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# **Frustrated Lewis Pairs**

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## Cationic Ti(IV) and neutral Ti(III) titanocene-phosphinoaryloxide frustrated Lewis pairs: hydrogen activation and catalytic amine-borane dehydrogenation<sup>†</sup>

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Titanium–phosphorus frustrated Lewis pairs (FLPs) based on titanocene–phosphinoaryloxide complexes have been synthesised. The cationic titanium(IV) complex  $[Cp_2TiOC_6H_4P(^{t}Bu)_2][B(C_6F_5)_4]$  **2** reacts with hydrogen to yield the reduced titanium(III) complex  $[Cp_2TiOC_6H_4P(^{t}Bu)_2][B(C_6F_5)_4]$  **5**. The titanium(III)–phosphorus FLP  $[Cp_2TiOC_6H_4P(^{t}Bu)_2]$  **6** has been synthesised either by chemical reduction of  $[Cp_2Ti(Cl)OC_6H_4P(^{t}Bu)_2]$  **1** with  $[CoCp^*_2]$  or by reaction of  $[Cp_2Ti(SiMe_3)_2]$  with  $2-C_6H_4(OH)\{P(^{t}Bu)_2\}$ . Both **2** and **6** catalyse the dehydrogenation of Me<sub>2</sub>HN·BH<sub>3</sub>.

#### Introduction

Solution phase combinations of sterically hindered Lewis acid-Lewis base pairs, so-called Frustrated Lewis Pairs (FLPs), have been the subject of recent interest, particularly because of the high latent reactivity of such species in the activation of small molecules. Initial studies have focused on the reversible heterolytic cleavage of dihydrogen, which offers the promise of metalfree catalytic hydrogenation.<sup>1-4</sup> However, the diversity of the reactions reported is now large and continues to grow.<sup>5</sup> The bulky phosphine and fluorinated borane systems (such as P<sup>t</sup>Bu<sub>3</sub>/  $B(C_6F_5)_3$  pioneered by Stephan have been modified so that the specific reactivity of FLP systems can be controlled by subtle steric and electronic alterations to either the Lewis acidic or basic components.<sup>6,7</sup> A great deal of work has also focused on extending the range of main group FLPs to other main group Lewis acids (*e.g.* simple alkyl boranes,  $alanes^{8,9}$  allenes<sup>10</sup>) or bases (*e.g.* amines<sup>11</sup> carbenes<sup>12</sup> and sulfides<sup>13</sup>). Linking the two components of the FLP into a single amphoteric molecule has also led to interesting results.<sup>14,15</sup>

We have been exploring the chemistry of cationic group 4 (Zr and Hf) metallocene–phosphinoaryloxide complexes as analogues of linked main group FLPs where the Lewis acidic borane component is replaced with an electrophilic transition metal centre. Our initial results have established the analogy with main group FLPs<sup>16,17</sup> but also demonstrated additional reactivity, for example the catalytic dehydrogenation of amineboranes,<sup>17</sup> a reaction only achieved in a stoichiometric sense with main group FLP systems.<sup>18,19</sup> It is our view that combining the ability of FLPs to activate substrate molecules *via* ditopic

activation offers an exciting extension of FLP chemistry with new possibilities for exploitation in activation pathways and reactivity patterns.

During our study of cationic Zr and Hf metallocene–phosphinoaryloxy complexes we have noted that both the nature of the metal and ancillary ligands have a dramatic effect on the reactivity of such complexes.<sup>20</sup> We were keen to complete the series by examining the reactivity of the analogous Ti complex but were limited by the synthetic challenge of obtaining pure samples of such complexes. Adopting a modified synthesis based on chloride abstraction from the parent compound  $[Cp_2Ti\{OC_6H_4P-({}^{t}Bu)_2\}Cl]$  **1** with  $[Ph_3Si][B(C_6F_5)_4]$  has finally allowed us to access this complex **2** (Scheme 1), as we reported recently.<sup>21</sup> With this compound now in hand, we report here our initial exploration of its FLP-type reactivity and, in particular, facile reduction chemistry to Ti(III).



