Synthesis of a four-coordinate titanium(IV) oxoanion *via* deprotonation and decarbonylation of complexed formate†‡

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Deprotonation of the titanium formate complex $[Ar(t\text{-}Bu)N]_3TiOC(O)H$ with $LiN(i\text{-}Pr)_2$ resulted in the release of free CO and the formation of a titanium(IV) oxoanion complex, isolated as its lithium salt.

In recent years, both transition metal formates and oxos have been studied intensively; the former as model compounds in the rich and varied chemistry of syngas on metal surfaces,[1–3] and the latter due to their importance in biological[4] and industrial oxidations.[5] Historically, the oxo ligand has been encountered primarily in conjunction with the middle metals of the transition series;[6] this observation has motivated a number of recent syntheses of both early-[7–9] and late-metal[10,11] oxos. We report here on an unprecedented, base-triggered formate decarbonylation, resulting in the synthesis of the first anionic oxo of titanium(IV). DFT calculations have been carried out in order to elucidate the electronic structure of the new compounds.

Our synthesis commences with treatment of an emerald green ethereal solution of $Ti[N(t\text{-}Bu)Ar]_3$ (Ar = $3,5\text{-}Me_2C_6H_3$, **1**)[12] with 1 equiv. of *t*-butyl formate at 25 °C, resulting in an immediate color change to red-brown, followed by precipitation of a yellow solid over the course of a few minutes. On the basis of ^1H and ^{13}C NMR spectroscopy, X-ray crystallography, and elemental analysis, this solid is identified as $[Ar(t\text{-}Bu)N]_3TiOC(O)H$, **2**.§ Key spectroscopic features are the formate proton resonance at 8.36 ppm and the OCO stretch observed by FTIR at 1685 cm^{-1}.

The formation of formate **2** can be accounted for *via* initial generation of a titanium-stabilized ketyl radical, followed by *t*-Bu radical ejection to generate the observed product (see Scheme 1). A similar sequence of events has been observed upon treatment of **1** with $O_2Mo(O–t\text{-}Bu)_2$.[13] In both cases, the final product is the result of formal displacement of CMe_3 radical by **1**.

The solid-state structure of formate **2** is shown in Fig. 1.[14] The molecule crystallizes on a crystallographic 3-fold axis, with the result that the formate moiety is disordered over three positions. The geometry at titanium is approximately tetrahedral with an O(1)–Ti(1)–N(1) angle of 110.7(47)°. The observed Ti–O distance of 1.868(4) Å is similar to that observed in other compounds containing the tris-*t*-butylanilide ligand set.[13,15] The three-fold disorder, which we have not been able satisfactorily to resolve, prevents discussion of additional metrical parameters.

The successful deprotonation of **2** would provide a compound in which the CO_2 anion is stabilized by coordination to a Ti center. Such a compound would be of considerable interest in that the reduction potential of free CO_2 is −1.90 V *vs.* NHE.[16,17] In any event, treatment of **2** with a slight excess of $LiN(i\text{-}Pr)_2$ in Et_2O resulted in the formation of a new crystalline product whose ^1H NMR spectrum displayed a single N(*t*-Bu)Ar environment. An X-ray diffraction study revealed the product to be titanium(IV) oxoanion **3**, likely formed by facile CO ejection subsequent to deprotonation. We have previously observed decarbonylation of isoelectronic $[(Ar[t\text{-}Bu]N)_3Nb=N=C=O]^-$ to form an anionic nitridoniobium complex.[18] Detection of liberated CO in the present system was carried out by vacuum transfer of the volatiles onto $(Ph_3P)_3RhCl$ (Wilkinson's catalyst), resulting in formation of $(Ph_3P)_2Rh(CO)Cl$ as documented in the literature.[19] The generation of $HN(i\text{-}Pr)_2$ was confirmed in a separate experiment.
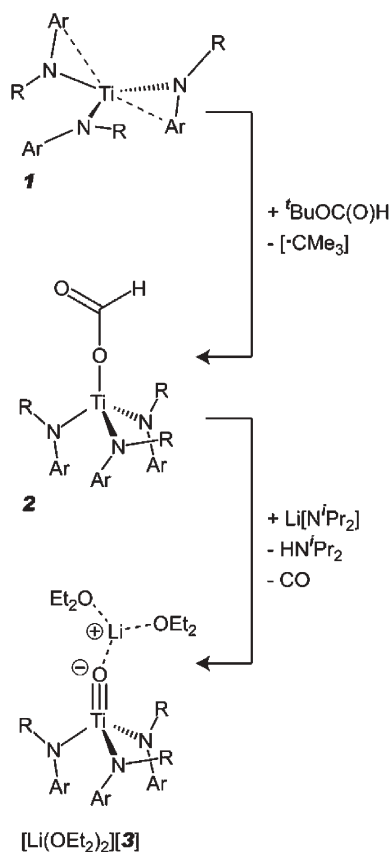
Scheme 1 Synthesis of **2** and **3**. R = *t*-Bu, Ar = $3,5\text{-}C_6H_3Me_2$.
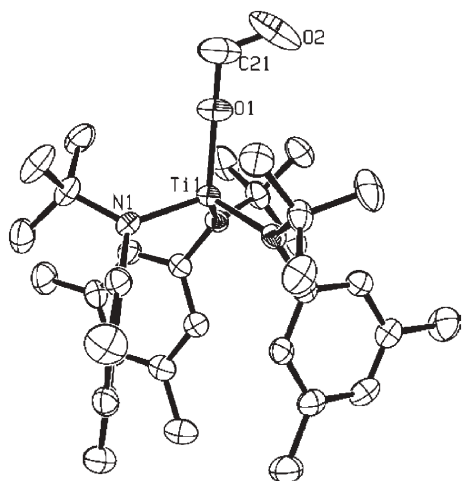

