



Communication

Synthesis and structure of V(V) and Mn(III) NHC complexes supported by a tridentate *bis*-aryloxy-N-heterocyclic carbene ligand

Stéphane Bellemin-Lapponnaz^{a,*}, Richard Welter^a, Lydia Brelot^b, Samuel Dagorne^{a,*}^a Laboratoire DECOMET, Institut de Chimie CNRS – Université de Strasbourg 1, rue Blaise Pascal, 67000 Strasbourg, France^b Service de Radiocristallographie, Institut de Chimie CNRS – Université de Strasbourg 4, rue Blaise Pascal, 67070 Strasbourg, France

ARTICLE INFO

Article history:

Received 6 November 2008

Received in revised form 17 December 2008

Accepted 18 December 2008

Available online 30 December 2008

Keywords:

Carbene ligands

Tridentate ligands

Vanadium

Manganese

ABSTRACT

Vanadium (V) and manganese (III) metal complexes (**2**, [^tBu(OCO)]V(=O)Cl; **3**, [^tBu(OCO)]Mn(acac)), which are supported by a tridentate *bis*-aryloxy-N-heterocyclic carbene ligand ([^tBu(OCO)]²⁻=[η³-O,C,O-((3,5-di-*tert*-butyl-C₆H₂O)₂N₂C₃H₄)]²⁻) have been prepared and structurally characterized. Both complexes were efficiently synthesized in a straightforward and smooth manner involving the direct reaction of the imidazolium proligand 1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)imidazolium chloride **1**, easily accessible in a two-step synthesis with an overall good yield, with (^tPrO)₃V=O and Mn(acac)₃, respectively.

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1. Introduction

Due to their unique electronic properties, N-heterocyclic carbenes (NHCs) have recently emerged as an important family of supporting ligands for the development of transition metal catalysts [1]. Their bonding to most late transition metals has proven to be kinetically inert, thus rendering them a 'privileged' motif for catalyst design with such metals [2]. In contrast, the use of NHC ligands for coordination to high-oxidation-state metals has been much less studied which may be ascribed, at least in part, to the presumed ease of dissociation of the M–C_{carbene} bond in such complexes [3]. In order to reduce the tendency for ligand dissociation, potentially bidentate or tridentate NHC-donor systems, which incorporate a neutral carbene donor surrounded by one or two anionic ligand(s), are now witnessing a growing interest as they may yield robust and stable high-oxidation-state metal NHC-based chelate complexes of potential interest in catalysis [4–6]. In addition, the possible electronic and steric tunability of both the anionic and NHC moieties should allow access to a wide variety of such chelating ligands, thereby opening the way to rich and versatile transition-metal coordination chemistry.

In search for new potentially tridentate pincer-type NHC anionic ligand, we focused our attention on *bis*-aryloxy–NHC chelating ligands of type **A** (Scheme 1) as the combination of anionic aryloxides, able to anchor the ligand onto oxophilic high-oxida-

tion-state metals, with a neutral NHC soft donor may render this class of ligands suitable for coordination to various metals across the periodic table. In addition, *bis*-aryloxy–NHC-type ligands have thus far been the subject of very few studies. Efforts in this area include: (i) the synthesis of stable Zr and Ti complexes incorporating the tridentate ligand **C** (Scheme 1). The latter ligand however exhibits a limited stability and readily decomposes via 1,2-alkyl migration [7]; such a decomposition pathway may be greatly disfavoured in the case of type-**A** ligands as the phenol rings (C_{sp2}) are directly bound to the NHC nitrogen atoms and (ii) the synthesis of the *bis*-aryloxy–NHC palladium complex **B** (Scheme 1) has recently been reported, thus showing the suitability of such a ligand structure for late transition metals [8].

Due to the potentially versatile coordination properties of type-**A** ligands, we have developed a straightforward synthesis of the corresponding imidazolium proligands so that to study their coordination chemistry with various metals and, possibly, to probe the potential interest in catalysis of the derived complexes. As part of preliminary studies in this area, we report herein on the synthesis and structural characterization of V(V) and Mn(III) NHC complexes supported by a type-**A** ligand.

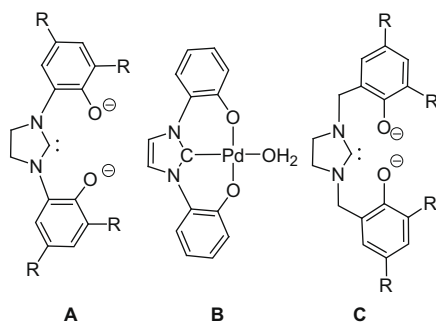
2. Results and discussion

2.1. Synthesis of the imidazolium proligand **1**

The type-**A** NHC proligand 1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)imidazolium chloride **1** (Scheme 1) was found to be accessible in straightforward manner in a two-step and overall

* Corresponding authors.