Scheme 1 Synthesis of 2 (ref. 21).

#### **Results and discussion**

#### Hydrogen activation with [Cp<sub>2</sub>TiOC<sub>6</sub>H<sub>4</sub>P(<sup>t</sup>Bu)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 2

The archetypal reaction of FLPs is arguably the heterolytic cleavage of dihydrogen and we have already reported analogous

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Scheme 2 Attempted reaction of  $H_2$  with 2, 3 and 4, and suggested mechanism for the reduction of 2 by  $H_2$  to give 5. *Reagents and conditions*: PhCl, 1–3 bar  $H_2$ , 25 °C, 20 h.

reactivity when our Zr and Hf complexes have at least one Cp\* ligand. By contrast, the Cp derivatives 3 and 4 do not appear to react with  $H_2$  under the conditions tested to date (1-3 bar, -30 to 50 °C, weeks). Given this apparent inertness of 3 and 4, we were surprised to find that 2 reacts smoothly with even low pressures of H<sub>2</sub> over the course of 20 hours (Scheme 2). During the course of the reaction, the intense purple colour of 2 slowly faded to a light brown colour and the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR indicated complete conversion of 2 to a new species. However, the complete loss of the Cp resonances and broadening of the aromatic signals in the <sup>1</sup>H NMR spectrum for this new species suggest it is a paramagnetic Ti(III) complex, observations which are also consistent with the genuine Ti(III) species **6** (*vide infra*) and other related compounds.<sup>22,23</sup> A weak signal in the  ${}^{31}P{}^{1}H{}$ NMR spectrum at  $\delta$  22.5 ppm is indicative of a P-H centre. The product was crystallized and unambiguously determined by X-ray crystallography to be 5 (Fig. 1).

Clearly, **2** is reduced under the reaction conditions to **5**. It is possible that the reduction occurs *via* an initial heterolytic activation of H<sub>2</sub>, followed by Ti–H bond homolysis to give a hydrogen radical (and ultimately hydrogen after dimerization)<sup>24</sup> and a cationic Ti(III) species. The formation of  $[Cp_2TiH_2]_2$  by the hydrogenation of  $[Cp_2TiMe_2]$  provides a related example in which a one-electron reduction of a Ti(IV) species is affected by hydrogen.<sup>25</sup>

#### Synthetic routes to neutral [Cp<sub>2</sub>TiOC<sub>6</sub>H<sub>4</sub>P(<sup>t</sup>Bu)2] 6

Despite being less electrophilic, the group 4 M(III) compounds (of the type [Cp<sub>2</sub>MX]) may still be considered as Lewis acids.<sup>26</sup> For example, intramolecular hydroaminations that are typical of the highly Lewis acidic group 4 M(IV) complexes are still possible with Ti(III) compounds.<sup>27</sup> Furthermore, it was anticipated the presence of a d-electron would facilitate the binding of  $\pi$ -acceptor ligands such as CO, hydrogen, ethene, and even nitrogen, opening new reaction pathways for FLP chemistry. Ti(III) compounds are mildly reducing and it is conceivable that a reduction may accompany an FLP-type activation of a small molecule with these compounds. The unexpected reduction with H<sub>2</sub> described in the previous section led us to investigate reliable routes to neutral Ti(III) titanocene–phosphinoaryloxy complexes.



Fig. 1 Molecular structure of 5. The borate anion and all hydrogen atoms (except P–H) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ti1–O1 1.941(2), C16–P1 1.773(2), P1–C17 1.846(3), C21–P1 1.850(3), Cp–Ti1 2.039. Angles (°): Ti1–O1–C11 141.7(1), C16–P1–H25 107(1), H25–P1–C17 104(1), H25–P1–C21 103(1), C16–P1–C17 110.0(1), C21–P1–C16 111.8(1), C21–P1–C17 119.8(1), Cp–Ti1–Cp 138.54.



