Dihydrogen cleavage by a dimetalloxycarbene-borane frustrated Lewis pair

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COMMUNICATION

Dihydrogen cleavage by a dimetalloxycarbene-borane frustrated Lewis pair

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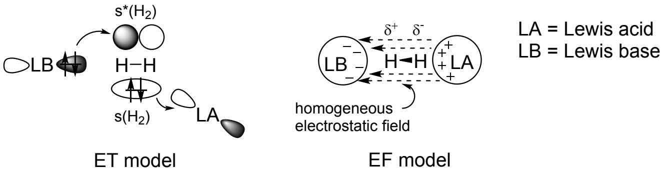
A frustrated Lewis pair of dititanoxycarbene [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-CO$_2$)] (Ar = 3,5-Me$_2$C$_6$H$_3$) and B(C$_6$F$_5$)$_3$ cleaved dihydrogen under ambient conditions to give the zwitterionic formate [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-OCHO-η*O*:η*O´*)(B(C$_6$F$_5$)$_3$)] and the hydrido borate [Ti(N[^{t}Bu]Ar)$_3$][HB(C$_6$F$_5$)$_3$].

The long-held dogma that H_2 activation requires a metal was definitively refuted in 2006. In a series of seminal publications, Stephan and co-workers introduced the heterolytic H_2 cleavage with simple main group compounds.[1] For that, frustrated Lewis pairs (FLPs) were used where recombination to the classical adducts through dative bonding was aggravated by the steric bulk of the substituents. The reaction of H_2 with a stoichiometric mixture of P-donors and B-acceptors gave the corresponding phosphonium borates. The field of small molecule activation[2] and catalysis[3] using the FLP principle has rapidly expanded ever since. The Lewis bases of choice are phosphines, (cyclic) amines, N-heterocyclic carbenes (NHCs) and O donors while, apart from Al and Si acceptors, the Lewis acids are mostly confined to boranes. Notably, the aluminum analogues have recently attracted attention as viable FLP systems for reaction with organic molecules[4] and for catalysis.[5]

Amongst the many reactions now known for FLPs, the mechanism for the H_2 activation has experienced special scrutiny. There are two models brought forward to explain the heterolytic cleavage, *viz*. the electron transfer (ET) model and the electrostatic field (EF) model.[6] The ET model is inspired by H_2 activation at transition metal centers where the filled and empty d orbitals are involved. It proposes a simultaneous push-pull transfer of electrons from the lone pair of the Lewis base into the antibonding σ* orbital of H_2, and donation from the bonding σ orbital of H_2 into the Lewis acid (Scheme 1, left). The disadvantages of the ET model are that it is geometrically restrictive, in that it requires a side-on approach of the Lewis acid, and that the gradual electron transfer is energetically rather unfavorable. The EF model, on the other hand, explains the low activation barrier for the H_2 cleavage by invoking an instant polarization of H_2 when it enters the homogeneous electrostatic field between the Lewis pairs (Scheme 1, right).



Scheme 1. FLP H_2 activation models: electron transfer (ET) and electrostatic field (EF).

This favorable charge separation facilitates the ensuing heterolytic cleavage of H_2. The EF model thus operates with geometrically early transition states (TS) and eliminates the need for the rather unfavorable late TS. The consequences for the EF-TS are a short H_2-like H-H separation, and an end-on acid /end-on base H_2 activation. This stands in opposition to a considerably elongated H-H distance and a side-on acid attack of the acid for the ET-TS. With its improved allocation of the TS, the EF model has been successfully employed in the prediction of H_2 activations performed even by weakly associated classical Lewis adducts.[6d]

We decided to test the models by using the recently developed “masked” dimetalloxycarbene [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(CO$_2$)] (Ar = 3,5-Me$_2$C$_6$H$_3$, **1**) as the Lewis base.[7] In this previous study, the carbene carbon of the bridging carbonite (CO_2^{2-}) ligand[8] had acted as a nucleophilic carbene. It had attacked free CO$_2$ to form the oxalate complex [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-C$_2$O$_4$-κ*O*,*O´*)] and could be protonated by [H$_2$N[^{t}Bu]Ar][B(C$_6$F$_5$)$_4$] to give the bridging formate complex [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-HCO$_2$-κ*O*,*O´*)][B(C$_6$F$_5$)$_4$]. While, in the solid state, the carbene carbon coordinates to only

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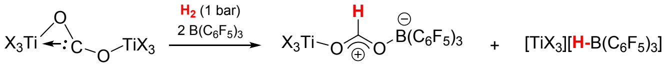
one of the $[Ti(N[^tBu]Ar)_3]^+$ fragments, NMR spectroscopic studies and DFT calculations confirmed a low-barrier transition state for alternating bonding to both metal centers, thus providing, in average, a free dioxycarbene in solution. Here, we report the first facile, heterolytic, FLP-type H_2 cleavage where the Lewis base is a dimetalloxycarbene.

