

Amine elimination synthesis of a titanium(IV) N-heterocyclic carbene complex with short intramolecular Cl...C_{carbene} contacts

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Received (in Cambridge, UK) 13th November 2003, Accepted 27th November 2003

First published as an Advance Article on the web 15th January 2004

The reaction of 1,3-dimesitylimidazolium chloride with Ti(NMe₂)₄ results in the 1,3-dimesitylimidazol-2-ylidene complex of Ti(NMe₂)₂Cl₂ (**3**); the X-ray crystal structure of **3** evidences short intramolecular Cl...C_{carbene} contacts.

N-heterocyclic carbenes are now used widely as ligands in transition-metal-based catalysts for effecting *e.g.* carbon-carbon bond formation.¹ In contrast to these extensively studied systems that feature transition metal centres in low oxidation states, very little information is available regarding high-oxidation-state transition metal N-heterocyclic carbene complexes. To date, we are aware of only three synthetic studies^{2,3,4} and one spectroscopic study⁵ of such complexes. In each case, the pertinent complexes were formed by direct reaction of a preformed or *in situ* generated N-heterocyclic carbene with the appropriate transition metal substrate. Surprisingly, X-ray crystallographic data are only available for V(O)Cl₃(carbene) (**1**, carbene = 1,3-dimesitylimidazol-2-ylidene),³ and Re(N)Cl₂(PMe₂Ph)₂(carbene) (**2**, carbene = 1,3,4-triphenyl-1,2,4-triazol-5-ylidene)⁴ and Re(N)(NCS)(carbene)(carbene-H) (carbene = 1,3,4-triphenyl-1,2,4-triazol-5-ylidene).⁴ Despite the small number of structurally characterized high-oxidation-state transition metal complexes of N-heterocyclic carbenes, the available information indicates that these species possess some remarkable properties. In addition to their exceptional stability towards air and moisture, both **1** and **2** (*vide infra*) have been found to exhibit bonding interactions between the carbene carbon and adjacent Cl ligands.^{3,4}

Herein we report a new approach to titanium(IV) complexes that employs an imidazolium salt, thereby avoiding the isolation and purification of the corresponding N-heterocyclic carbene. The titanium(IV) complex, Ti(NMe₂)Cl₂(carbene) (**3**, carbene = 1,3-dimesitylimidazol-2-ylidene), was prepared by treatment of Ti(NMe₂)₄ with two equivalents of 1,3-dimesitylimidazolium chloride in THF solution at ambient temperature as summarized in Scheme 1. Previously, it has been shown that imidazolium salts react with chromocene⁶ or nickelocene⁷ to form N-heterocyclic carbene complexes *via* cyclopentadiene elimination. The present work usefully extends this type of reaction to include amine elimination. Since amides are available for all the early transition metals in high oxidation states, this method represents a general entry point into their coordination chemistry with N-heterocyclic carbenes.

Initial support for the proposed formulation for **3** was indicated by ¹H NMR spectroscopy which showed the presence of two NMe₂ groups and one carbene ligand.[†] Confirmation of this structure assignment was provided by an X-ray crystal structure determina-

tion.[‡] The crystalline state of **3** comprises individual molecules and there are no unusually short intermolecular contacts. The environment around titanium in **3** is that of a distorted trigonal bipyramid (TBP) in which the NMe₂ groups and the carbene ligand occupy the equatorial sites; however, the N(3)-Ti(1)-N(4) bond angle of 109.30(18)[°] is considerably more acute than the ideal equatorial TBP angle of 120[°]. Similarly, the axial Cl(1)-Ti(1)-Cl(2) moiety, with a bond angle of 163.93(6)[°], is distinctly non-linear. As in the case of the structure of *e.g.* [Ti(η⁵-Ind)(NMe₂)Cl₂],⁸ the NMe₂ groups in **3** adopt a trigonal planar geometry; however, the N(3)-Ti(1)-N(4) bond angle of 109.30(18)[°] is considerably more acute than the ideal equatorial TBP angle of 120[°]. Similarly, the axial Cl(1)-Ti(1)-Cl(2) moiety, with a bond angle of 163.93(6)[°], is distinctly non-linear. To our knowledge, there are no published values for N-heterocyclic carbene-Ti(IV) bond distances. As expected on the basis of ionic radii, the Ti-C_{carbene} bond distance in **3** (2.313(5) Å) is longer than the V-C_{carbene} bond distance in the vanadium(V) complex **1** (2.137(2) Å), the only other example of an isolated high-oxidation-state first-row early transition metal N-heterocyclic carbene complex. As in the case of **1**, the axial Cl ligands in **3** are orientated approximately at right angles with respect to the plane of the carbene ligand. Moreover, the Cl(1)...C(1) and Cl(2)...C(1) distances of 3.120(5) and 3.103(5) Å, respectively, are considerably shorter than the sum of van der Waals radii for carbon and chlorine (3.65 Å),⁹ thus suggesting the existence of Cl...C_{carbene} intermolecular interactions. The nature of the implied Cl...C_{carbene} interactions was probed by a number of theoretical approaches, of which the DFT method with the 6-31 G++(d,p) basis set proved to be the most satisfactory. In the interest of computational efficiency, these calculations were performed on the model complex, Ti(NMe₂)₂Cl₂(carbene) (**4**, carbene = 1,3-dimethylimidazol-2-ylidene). The global minimum for **4** is in very good agreement with the experimental structure of **3**, both in terms of the overall geometry and also from the standpoint of metrical parameters; calculated for **4**: Ti-C_{carbene} 2.268 Å, Ti-Cl 2.386 Å, Ti-N 1.890 Å, C_{carbene}...Cl(1) 2.990 Å, C_{carbene}...Cl(2) 2.980 Å, Cl-Ti-Cl 159.75[°], N-Ti-N 111.06[°]. (c.f. experimental data in Fig. 1 caption). The interaction between the chloride lone pairs and the

