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Titanium complexes with imidazolin-2-iminato ligands

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The reaction of 1,3-di-*tert*-butylimidazolin-2-ylidene with trimethylsilyl azide furnishes the corresponding *N*-silylated 2-iminoimidazoline which reacts with titanium(IV) chlorides to yield imidazolin-2-iminato titanium complexes.

The coordination chemistry of phosphoraneiminato ligands, R_3PN^-, has developed into a broad area of research which has produced a large number of structurally diverse main group element and transition metal complexes.[1] Due to their capability to act as 2σ,4π-electron donors, these anionic ligands can be regarded as monodentate analogues to cyclopentadienyls, C_5R_5, and this relationship has been described as a pseudo-isolobal phenomenon.[2] Accordingly, the use of phosphoraneiminato instead of the traditional cyclopentadienyl ancillary ligands could produce complexes of modified and potentially enhanced catalytic activity. This concept was proved successful by the synthesis of extremely active titanium catalysts for olefin polymerization.[3]

Another concept, which has been extremely useful for boosting the performance of numerous transition metal catalysts, is based on the striking similarity between electron-rich organophosphanes and nucleophilic carbenes of the imidazolin-2-ylidene type in terms of their ligand properties.[4] In many cases, replacement of phosphane by *N*-heterocyclic carbene ligands has created transition metal complexes with improved stability and significantly enhanced catalytic activity. Similarly, substitution of the R_3P for an imidazolin-2-ylidene moiety in phosphoraneimides gives imidazolin-2-imides of type **I**, which can be described by the two limiting mesomeric structures **IA** and **IB** (Fig. 1). The ability of an imidazolium ring to stabilize a positive charge in a more effective manner than a phosphonium group should increase the negative charge on the nitrogen atom and thus lead to the formation of ligands with enhanced basicity and electron donating capacity. However, only a surprisingly small number of publications has been devoted to the preparation of imidazolin-2-iminato transition metal complexes,[5] and these reports have been confined to the use of the ligand precursor 2-imino-1,3-dimethylimidazoline.[6]

With this contribution, we present a novel and versatile method for the preparation of imidazolin-2-iminato ligands employing imidazolin-2-ylidenes as readily available starting materials. The reaction of the stable carbene 1,3-di-*tert*-butylimidazolin-2-ylidene (**1**)[7] with trimethylsilyl azide in boiling toluene (110 °C) for 24 h furnishes the *N*-silylated 2-iminoimidazoline **2** in a similar way as described for the preparation of silylated phosphoraneimines (Scheme 1).[1c] Recrystallization from hexane affords **2** as colourless needle-shaped crystals. The conversion of the carbene **1** can easily be followed by ^1H NMR spectroscopy as a pronounced high-field shift is observed for the resonance of the NCH hydrogen atoms at 6.75 ppm upon formation of the imine **2**. The ^1H NMR spectrum of **2** exhibits three resonances at 6.03, 1.36 and 0.48 ppm for the NCH, CCH_3 and $SiCH_3$ protons, respectively, either indicating that **2** does contain a mirror plane or that rotation around the N1–C1 axis is fast on the NMR timescale.†

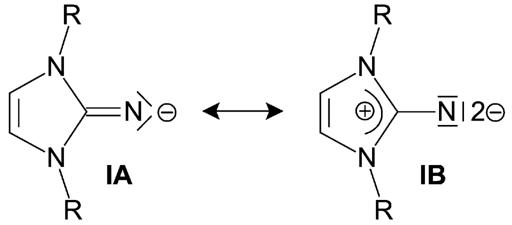
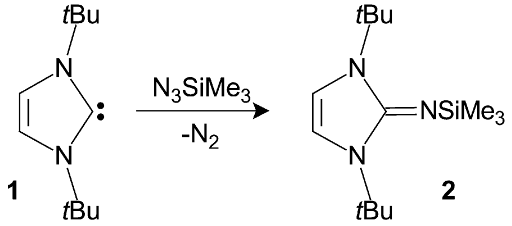


Fig. 1 Mesomeric structures for imidazolin-2-iminato ligands **I**.

Crystals of **2** were subjected to an X-ray diffraction analysis,‡ and the molecular structure of **2** is shown in Fig. 2. The exocyclic C1–N1 bond distance of 1.275(3) Å is shorter than the corresponding distance in 2-imino-1,3-dimethylimidazoline [1.296(2) Å][6] despite the steric bulk of the *tert*-butyl and trimethylsilyl substituents. The C1–N1–Si angle of 169.3(2)° in **2** is close to linearity and thereby significantly larger than the corresponding P–N–Si angles in silylated iminophosphoranes with values of 128 to 150°. A more detailed structural comparison with $Ph_3PNSiMe_3$ [P–N 1.542(2) Å, N–Si 1.686(2) Å, P–N–Si 140.2(2)°][8] and $(C_6H_{11})_3PNSiMe_3$ [P–N 1.549(4) Å, N–Si 1.656(4) Å, P–N–Si 149.8(2)°][9] confirms the expected electron donor trend,[10] which increases in the order $PPh_3 < P(C_6H_{11})_3 <$ **1** (*vide supra*).