At the outset, the possible formation of methanediolate $[(Ti(N[^tBu]Ar)_3)_2(\mu\text{-}H_2CO_2\text{-}\kappa O,O')]$[9] which might be triggered by minute free cationic $[Ti(N[^tBu]Ar)_3]^+$ in solution[10] was excluded. A toluene solution of dititanoxycarbene $[(Ti(N[^tBu]Ar)_3)_2(CO_2)]$ (Ar = 3,5-$Me_2C_6H_3$, **1**) was exposed to up to 40 bar H_2 and did not react. There is also no evidence for the formation of a classical adduct between **1** and $B(C_6F_5)_3$.[11] Their ^1H and ^{19}F NMR spectroscopic shifts remained unchanged in an equimolar mixture in benzene-d_6 and the compounds were recovered unreacted. However, under an atmosphere of 1 bar H_2 the thawing orange suspension gradually turned into a red solution when warming to room temperature. The ^1H NMR spectrum of the crude reaction mixture in chloroform-d_1 showed signals for several species which did not match the expected hydridoborate product $[(Ti(N[^tBu]Ar)_3)_2(\mu\text{-}H_2CO_2\text{-}\kappa O,O')]$-$[HB(C_6F_5)_3]$. However, with two equivalents $B(C_6F_5)_3$ and an excess of 1 bar H_2, **1** was cleanly converted into $[(Ti(N[^tBu]Ar)_3)_2(\mu\text{-}OCHO\text{-}\kappa O,O')(B(C_6F_5)_3)]$ (**2**) and $[Ti(N[^tBu]Ar)_3][HB(C_6F_5)_3]$ (**3**$[HB(C_6F_5)_3]$) in 62% and 60% isolated yield, respectively (Scheme 2). Apparently, the substitution of a $[Ti(N[^tBu]Ar)_3]^+$ fragment by free borane to form **2** is favorable via a putative cationic, formate-bridged intermediate. Hence the necessity for the second equivalent of $B(C_6F_5)_3$. The released $[Ti(N[^tBu]Ar)_3]^+$ recombines with hydrido borate to give **3**$[HB(C_6F_5)_3]$.



1 **2** (62%) **3**$[HB(C_6F_5)_3]$ (60%)

Scheme 2. H_2 cleavage with the FLP-system **1** · $B(C_6F_5)_3$ (X = $N[^tBu]Ar$, Ar = 3,5-$Me_2C_6H_3$).

The products were separated by extracting **2** with *n*-pentane. Red crystals of the residual ionic **3**$[HB(C_6F_5)_3]$ were obtained by recrystallizing from diethyl ether at −40 °C. Compound **2** was isolated as red crystals after removal of *n*-pentane from the filtrate, and recrystallization of the orange residue from diethyl ether at –40 °C. The molecular structures of **2** (Figure 1, left) and **3**$[HB(C_6F_5)_3]$ (Figure 1, right) were determined through X-ray diffraction on single crystals.

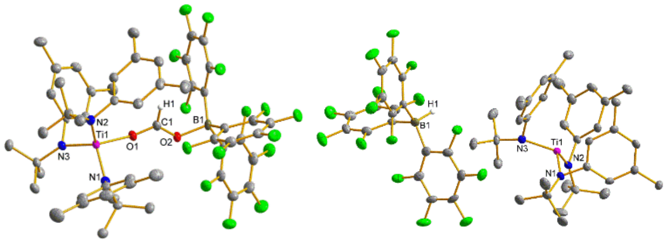


Figure 1. Molecular structures of **2** and **3**$[HB(C_6F_5)_3]$. Displacement parameters shown at the 50% probability level. All hydrogen atoms with the exception of H1 for both compounds and co-crystallized diethyl ether for **2** are omitted for clarity. Selected interatomic distances (Å) and angles (°): **2**: Ti1–O1 2.004(3), O1–C1 1.233(4), C1–O2 1.269(4), O2–B1 1.554(5), C1–H1 1.04(5); Ti1-O1-C1 149.7(3), O1-C1-O2 121.3(4), C1-O2-B1 123.9(3). **3**$[HB(C_6F_5)_3]$: Ti–N1/N2/N3 1.870(3), Ti1–plane(N1-N2-N3) 0.58(1).