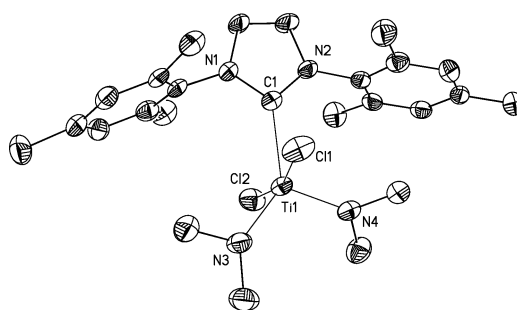
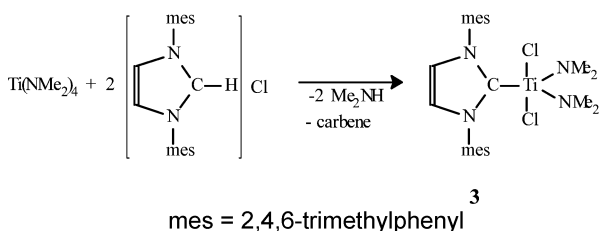


Fig. 1 View of the molecular structure of **3** showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The hydrogen atoms have been removed for clarity. Important bond distances (Å) and angles (°): Ti(1)-C(1) 2.313(5), Ti(1)-N(3) 1.874(4), Ti(1)-N(4) 1.878(4), Ti(1)-Cl(1) 2.3680(16), Ti(1)-Cl(2) 2.3649(17), C(1)-Ti(1)-Cl(1) 83.60(12), C(1)-Ti(1)-Cl(2) 83.09(12), Cl(1)-Ti(1)-Cl(2) 163.93(6), N(3)-Ti(1)-N(4) 109.30(18).



Scheme 1

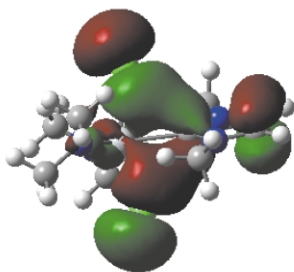


Fig. 2 The HOMO-8 orbital of **3** showing the interaction between chloride lone pairs and the carbenic 2p orbital.

formally vacant C(2p) orbital on the carbene ligand can be discerned in the HOMO-8 orbital of **4** (Fig. 2) where there is clear evidence for overlap between chloride lone pairs and the carbenic 2p orbital. A similar type of interaction has been reported by Abernethy *et al.* for **1**.³ Furthermore, although not commented on by Braband and Abram,⁴ we have found that **2** also exhibits a short Cl...C_{carbene} interaction. Analysis of the supplementary X-ray data for **2** reveals that for the C_{carbene} and the Cl ligand positioned approximately perpendicular to the heterocyclic ring of the carbene (Cl–Re–C_{carbene}–N torsional angle = 74.0°), the C_{carbene}...Cl distance is 3.022 Å and the Cl–Re–C_{carbene} angle is 81.61°. It appears, therefore, that such Cl...C_{carbene} interactions are a pervasive feature of the N-heterocyclic carbene complexes of high-valent transition metal chlorides. Since these interactions may be considered to represent nucleophilic attack by the chloride ligands on C_{carbene}, they indicate that the carbenic centre is electrophilic. Accordingly, the structure of **3** gives further support to the view that complexes of N-heterocyclic carbenes with high-oxidation-state transition metals should be considered to be Fischer-type carbene complexes rather than the Schrock-type alkylidenes that are usually associated with high-oxidation-state transition metal systems.¹⁰ A full description of the reactivity of high-oxidation-state transition metal N-heterocyclic carbene complexes towards both electrophiles and nucleophiles will be presented in due course.¹¹

We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support and to Dr. Vincent Lynch for refining the structure of **3**.

Notes and references

† A suspension of 3.0 g (8.8 mmol) of 1,3-dimesitylimidazolium chloride in 100 mL of THF was added *via* cannula to a solution of 1.0 g (4.46 mmol) of Ti(NMe₂)₄ in 30 mL of THF at room temperature. The reaction mixture, which had assumed an immediate red colour, was allowed to stir overnight at ambient temperature, following which it was filtered through Celite.[®] Removal of THF from the filtrate under reduced pressure afforded crude **3** as a dark red powder. Pure, crystalline **3** was obtained by recrystallization from a saturated toluene solution at –20 °C. Yield, 1.04 g (45.1% based on Ti(NMe₂)₄ consumed); mp 81–83 °C. Anal. Calcd for C₂₅H₃₆Cl₂N₄Ti: %C = 58.72, %H = 7.10, Found: %C = 58.94, %H = 6.97.

‡ *Crystal data*: C₂₅H₃₆Cl₂N₄Ti, monoclinic, space group *P2₁/n*, *a* = 11.492(2) Å, *b* = 14.182(3) Å, *c* = 16.649(3) Å, β = 92.34(2)°, *V* = 2711.2(9) Å³, *D*_{calcd} = 1.253 g cm^{–3}, *Z* = 4, λ (Mo–Kα) = 0.71073 Å, μ (Mo–Kα) = 0.570 mm^{–1}. A total of 8944 independent reflections was collected on a Siemens P4 diffractometer at 293(2) K with 2θ ranging between 6.24 and 50.1°. The structure was solved by direct methods and refined by full matrix least squares on *F*² to *R*₁ = 0.0942 and *wR*₂ = 0.2235. CCDC 224825. See <http://www.rsc.org/suppdata/cc/b3/b314558a/> for crystallographic data in .cif or other electronic format.

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