E-mail addresses: bellemin@chimie.u-strasbg.fr (S. Bellemin-Lapponnaz), dagorne@chimie.u-strasbg.fr (S. Dagorne).



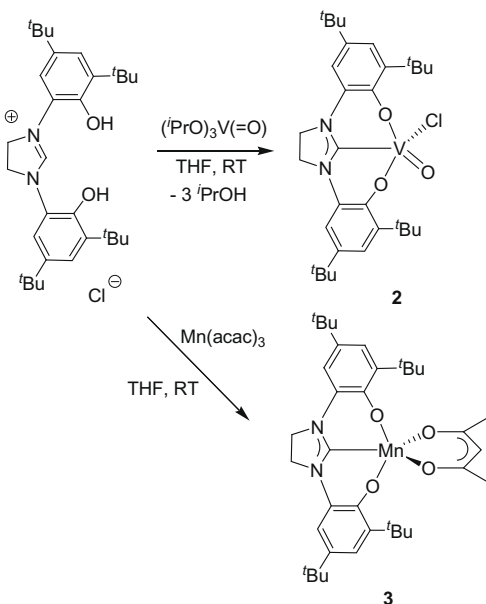
Scheme 1.

high-yield synthesis. Thus, compound **1** was prepared in 80% yield from *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl) ethylenediamine, recently reported by Wieghardt and colleagues [9], using HCl and then $(\text{EtO})_3\text{CH}$ [10]. Spectroscopic data are consistent with the proposed structure for **1**. For instance, the NMR resonance of the C2-*H* proton of the imidazolium ring (δ 8.16) and that of the corresponding carbon (δ 158.8) are characteristic for this type of moiety.

2.2. Synthesis and structural characterization of a V(V) bis-aryloxide-NHC complex derived from proligand **1**

Although there are a few examples of well-characterized vanadium V(III) and V(IV) NHC complexes, [3a,4d,5g,11] the report by Abernethy and colleagues on an air-stable trichloro-oxo-vanadium (V) NHC complex supported by a monodentate NHC ligand constitutes the only example of vanadium(V) NHC species [3d]. It thus appeared interesting to us to probe the suitability of the tridentate NHC anionic ligand $[\text{t}^{\text{Bu}}(\text{OCO})]^{2-}$ for the formation of a robust V(V)-NHC chelate.

The V(V) NHC complex $[\text{t}^{\text{Bu}}(\text{OCO})\text{V}(=\text{O})\text{Cl}][\text{t}^{\text{Bu}}(\text{OCO})]^{2-} = [\eta^3\text{-O,C,O}\{-\{(3,5\text{-di-}t^{\text{Bu}}\text{-C}_6\text{H}_2\text{O})_2\text{N}_2\text{C}_3\text{H}_4\}\}^{2-}]$ (**2**, Scheme 2) was readily and quantitatively synthesized in a straightforward and smooth manner via an alcohol elimination route involving the reaction of the imidazolium **1** with 1 equiv. of $(\text{t}^{\text{Bu}}\text{PrO})_3\text{V}(=\text{O})$, along with 3 equiv. of $\text{t}^{\text{Bu}}\text{PrOH}$. Compound **2** could be obtained as



Scheme 2.

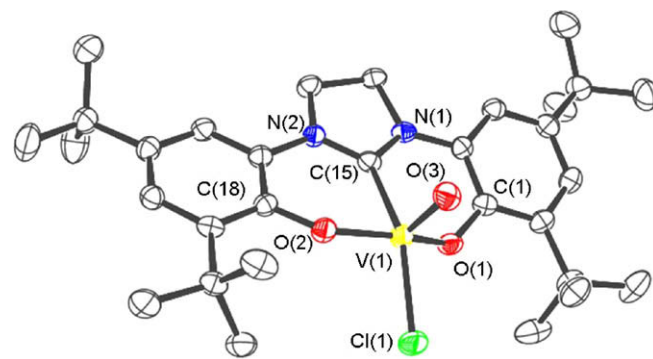


Fig. 1. ORTEP view of complex **2** with partial atom labeling. Thermal ellipsoids drawn at 50% probability; hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): C(15)–V(1), 2.095(3); O(2)–V(1), 1.810(2); O(1)–V(1), 1.817(2); Cl(1)–V(1), 2.3077(10); O(3)–V(1), 1.589(2); O(3)–V(1)–Cl(1), 109.05(9); O(3)–V(1)–O(2), 103.73(11); O(3)–V(1)–O(1), 101.60(11); O(2)–V(1)–O(1), 150.96(10).

an analytically pure dark orange solid upon evaporation of volatiles in vacuo. It is indefinitely air-stable whether in the solid state or in benzene solution.