Cationic **3**, as previously reported,[7] is trigonal pyramidal with titanium located 0.58(1) Å above the plane spanned by the three nitrogen atoms. This motif for cationic titanium *tris*(anilide) is caused by electron donation from the occupied non-bonding nitrogen orbitals into the empty d orbitals of the electron deficient metal center.[10] In its ^1H NMR spectrum in chloroform-d_1, the locked N–Cipso rotation causes a split of the ArMe2 and the ortho-CH resonances each into two broad singlets of equal intensity.[12] The $^{11}B\{^1H\}$ NMR spectrum features a sharp singlet at δ −24.73 ppm, which appears as a doublet with $^1J_{BH}$ = 88.0 Hz in the ^{11}B NMR spectrum. The B–H stretch vibrations of **3**$[HB(C_6F_5)_3]$ between ν = 2417 and 2351 cm^{-1} in the NIR spectrum support the presence of boron-bound hydride.[13]

The C–O distances in **2** (1.233(4) Å, 1.269(4) Å) are typical for formate[14] and the B1–O2 distance (1.554(5) Å) is within 3σ of the sum of covalent radii for a boron-oxygen single bond (1.48 Å).[15] The overall neutral formate-bridged complex **2** is structurally related to the reported cationic $[(Ti(N[^tBu]Ar)_3)_2(\mu\text{-}HCO_2\text{-}\kappa O,O')][B(C_6F_5)_4]$,[7] **4**$[B(C_6F_5)_4]$, in that two of the anilido aryl moieties are tilted and directed towards the bridging formate unit. Similar to the latter, **2** was readily obtained in 96% isolated yield by treatment of the terminal formate complex $[Ti(N[^tBu]Ar)_3(OCHO)]$[16] with $B(C_6F_5)_3$. The isotopically labelled **^{13}C-2** formed accordingly with $[Ti(N[^tBu]Ar)_3(O^{13}CHO)]$. The asymmetric C-O stretch bands $\nu_{as}(^{12/13}CO)$ were identified by comparing the NIR spectra of **2** and **^{13}C-2**, i.e. $\nu_{as}(CO)$ = 1617 cm^{-1} and $\nu_{as}(^{13}CO)$ = 1574 cm^{-1}. The $^{11}B\{^1H\}$ NMR spectrum of **2** in chloroform-d_1 features a broad singlet at δ −1.75 ppm in the characteristic region for borates.[17]

The ^1H NMR spectrum of **2** exhibits chemically equivalent anilide environments. At δ 5.84 ppm, the formate resonance appears as a doublet with $^1J_{CH}$ = 218.9 Hz for **^{13}C-2**, whereas it is a singlet for **2**. This is a distinct upfield shift when compared to the chemical shift of the terminal formate complex,[16] and a feature **2** has in common with the reported **4**$[B(C_6F_5)_4]$.[7] However, for neutral polyhedral boranes, aromatic solvent induced NMR shifts (ASIS) are also known for the bridging hydrogens, which bear a partial positive charge and are acidic.[18] In the case of **2**, the magnetic shielding of the formate proton is due to π interactions[19] with the anilide aryls. Here, ASIS is not relevant because the upfield shift observed in the aromatic solvents benzene-d_6 (6.04 ppm) and toluene-d_8 (δ 5.99 ppm) also occurred in the chlorinated hydrocarbons dichloromethane-d_2 (δ 5.87 ppm) and chloroform-d_1 (δ 5.84 ppm). The π interaction is only possible because of the tilt of two anilides, which itself is a result of electron density donation from the nitrogen lone pairs into the electron-poor metal center.[10] This further corroborates a retention of this structural feature in solution on the time-scale of the NMR experiment. The combined structural and spectroscopic data suggest that **2** is zwitterionic, with its boron negatively charged and the bridging formate unit bearing a delocalized positive charge. The latter is a consequence of electron pair delocalization over the formate ligand as also found in **4**$[B(C_6F_5)_4]$.

It is noteworthy that $B(C_6F_5)_3$ partially dissociates from $[Ti(N[^tBu]Ar)_3(OCHO)]$ when dissolved in coordinating THF-d_8, and thus features a separate resonance set in the ^{19}F NMR spectrum. The ^1H NMR spectrum displayed free $[Ti(N[^tBu]Ar)_3(OCHO)]$ and **2** in an equilibrium, which favors **2** in a 2:1 ratio. The dynamic behavior in solution caused a broadening of the resonances which precluded a detection of the formate resonance of **2**. Compound **2** was recovered unreacted after removal of the solvent under reduced pressure, as ascertained through ^1H NMR spectroscopy on the residue in benzene-d_6.

The consumption profiles for **1** with excess H_2 or D_2 in the presence of two equivalents of $B(C_6F_5)_3$ at 50 °C are shown in the ESI. D_2 gave the analogous $[(Ti(N[^tBu]Ar)_3)_2(\mu\text{-OCDO-}\kappa O,O')(B(C_6F_5)_3)]$ (**D-2**) and **3**$[DB(C_6F_5)_3$.