Scheme 3 Synthesis of 6. *Reagents and conditions*: (a) 1 eq.  $[CoCp*_2]$ , benzene, 25 °C, 20 h. (b) 2 eq. KHMDS, THF, 25 °C, 20 h. (c) 1 eq. *t*-Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH, hexanes, 25 °C, 30 min. (d) 0.98 eq.  $[(C_5H_4Me)_2Fe][B(C_6F_5)_4]$ , PhCl, 25 °C, 5 min.

The mixed alkoxy/chloride precursor **1** provides a convenient, highly soluble precursor for the synthesis of the Ti(III) compound **6**. Treatment of **1** with a stoichiometric quantity of  $[CoCp*_2]$  resulted in clean reduction, evidenced by the recovery of almost exactly one equivalent of the expected by-product  $[CoCp*_2][Cl]$  (Scheme 3). The reaction is reversible, so that treatment of **6** with 1 eq  $[(C_5H_4Me)_2Fe][B(C_6F_5)_4]$  gave quantitative conversion to the Ti(IV) species **2**. This reduction procedure was free of side reactions but is a rather uneconomical route to **6** because of the expense of  $[CoCp*_2]$ . An alternative, and potentially more general, synthesis of **6** was realised by protonolysis of  $[Cp_2Ti(N-(TMS)_2)]$  by *t*-Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH. This procedure provided a convenient method to prepare **6** in high yield and excellent purity. Deep purple single crystals suitable for X-ray diffraction were

confirmed (Fig. 2). The X-ray structure shows the monomeric structure of **6** and the presence of a very long Ti–P interaction (2.907(2) Å) exists in the solid state.<sup>28</sup> The presence of the 5-membered ring in **6** creates an unusually acute Ti–O–C bend angle compared to the simple alkoxy-analogues  $A^{22}$  and  $B^{23}$  (Fig. 3). In addition, **6** contains a rather long Ti–O bond in comparison to these other two compounds. It has been suggested<sup>30,31</sup> that the extent of Ti  $\leftarrow$  O donation is proportional to the polarity of the Ti–O bond, and hence the electron donor capability of the

Ti–O bond, and hence the electron donor capability of the O-atom. Importantly, these studies concluded that the Ti  $\leftarrow$  O donation is largely unaffected by the Ti–O–C angle, although a coincidental correlation is observed in the complexes presented

here. This may explain why the Ti-O bond is longer in 6

obtained from hexane at low temperature and the structure



**Fig. 2** Molecular structure of **6**. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. For selected bonds lengths and angles see Table 1.



**Fig. 3** Schematic representation of the three important angles in  $[Cp_2ML_2]$  complexes (left) and examples of other  $[Cp_2TiOR]$  complexes, **A** and **B**.<sup>22,23</sup> The two angles,  $\alpha_1$  and  $\alpha_2$ , refer to the angles made between the ligand, M centre and the imaginary normal that bisects the two Cp rings in a staggered conformation. The 2a<sub>1</sub> frontier orbital is calculated to extend in this direction.<sup>29</sup>

compared with A, but not why it is longer than in B, where the electron donor capabilities are expected to be very similar. The long Ti-O bond is best explained by the presence of the Ti-P interaction in 6. The bonding picture in complexes of the type  $[Cp_2ML]$  and  $[Cp_2ML_2]$  has been studied in some detail.<sup>29</sup> and the MO pictures 30,31 of these complexes help to explain these observations. Accommodation of the extra pair of electrons from the Ti-P bond in 6 is expected to result in population of the b<sub>2</sub> orbital, reducing its availability to participate in a stabilizing Ti  $\leftarrow$  O  $\pi$ -bonding interaction. The net result is an elongated Ti–O bond and a geometry that is very similar to the M(IV) analogues (Table 1). The absence of paramagnetic broadening of the  ${}^{31}P$ resonance in the  ${}^{31}P{}^{1}H$  NMR spectra of 6 suggests that this interaction is not present in solution. This was later confirmed by an ESR experiment in which no  $^{31}\text{P}-^{47}\text{Ti}$  or  $^{31}\text{P}-^{49}\text{Ti}$  fine or hyper-fine coupling was observed.<sup>32</sup>

