used without further purification [18]. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^1H) and 75 ($^{13}C\{^1H\}$) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University.

2.1.1. $Nb(hpp)Cl_4$ (**1**)

2.1.1.1. Method 1. ^{n}BuLi (1.44 mL of a 2.5 M solution in hexane, 3.6 mmol) was added to a solution of hppH (0.50 g, 3.6 mmol) in THF at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h, after which time the solvent was removed to afford a white powder of the lithium salt, '$hppLi(THF)_n$'. This product was slurried in toluene and added to a solution of $NbCl_5$ (0.97 g, 3.6 mmol) in toluene at −78 °C. After stirring at ambient temperature for 20 h, the volatile components were removed and the product extracted with dichloromethane. Removal of the volatiles afforded crude **1** as a brown solid. Yield 0.24 g, 18% (see Fig. 1).