Fig. 1 ORTEP drawing of compound **2** with ellipsoids at the 50% probability level. The formate ligand is positionally disordered about the C_3 axis. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1) 1.874(4), Ti(1)–N(1) 1.928(3), O(1)–C(21) 1.285(8), C(21)–O(2) 1.282(13), O(1)–Ti(1)–N(1) 110.74(7), O(1)–C(21)–O(2) 114.3(7).

The solid-state structure of **3** (see Fig. 2), reveals the expected coordination of the titanoxide anion to the Li cation, with a Li–O distance of 1.801(6) Å.[20] The Li$^+$ ion is coordinated additionally by two molecules of Et$_2$O, adopting an overall trigonal planar geometry. The Ti–O distance, at 1.717(2) Å, is significantly contracted relative to **2**. While anionic titanium(IV) oxos have not been previously structurally characterized, typical Ti–O distances in neutral titanyls range from 1.61 to 1.68 Å.[6] Andersen *et al.* have prepared the anionic oxotitanium(III) compound [Cp*$_2$TiOLi(THF)]$_2$, which features an average Ti–O distance of 1.787 Å,[21] while Hoskin and Stephan's oxozirconium(IV) anion, [Cp*$_2$Zr(H)OLi(THF)]$_2$, exhibits a Zr–O distance of 1.847 Å.[22]

These comparisons suggest that the Ti–O interaction in **3** is best viewed as a multiple bond.

To further address this issue, we have carried out DFT calculations on the model compounds H(O)COTi(NH$_2$)$_3$ (**2-m**) and [Li(OMe$_2$)$_2$][OTi(NH$_2$)$_3$] (**3-m**).¶ The key features of the experimental structures are satisfactorily reproduced at the BP86 level of density functional theory.[23] Inspection of the Laplacian of the electron density[24] indicates that, in both cases, the Ti–O bond is characterized by considerable ionic character, as anticipated based on the large difference in electronegativities between Ti and O. On moving from **2-m** to **3-m**, however, the value of the electron density at the bond critical point increases from 0.1134 to 0.1815 a.u., consistent with a substantial increase in bond order and, thus, covalency. Additionally, a pair of degenerate orbitals corresponding to orthogonal Ti–O π bonds is observed in the DFT analysis. Since the electron localization function (ELF) has been particularly valuable for illuminating complex issues of chemical bond multiplicity,[25] we provide in Fig. 3 an ELF isosurface plot for **3-m**.[26] In the ELF, triple bonds give rise to a toroidal basin surrounding the bond axis. In Fig. 3 it is seen that such a toroidal basin is present and is shifted close to the O atom, nearly merging with the oxygen lone pair basin. By all accounts, the titanoxide anion of interest herein manifests a quite polar triple bond.