The molecular structure of the V(V) complex **2**, as determined by single crystal X-ray crystallographic studies (Fig. 1) confirmed the coordination to vanadium of the tridentate NHC ligand [O(1)–V(1)–O(2) bite angle of $150.96(10)^\circ$] in a *mer*-fashion along with a distortion of the {OCO}V metallacycle [for instance, C(18)–O(2)–O(1)–C(1) = 63.1°]. The vanadium atom in complex **2** adopts a slightly distorted square-pyramidal geometry and is displaced from the tetragonal plane formed by C(15), O(1), O(2) and Cl(1) by only 0.46(2) Å. The V– $\text{C}_{\text{carbene}}$ bond distance (2.095(3) Å) is bit shorter than that in the other V(V)-NHC complex X-ray characterized so far [3d], probably reflecting, in the present case, geometrical constraints imposed by the tridentate NHC ligand. The oxovanadium V=O bond is nearly perpendicular to the plane of the heterocyclic carbene ring [centroid_{NHC}–V(1)–O(1) = $95(2)^\circ$]. The distance of the V=O oxygen atom to the $\text{C}_{\text{carbene}}$ atom (2.77(1) Å) appears to be well within the sum of van der Waals radii for carbon and oxygen (3.20(1) Å). A similar observation was reported in the case of the trichloro-oxo-V(V) NHC complex with short distances between the $\text{C}_{\text{carbene}}$ and the *cis* chlorides. In the latter case, DFT calculations clearly showed the presence of interligand bonding interactions between chloride electron density and the formally vacant molecular orbitals of the $\text{C}_{\text{carbene}}$ [3d]. In the case of complex **2**, such bonding interactions between the V=O and the $\text{C}_{\text{carbene}}$ may also account for the rather short contacts between the $\text{C}_{\text{carbene}}$ and the V=O oxygen.

2.3. Synthesis and structural characterization of a Mn(III) bis-aryloxide-NHC complex derived from proligand **1**

The possibility to access low-oxidation-state NHC Mn complexes has been known for thirty years with a report by Lappert and colleagues on the synthesis of Mn(0) NHC complexes [12]. Several Mn(0), Mn(I) and a few Mn(II) NHC complexes have since then been characterized [13]. However, to the best of our knowledge, no Mn(III) NHC complex has been thus far reported which is rather surprising in view of the potential interest of Mn(III) complexes in catalysis when chelated by an appropriate multidentate ligand such as, for instance, the salen ligand [14]. We thus became interested in the synthesis of Mn(III) bis-aryloxide-NHC complexes as such derivatives may well be of interest in catalysis.

The imidazolium **1** was found to smoothly react (room temperature, THF) with 1 equiv. of $\text{Mn}(\text{acac})_3$ to afford the Mn(III)-bis-aryloxide-NHC complex **3** (Scheme 2), which was isolated in

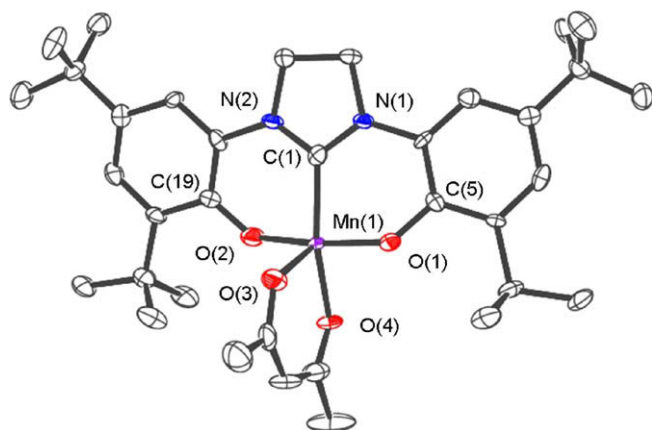


Fig. 2. ORTEP view of complex **3** with partial atom labeling. Thermal ellipsoids drawn at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Mn(1), 1.999(8); O(1)–Mn(1), 1.848(6); O(2)–Mn(1), 1.860(6); O(4)–Mn(1), 1.965(6); O(3)–Mn(1), 2.069(6); O(1)–Mn(1)–O(2), 168.7(3); O(1)–Mn(1)–O(4), 89.2(3); O(1)–Mn(1)–C(1), 87.4(3); O(1)–Mn(1)–O(3), 91.4(3); O(3)–Mn(1)–O(4), 90.1(3).