We turned to computational methods to elucidate the FLP-type mechanism of the heterolytic cleavage. We further sought to establish which of the two models apply, i.e. the electron transfer (ET) or the electrostatic field (EF) model. DFT calculations on the B3PW91 level showed that, when compared to the starting materials, the products are thermodynamically clearly favored by $\Delta H^0 = -219$ kJ·mol^{-1}. The transition state **TS-1** (see ESI, Figure S68) features an orientation along the H-H axis which is typical for a low-energy "early" TS of the EF model, i.e. an end-on attack by the carbene Lewis base (C1-H1-H2 175.1°) and an only partially side-on located Lewis acid (B1-H2-H1 145.9°). The low activation barrier of $\Delta H^{\ddagger} = 39$ kJ mol^{-1} and the distinct charge separation at H1 (+0.42) and H2 (−0.42) additionally corroborate an EF regime. The EF model generally requires an H-H distance comparable to the H-H bond length in free H_2 of 0.76 Å.[6d] However, the H1-H2 separation of 1.72 Å in **TS-1** is more than twice as long and indicates a fully cleaved H-H bond. It is also larger than the calculated H-H distance in the reported TS with the classical Lewis adduct $Me_3P\text{-}BF_3$ (0.98 Å), which itself had been the largest in a series of calculated TS H-H separations.[6d] The latter had been assigned as a high-energy "late" TS, which is characteristic for an ET regime. In **TS-1**, the C-H (1.35 Å) and B-H (1.52 Å) contacts are well longer than the corresponding sum of covalent radii for single bonds, i.e. 1.07 Å and 1.17 Å,[20] respectively, which is in accord to reported high-energy "late" TS.[6d] **TS-1** can therefore be described as an unusual low-energy "*very* late" TS, where the arrangement of the Lewis partners is characteristic for the EF model. It further supports the notion formulated by De Vleeschouwer, Pinter and co-workers that a reaction coordinate based on the H-H separation is, mechanistically, not substantial for this reaction.[6d]

In conclusion, dioxycarbene, $[(Ti(N[^tBu]Ar)_3)_2(CO_2)]$, has been employed as Lewis base for the facile FLP-type heterolytic cleavage of H_2 at ambient conditions. This is another example showing dititanoxycarbene to act as a nucleophilic carbene. Computational studies on the activation mechanism for the H_2 cleavage step indicated an atypical EF regime for this FLP. The "late" TS featured H_2 fully cleaved into hydride and a proton, which were suspended in the strong homogeneous EF between Lewis acid and base. At the same time, the low activation energy of $\Delta H^{\ddagger} = 39$ kJ mol^{-1} and the end-on base/(mostly) end-on acid-geometry of **TS-1** suggested a low-energy TS. This work further corroborates that, for the FLP-type activation of H_2, the H-H distance is inconsequential as a reaction coordinate. Instead, the strength of the homogeneous EF matters. Here, dioxycarbene contributed to such a strong EF that the spatial and the charge separations in the activated H_2 were well advanced at the transition state.

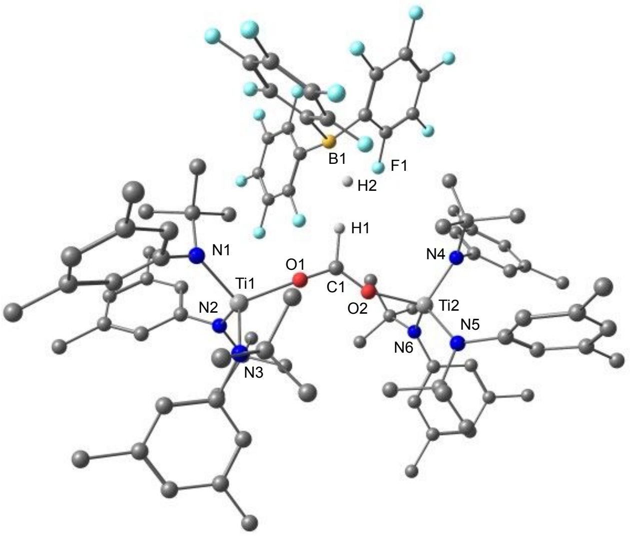


Figure 2. Calculated structure of the transition state TS-1. Selected interatomic distances (Å) and angles (°): H1...H2 1.72, B1-H2 1.52, C1-H1 1.35; B1-H2-H1 145.9, C1-H1-H2 175.1.

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Conflict of Interest

There are no conflicts to declare.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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