The chemistry presented herein provides precedent for bound formate decarbonylation as triggered by deprotonation. The existence of such a transformation may be significant with regard to the reactions of CO and CO$_2$ on metal surfaces.[1–3] Furthermore, oxoanion **3** is likely to be a potent nucleophile as
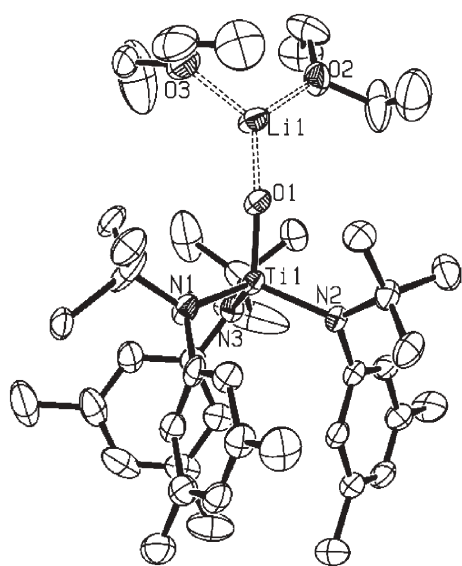

Fig. 2 ORTEP drawing of ion pair [Li(OEt$_2$)$_2$] **3** with ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1) 1.717(2), Ti(1)–N(1) 1.986(3), Ti(1)–N(2) 1.989(2), Ti(1)–N(3) 1.990(3), O(1)–Li(1) 1.801(6), Ti(1)–O(1)–Li(1) 167.8(2).
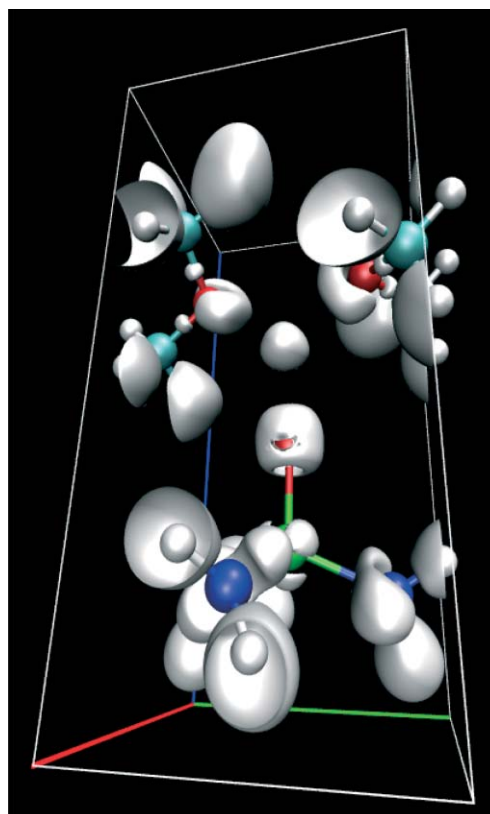

Fig. 3 A plot of the isosurface corresponding to ELF = 0.84 for **3-m**. Color scheme: green, Ti; dark blue, N; light blue, C; red, O; white, H.

well as an interesting metallo-ligand, prospects currently under investigation. Finally, the valence-isoelectronic relationship of $[OTi(N[t\text{-Bu}]Ar)_3]^{1-}$ to the previously described neutral $[OV(N[t\text{-Bu}]Ar)_3]$ and cationic $[OMo(N[t\text{-Bu}]Ar)_3]^{1+}$ complexes reveals **3** to be the newest member of an intriguing series of four-coordinate oxometal entities.[27,28]

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Notes and references

§ All manipulations were carried out under an atmosphere of dry nitrogen using solvents purified by standard methods. The new compounds **2** and **3** gave satisfactory elemental analyses (C, H, and N).

¶ Calculations were carried out using the ADF2004.01[29] software package. Visualization of the Laplacian and determination of bond critical points were performed using the Xaim software package.[30] The ELF isosurface was generated using the DGRID software package.[31]

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14 **Crystal data**. $C_{37}H_{54}N_3O_2Ti$, $M = 620.73$, rhombohedral, $a = 15.7365(7)$, $b = 15.7365(7)$, $c = 24.686(2)$ Å, $U = 5294.1(6)$ Å^3, $T = 193$ K, space group $R\bar{3}$, $Z = 6$, $\mu(\text{Mo-K}\alpha) = 0.277$ mm^{-1}, 4300 reflections measured, 1423 unique ($R_{int} = 0.043$) which were used in all calculations. The final w$R(F^2)$ was 0.134 (all data). Due to the disorder, the formate hydrogen atom was not included in the refinement. CCDC 267713. See http://dx.doi.org/10.1039/b504492h for crystallographic data in CIF or other electronic format.
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