a reasonable yield as analytically pure dark purple crystals. The molecular structure of complex **3** was determined by single crystal X-ray diffraction and is illustrated in Fig. 2. The geometry at the Mn atom in compound **3** is best described as slightly distorted square-pyramidal with the metal center being displaced from the tetragonal plane formed by C(1), O(1), O(2) and O(4) by only 0.27(2) Å. The *mer*-coordination of the tridentate NHC ligand results in the formation of a {OCO}Mn metallacycle significantly distorted from planarity [for instance, |C(19)–O(2)–O(1)–C(5)| = 59.0°]. As expected, the Mn–C_{carbene} bond distance (1.999(8) Å) is shorter than that in Mn–NHC complexes X-ray characterized thus far (average 2.20 Å) due to constraints imposed by the tridentate {OCO}²⁻ chelating ligand. It is noteworthy that the Mn–O bond distances within the Mn(acac) moiety are quite different from one another with Mn(1)–O(3) (2.069(6) Å), O(3) being the top of the square-pyramidal, around 0.1 Å longer than Mn(1)–O(4) (1.965(6) Å). This structural difference presumably reflects a Jahn–Teller distortion typically observed for high-spin d⁴ Mn(III) chelate compounds [15].

3. Conclusion

The tridentate *bis*-aryloxyde–NHC [^{tBu}(OCO)]²⁻ (type **A**, Scheme 1) may be a suitable supporting ligand for the synthesis of high-oxidation-state transition metal complexes such as the V(V) derivative **2**, which was found to be a robust and air-stable species. This ligand appears to be quite versatile as it also readily chelates Mn(III) to afford the first structurally characterized Mn(III) NHC complex. Both V(V) and Mn(III) complexes **2** and **3** were efficiently synthesized in a straightforward and smooth manner involving the direct reaction of the imidazolium proligand, easily accessible in a two-step synthesis with an overall good yield, with an appropriate metal precursor.

Further work in this area will keep on studying the coordination chemistry of tridentate *bis*-aryloxyde–NHC with various metals as well as the potential interest in catalysis of these robust NHC metal complexes.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.049.