#### Catalytic dehydrocoupling of Me<sub>2</sub>NHBH<sub>3</sub> by 2 and 6

We have already reported that transition metal FLPs are active catalysts for the dehydrocoupling of amine-boranes, in contrast to main group systems which only mediate this reaction in a stoichiometric sense.<sup>16</sup> Our investigations into the mechanism of this catalysis suggest that these systems are operating *via* an FLP-type mechanism, in contrast to the superficially related  $[Cp_2M(II)]$  (M = Ti, Zr and Hf) systems reported by Manners *et al.*<sup>33</sup> and Chirik *et al.*<sup>34</sup> In both these literature examples, Ti is the most active metal, with little or no activity observed with the analogous Zr(IV) and Hf(IV) systems. These trends have been rationalized in terms of the relative stability of +2 and +4 oxidation states of the group 4 metallocenes and thus the relative accessibility of an M(II)/M(IV) redox manifold during catalysis.<sup>33,35</sup> Both **2** and **6** were found to be active catalysts (entries 3 and 4, Table 2), albeit with substantially decreased activity

Table 2 Comparison of the catalytic activities for the dehydrocoupling of  $Me_2NHBH_3$  to cyclo- $[Me_2NBH_2]_2$ 

Entry	Compound	Loading/mol%	Solvent	TOF <sup>a</sup> /h <sup>-1</sup>
1	3	2	PhCl	384
2	4	2	PhCl	42
3	2	2	PhCl	12
4	6	10	$C_6D_6$	0.8

 $^a$  Calculated from monitoring of conversion by NMR spectroscopy at 23 °C.

Table 1	Comparison	of some relevant	t structural	parameters	for 2, 3	3, 4	, 6	, A and	В
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Compound	d(M_O)/Å	$d(Cn-M)/Å^a$	M_O_C/°	a./°	<i>a_</i> /°	A/°	/°
Compound		u(cp wi)//	M O C/	<i>α</i> <sub>1</sub> /	u2/	0/	$\psi_{\prime}$
6	2.028(6)	2.07	124.3(5)	41.7	27.66	136.3	69.4(2)
Α	1.810(3)	С	175.4(11)	$0^b$	n/a	С	c
В	1.892(2)	2.36	142.3(2)	$0^b$	n/a	135.5	С
2	1.901(5)	2.06	122.5(4)	43.5	28.0	129.3	71.5(1)
3	1.9972(1)	2.20	124.51(1)	42.4	27.8	128.2	70.18(4)
4	1.989(2)	2.19	121.7(2)	42.6	28.5	128.1	71.16(5)

<sup>a</sup> Mean of the two M–Cp centroid distances. <sup>b</sup> Estimated from the available X-ray structural data. <sup>c</sup> Data not available.

relative to both the Zr and Hf systems reported previously by us (compounds 3 and 4, entries 1 and 2), and indeed those of Manners<sup>33</sup> and Chirik.<sup>34</sup>