Silylated iminophosphoranes have been widely used for complexation reactions with various metal halides to yield phosphoraneiminato complexes together with the elimination of trialkylsilyl halides.[1] Accordingly, treatment of a $TiCl_4$ solution in hexane with one eq. of the imine **2** at room temperature results in the instantaneous precipitation of complex **3** as an orange crystalline solid in almost quantitative yield (Scheme 2). Desilylation and coordination to the metal center results in a pronounced down-field shift of the resonances observed for the NCH hydrogen as well as for the ring carbon atoms as expected for a strong electron release



Scheme 1

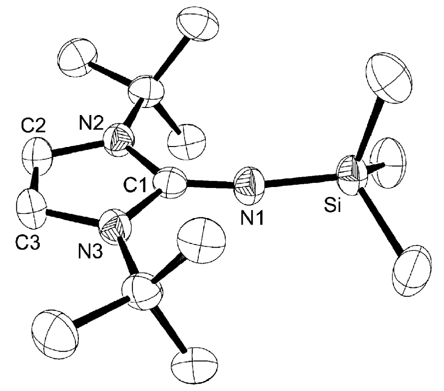


Fig. 2 ORTEP drawing of **2** with thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: C1–N1 1.275(3), N1–Si 1.655(2), C1–N2 1.394(2), C1–N3 1.393(3), N2–C2 1.387(3), N3–C3 1.387(3), C2–C3 1.326(4); C1–N1–Si 169.3(2), N2–C1–N3 104.5(2).

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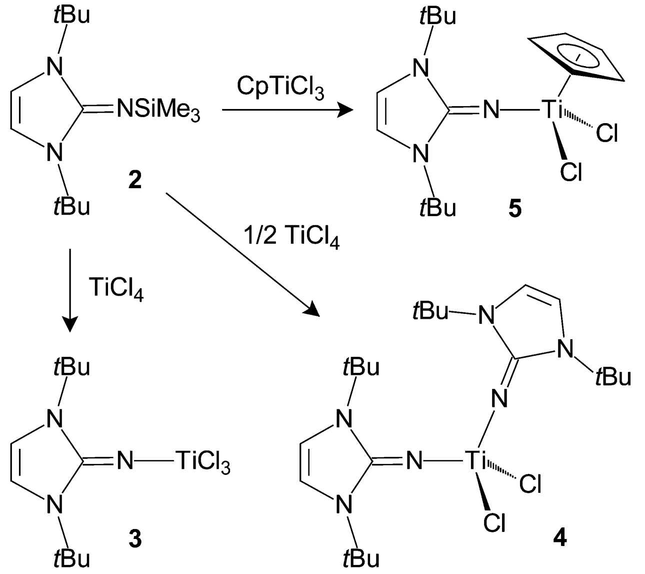
towards the metal center.† Introduction of a second imidazolin-2-iminato ligand requires more forcing reaction conditions, and prolonged heating (48 h) in boiling toluene quantitatively affords complex **4** as an orange solid.

In a similar fashion, the cyclopentadienyl titanium complex **5** can be isolated from the reaction of [(η-C_5H_5)$TiCl_3$] with **2** in toluene at room temperature overnight. Single crystals obtained at 4 °C from a saturated toluene solution were subjected to an X-ray diffraction analysis,‡ and the molecular structure of **5** is shown in Fig. 3. The metal center is pseudotetrahedrally coordinated with Cl–Ti–Cl and Cl–Ti–N1 angles of 102.10(3) and 103.47(5)°, respectively. A short Ti–N1 distance [1.765(3) Å] and an almost linear Ti–N1–C1 arrangement [170.7(2)°] are indicative of efficient π-donation to the metal center confirming that the ligand can be regarded as a six-electron donor. The structural characterization of a similar complex containing a saturated imidazolidin-2-iminato ligand attached to the [(η-C_5H_5)$TiCl_2$] complex fragment reveals a significantly longer Ti–N distance [1.792(2) Å] and a stronger deviation from a linear Ti-N-C orientation.[11] In contrast, closely related structural parameters have been observed for complexes of the type [(η-C_5H_5)$TiCl_2$(NPR_3)] (R = C_6H_{11}, *i*Pr, *t*Bu) containing trialkylphosphoraneiminato ligands with Ti–N distances ranging from 1.750(3) to 1.775(11) Å.[3a]