References

- [1] (a) A.J. Arduengo III, *Acc. Chem. Res.* 32 (1999) 913; (b) D. Bourissou, O. Guerret, F. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39; (c) C.M. Crudden, D.P. Allen, *Coord. Chem. Rev.* 248 (2004) 2247; (d) S. Díez-González, S.P. Nolan, *Coord. Chem. Rev.* 251 (2007) 874; (e) F. Glorius, *Top. Organomet. Chem.* 21 (2007) 1.
- [2] (a) W.A. Herrmann, *Angew. Chem., Int. Ed.* 41 (2002) 1290; (b) M.C. Perry, K. Burgess, *Tetrahedron: Asymmetr.* 14 (2003) 951; (c) V. César, S. Bellemin-Laponnaz, L.H. Gade, *Chem. Soc. Rev.* 33 (2004) 619; (d) L.H. Gade, S. Bellemin-Laponnaz, *Top. Organomet. Chem.* 21 (2007) 117.
- [3] (a) For recent d⁰ early transition metal complexes stabilized by a monodentate NHC ligand, see, for instance: W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, *J. Organomet. Chem.* 480 (1994) C7; (b) M. Niehues, G. Erker, G. Kehr, P. Schwab, R. Fröhlich, O. Blacque, H. Berke, *Organometallics* 21 (2002) 2905; (c) M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, *J. Organomet. Chem.* 663 (2002) 192; (d) C.D. Abernethy, G.M. Codd, M.D. Spicer, M.K. Taylor, *J. Am. Chem. Soc.* 125 (2003) 1128; (e) P. Shukla, J.A. Johnson, D. Vidovic, A.H. Cowley, C.D. Abernethy, *Chem. Commun.* (2004) 360.
- [4] (a) For d⁰ early transition metal complexes stabilized by an NHC-incorporating anionic bidentate ligand, see: P.L. Arnold, M. Rodden, C. Wilson, *Chem. Commun.* (2005) 1743; (b) D. Patel, S.T. Liddle, S.A. Mungur, M. Rodden, A.J. Blake, P.L. Arnold, *Chem. Commun.* (2006) 1124; (c) S.A. Mungur, A.J. Blake, C. Wilson, J. McMaster, P.L. Arnold, *Organometallics* 25 (2006) 1861; (d) S.P. Downing, S.C. Guadaño, D. Pugh, A.A. Danopoulos, R.M. Bellabarba, M. Hanton, D. Smith, R.P. Tooze, *Organometallics* 26 (2007) 3762; (e) J. Müller, I. Piotrowski, L. von Chrzanowski, *Z. Naturforsch.* 62b (2007) 467.
- [5] (a) For d⁰ early transition metal complexes stabilized by an NHC-incorporating tridentate ligand, see: H. Aihara, T. Matsuo, H. Kawaguchi, *Chem. Commun.* (2003) 2204; (b) L.P. Spencer, S. Winston, M.D. Fryzuk, *Organometallics* 23 (2004) 3372; (c) L.P. Spencer, M.D. Fryzuk, *J. Organomet. Chem.* 690 (2005) 5788; (d) R.J. Rubio, G.T.S. Andavan, E.B. Bauer, T.K. Hollis, J. Cho, F.S. Tham, B. Donnadieu, *J. Organomet. Chem.* 690 (2005) 5353; (e) L.P. Spencer, C. Beddie, M.B. Hall, M.D. Fryzuk, *J. Am. Chem. Soc.* 128 (2006) 12531; (f) D. Zhang, T. Aihara, T. Watanabe, T. Matsuo, H. Kawaguchi, *J. Organomet. Chem.* 692 (2007) 234; (g) D. Pugh, J.A. Wright, S. Freeman, A.A. Danopoulos, *Dalton Trans.* (2006) 775; (h) D. Zhang, *Eur. J. Inorg. Chem.* (2007) 4839; (i) I.S. Edworthy, A.J. Blake, C. Wilson, P.L. Arnold, *Organometallics* 26 (2007) 3684.
- [6] (a) For reviews, see: S.T. Liddle, I.S. Edworthy, P.L. Arnold, *Chem. Soc. Rev.* 36 (2007) 1732; (b) O. Kühl, *Chem. Soc. Rev.* 36 (2007) 792.
- [7] D. Zhang, H. Kawaguchi, *Organometallics* 25 (2006) 5506.
- [8] No information were given concerning the characterization of the imidazolium proligand and the X-ray characterized Pd complex **B**, see: T. Yagyu, S. Oya, M. Maeda, K. Jitsukawa, *Chem. Lett.* 35 (2006) 154.
- [9] K.S. Min, T. Weyermüller, E. Bothe, K. Wieghardt, *Inorg. Chem.* 43 (2004) 2922.
- [10] A.W. Waltman, R.H. Grubbs, *Organometallics* 23 (2004) 3105.
- [11] (a) For other V(III) and V(IV) NHC complexes, see: A. Wacker, C.G. Yan, G. Kaltentpoth, A. Ginsberg, A.M. Arif, R.D. Ernst, H. Prizkow, W. Siebert, *J. Organomet. Chem.* 641 (2002) 195; (b) D.S. McGuinness, V.C. Gibson, J.W. Steed, *Organometallics* 23 (2004) 6288.
- [12] M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 2172.
- [13] (a) For recent examples, see: A. Wacker, H. Prizkow, W. Siebert, *Eur. J. Inorg. Chem.* (1998) 843; (b) C.D. Abernethy, A.H. Cowley, R.A. Jones, C.L.B. Macdonald, P. Shukla, L.K. Thomson, *Organometallics* 20 (2001) 3629; (c) J. Chai, H. Zhu, H.W. Roesky, D. Vidovic, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* (2003) 4332; (d) J. Chai, H. Zhu, Y. Peng, H.W. Roesky, S. Singh, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* (2004) 2673; (e) J. Ruiz, G. Garcia, M.E.G. Mosquera, B.F. Perandones, M.P. Gonzalo, M. Vivanco, *J. Am. Chem. Soc.* 127 (2005) 8584; (f) B. Tumanskii, D. Sheberla, G. Molev, Y. Apeloig, *Angew. Chem., Int. Ed.* 46 (2007) 7408; (g) J. Ruiz, B.F. Perandones, G. Garcia, M.E.G. Mosquera, *Organometallics* 26 (2007) 5687.
- [14] (a) W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, *J. Am. Chem. Soc.* 112 (1990) 2801; (b) R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, *Tetrahedron Lett.* 31 (1990) 7345.
- [15] E.J. Larson, V.L. Pecoraro, *J. Am. Chem. Soc.* 113 (1991) 3810.