This striking decrease in activity between 3 or 4 and 2 was unexpected. If the Lewis acidity of the metal centre is key to the catalytic activity, then it is not clear why the Ti compound 2 should be so much less active than the Zr and Hf analogues 3 and 4.36 Although bond dissociation energies of M-L bonds are generally lowest for Ti compared to Zr and Hf, during the many attempts at preparing 2 it was noted that the Ti-C bonds appeared to undergo protonolysis far less readily than in either the Zr of Hf compounds. Consequently, the slow rate may be a factor of an increasing stable Ti-H bond that would be present in the cationic intermediate  $[Cp_2Ti(H)OC_6H_4PH'Bu_2]^+$  that is postulated to form upon dehydrogenation of Me<sub>2</sub>NHBH<sub>3</sub>.<sup>16</sup> Since the Ti-H bond is expected to be thermodynamically less stable than either Zr-H or Hf-H bonds, it is presumed that the stability is kinetic in origin and is a product of the smaller size of Ti. When following the catalysis using in situ <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy, the resonance for free Me<sub>2</sub>NHBH<sub>3</sub> was extremely broad in the presence of 2.37 In addition, upon mixing the reagents, an initial colour change from deep purple/black to light brown was accompanied by a very brief period of vigorous effervescence. One explanation is that the Me<sub>2</sub>NHBH<sub>3</sub> is able to reduce the Ti(IV) centre in 2 to a Ti(III) compound, akin to the reduction of 2 to 5 by hydrogenation. Amounts of [Me<sub>2</sub>NBH<sub>2</sub>]<sub>2</sub> consistent with the stoichiometric reduction of the catalyst were observed upon acquiring the NMR immediately afterward. Despite this evidence, the possible formation of 6 as the catalytically active species under the reaction conditions does not account for the observation that 2 exhibits a TOF about 15 times that of authentic 6. This Ti(III) compound shows low but repeatable and catalytic activity (10 turnovers). It is interesting to note that other Ti(III) sources such as [Cp2TiCl] and TiCl3 are completely inactive for this reaction.<sup>33</sup> Once again, this highlights and importance difference between these FLP-type compounds and those that depend on metal-centered redox events.

#### **Experimental section**

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of argon using standard Schlenk-line and glovebox (M-Braun, O<sub>2</sub> < 0.1 ppm, H<sub>2</sub>O < 0.1 ppm) techniques, and all glassware was oven dried (200 °C) overnight and allowed to cool under vacuum prior to use. The reagents  ${}^{t}Bu_{2}P(C_{6}H_{4})$  $OH^{38}$  and  $[CPh_3][B(C_6F_5)_4]^{39}$  were prepared according to the literature. Solvents were purified and pre-dried using an Anhydrous Engineering column purification system<sup>40</sup> then vacuum transferred from the appropriate drying agent (K/benzophenone aromatics, ethers, CaH<sub>2</sub> for hydrocarbons and chlorinated solvents) prior to use. NMR spectra were recorded using a JEOL ECP 300 spectrometer at 300 MHz, and Varian 400 and 500 spectrometers at 400 and 500 MHz, respectively, (using the appropriate deuterated solvent, purchased from Cambridge Isotope Labs or Sigma-Aldrich and purified by vacuum transfer from the appropriate desiccant) and referenced to an internal standard (residual solvent signal for <sup>1</sup>H, BF<sub>3</sub>·OEt<sub>2</sub> for <sup>11</sup>B, 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, and FCCl<sub>3</sub> for <sup>19</sup>F. NMR. Spectra of air and moisture sensitive

compounds were recorded using sealable J-Youngs tap NMR tubes. Microanalysis was carried out by the Microanalytical Laboratory, University of Bristol using a Carlo Elba spectrometer. X-ray diffraction experiments were carried out at 100 K on a Bruker Apex II Kappa CCD diffractometer using Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). Spectral data for the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] anion are reported separately:

<sup>13</sup>C {<sup>1</sup>H} (100 Hz, DCM-d<sub>2</sub>): δ 150.1 (dm, <sup>1</sup>*J*<sub>CF</sub> = 244 Hz, *o*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 139.7 (dm, <sup>1</sup>*J*<sub>CF</sub> = 246 Hz, *p*-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 137.8 (dm, <sup>1</sup>*J*<sub>CF</sub> = 247 Hz, *m*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 126.3 (m, *ipso*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>). <sup>11</sup>B{<sup>1</sup>H} (96 Hz, DCM-d<sub>2</sub>):  $\delta$  = 17.8 (s).

<sup>19</sup>F NMR (376 Hz, DCM-d<sub>2</sub>):  $\delta = -129.6$  (*o*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -162.0 (*p*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -165.8 (*m*-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>).