Scheme 2

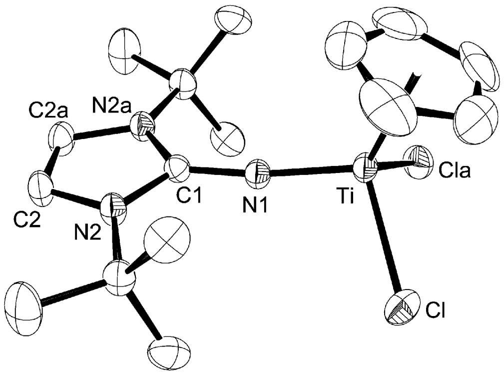


Fig. 3 ORTEP drawing of **5** with thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Ti–N1 1.765(3), Ti–Cl 2.3253(6), C1–N1 1.332(4), C1–N2 1.373(2), N2–C2 1.382(3), C2–C2a 1.331(3); Cl–Ti–Cla 102.10(3), Cl–Ti–N1 103.47(5), Ti–N1–C1 170.7(2), N2–C1–N2a 106.2(2). Symmetry operation to equivalent positions *a*: *x*, $\frac{1}{2}-y$, *z*.

In conclusion, we have presented a new and general method for the preparation of silylated 2-iminoimidazolines which can be used for the preparation of imidazolin-2-iminato transition metal complexes. These ligands are promising ancillary ligands for the design and preparation of homogeneous catalysts owing to their strong electron donating ability and to the ease of variability by employing stable carbenes of the imidazolin-2-ylidene type.

Notes and references

† *Spectroscopic data*: **2**: δ_H (C_6D_6): 6.03 (s, 2H, NC*H*), 1.36 (s, 18H, CC*H*$_3$), 0.48 (s, 9H, SiC*H*$_3$); δ_C (C_6D_6): 144.6 (s, N*C*N), 110.2 (s, N*C*H), 60.2 (s, N*C*CH$_3$), 29.6 (s, C*C*H$_3$), 4.4 (s, Si*C*H$_3$). **3**: δ_H ($CDCl_3$): 6.56 (s, 2H, NC*H*), 1.83 (s, 18H, CC*H*$_3$); δ_C (C_6D_6): 139.7 (s, N*C*N), 107.1 (s, N*C*H), 54.2 (s, N*C*CH$_3$), 28.1 (s, C*C*H$_3$). **4**: δ_H (C_6D_6): 5.82 (s, 2H, NC*H*), 1.60 (s, 18H, CC*H*$_3$); δ_C (C_6D_6): 142.9 (s, N*C*H), 107.7 (s, N*C*H), 57.0 (s, N*C*CH$_3$), 28.8 (s, C*C*H$_3$). **5**: δ_H ($CDCl_3$): 6.51 (s, 2H, NC*H*), 6.45 (s, 5H, C_5*H*$_5$), 1.67 (s, 18H, CC*H*$_3$); δ_C (C_6D_6): 146.6 (s, N*C*N), 115.6 (s, *C*$_5$H$_5$), 109.2 (s, N*C*H), 59.0 (s, N*C*CH$_3$), 29.8 (s, C*C*H$_3$).

‡ *Crystal data*: **2**: $C_{14}H_{29}N_3Si$, M = 267.49, triclinic, a = 9.0758(2), b = 9.4187(2), c = 11.0961(3) Å, α = 84.7122(12), β = 83.0332(13), γ = 63.7546(9)°, U = 843.66(4) Å^3, T = 173 K, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.053 g cm^{-3}, μ(*Mo*–K_a) = 0.130 mm^{-1}, 18531 reflections measured, 3097 unique (R_{int} = 0.042) which were used in all calculations. The final $wR(F^2)$ was 0.1367 (all data). CCDC 229688. **5**: $C_{16}H_{25}Cl_2N_3Ti$, M = 378.16, orthorhombic, a = 12.8780(2), b = 17.5935(2), c = 8.5676(1) Å, U = 1941.15(4) Å^3, T = 173 K, space group *Pnma* (no. 62), Z = 4, D_c = 1.294 g cm^{-3}, μ(*Mo*–K_a) = 0.716 mm^{-1}, 40109 reflections measured, 1848 unique (R_{int} = 0.050) which were used in all calculations. The final $wR(F^2)$ was 0.0901 (all data). Complex **5** is located on a crystallographic mirror plane passing through Ti, N1 and C1. CCDC 229689. See http://www.rsc.org/suppdata/cc/b4/b401041h/ for crystallographic data in .cif or other electronic format.

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