#### [(C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>Fe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

A Schlenk flask was charged with  $[CPh_3][B(C_6F_5)_4]$  (461 mg, 0.5 mmol), which was dissolved in fluorobenzene. To this, a fluorobenzene solution of  $[(C_5H_4Me)_2Fe]$  (109 mg, 0.51 mmol) was added dropwise with stirring, causing a colour change to deep emerald green. Once the addition was complete, the solution was left to stir for 30 min then layered with hexane (10 mL). After standing overnight, the light green supernatant was removed *via* cannula and the green crystals washed with several portions of hexane before drying *in vacuo* for 2 hours. Yield: 402 mg, 0.45 mmol, 90%. Elemental analysis: calc. C, 48.41; H, 1.58; found C, 48.53; H, 1.70.

#### [Cp<sub>2</sub>TiCl]<sub>2</sub>

This compound was prepared by a modification to the published procedure:<sup>41</sup> Cp<sub>2</sub>TiCl<sub>2</sub> (3 g, 12.05 mmol) and Al powder (0.8 g, 30 mmol) were weighed out into a Schlenk flask fitted with a condenser and filter stick. The apparatus was connected to a Schlenk line and THF (ca. 10 mL) was added by vacuum transfer from Na/benzophenone at -78 °C. The solution was allowed to warm to room temperature, then refluxed for 1 hour, during which time the red/silver suspension became a dark green solution. Stirring was continued for a further 20 hours before the solution was filtered and the filtrate concentrated to dryness. The resulting dark green powder was suspended in ether (20 mL), collected on a frit and washed with several portions of ether  $(3 \times 10 \text{ mL})$  until the colour of the washings had faded to a light olive green. The olive green powder was dried in vacuo for 1 hour. Yield: 2.01 g, 9.4 mmol, 78%. Satisfactory elemental analysis could not be obtained and the crude material was used in the next step.

#### [Cp<sub>2</sub>Ti(N(TMS)<sub>2</sub>)]

 $[Cp_2TiCl]_2$  (2.13 g, 5.0 mmol) and KN(TMS)<sub>2</sub> (1.99 g, 10.0 mmol) were weighed out into a swivel frit assembly. The apparatus was connected to a Schlenk line and THF (*ca.* 10 mL) was added by vacuum transfer from Na/benzophenone at -78 °C. The solution was allowed to warm to room temperature, during which time the green suspension turned black/brown with a grey precipitate. The suspension was stirred for a further 24 hours then concentrated to dryness. Pentane (*ca.* 15 mL) was

distilled onto the solids from Na/benzophenone/tetraglyme at 0 °C. The resulting brown suspension was stirred for 30 min at ambient temperature then filtered and the filtrate concentrated to dryness leaving a dark brown oil. The residue was sublimed at 90 °C,  $10^{-2}$  Torr as a deep brown/black microcrystalline solid. Yield (crude): 1.51 g, 4.45 mmol, 89%. <sup>1</sup>H NMR (300 Hz, toluene-d<sub>8</sub>):  $\delta$  0.10 (br s, C(CH<sub>3</sub>)<sub>3</sub>). Satisfactory elemental analysis could not be obtained even after repeated sublimation. The material obtained after one sublimation was of sufficient purity for use in the next stage.

#### $[Cp_{2}Ti{OC_{6}H_{4}P('Bu)_{2}}][B(C_{6}F_{5})_{4}] 2$

Equimolar quantities of 6 (0.02 mmol) and [(C5H4Me)2Fe]- $[B(C_6F_5)_4]$  were weighed into vials and each dissolved in PhCl (ca. 1 mL). The two solutions were mixed, resulting in a dark brown/black solution. The solution was layered with hexanes and allowed to stand overnight, precipitating large black/purple needles of 2. Yield: 0.0198 mmol, 99%. <sup>1</sup>H NMR (500 Hz, PhCl-benzene-d<sub>6</sub>, 5:1): HC3 HC4 and HC6 aromatic signals are obscured by PhCl signals and could be unambiguously identified.  $\delta$  6.27 (dd, 1H,  ${}^{3}J_{\text{HH}} = 8.2$  Hz,  ${}^{4}J_{\text{HH}} = 4.4$ , HC5), 5.87 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 0.99 (d,  ${}^{3}J_{\text{HP}} = 13.6$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>).<sup>13</sup>C {<sup>1</sup>H} (125 Hz, PhCl-benzene-d<sub>6</sub>, 5:1):  $\delta$  170.6 (d, <sup>2</sup>J<sub>CP</sub> = 15.6 Hz, C1), 133.2 (d,  ${}^{2}J_{CP}$  = 2.0 Hz, C5), 132.6 (d,  ${}^{3}J_{CP}$  = 2.5 Hz, C4), 124.2 (d,  ${}^{1}J_{CP} = 28.4$  Hz, C2), 123.0 (d,  ${}^{3}J_{CP} = 4.4$  Hz, C6), 116.6 (s, C<sub>5</sub>H<sub>5</sub>), 115.6 (d,  ${}^{2}J_{CP}$  = 4.9 Hz, C3), 39.4 (d,  ${}^{1}J_{CP}$  = 3.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 30.2 (d,  ${}^{2}J_{CP}$  = 3.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>).  ${}^{31}P{}^{1}H{}$ (161 Hz, PhCl-benzene-d<sub>6</sub>, 5:1):  $\delta$  70.2 (s). ESI-MS: 415.17 [M]. Elemental analysis: calc. C, 52.68; H, 2.95; found. C, 52.52; H, 3.27.

#### [Cp<sub>2</sub>Ti{OC<sub>6</sub>H<sub>4</sub>PH(<sup>t</sup>Bu)<sub>2</sub>}][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 5

**2** (139.0 mg, 0.2 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in PhCl and benzene-d<sub>6</sub> (*ca.* 0.5 and 0.2 mL, respectively) giving a deep purple solution. The tube was connected to a Schlenk line and subjected to three freeze–pump–thaw degassing cycles then backfilled with 2 bar H<sub>2</sub> at room temperature *via* liquid nitrogen trap. No conversion of **2** was detected after *ca.* 3 hours. After standing overnight, the solution had changed colour to orange/brown. The solution was layered with hexanes (*ca.* 6 mL), precipitating brown/purple plates which were collected and dried *in vacuo*. Yield: 130 mg, 94%. <sup>1</sup>H NMR (500 Hz PhCl–toluene-d<sub>8</sub>, 5:1): No aromatic signals (including C<sub>5</sub>H<sub>5</sub>) could be unambiguously identified due to paramagnetic broadening;  $\delta$  0.9 (br. s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 Hz, PhCl–toluene-d<sub>8</sub>, 5:1):  $\delta$  26.8 (s). Satisfactory elemental analysis could not be obtained.

#### $[Cp_2Ti\{OC_6H_4P(^tBu)_2\}] 6$

**Method A. 1** (633.0 mg, 1.41 mmol) and  $[CoCp*_2]$  (463.1 mg, 1.41 mmol) were combined in a Schlenk flask. Benzene (8 mL) was vacuum transferred onto the solids at 0 °C. Upon thawing of the solvent, a black suspension was formed, which was stirred for 24 hours. During this time, a yellow precipitate formed along with a small quantity of metallic mirror on the walls of the flask. The suspension was filtered and the solids washed with benzene. The yellow solids that remained were identified as essentially pure  $[CoCp*_2][Cl]$  by <sup>1</sup>H NMR (MeCN-d<sub>3</sub>,  $\delta$  2.02 ppm, s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>) and amounted to 84% of the expected mass. Solvent was removed from the filtrate under reduced pressure and the resulting purple microcrystalline solid **6** was washed with several small portions of hexane (1 mL) then dried *in vacuo*. Yield: 85 mg, 0.205 mmol, 41%.

Method B. Crude [Cp<sub>2</sub>Ti(N(TMS)<sub>2</sub>)] (169.1 mg, 0.5 mmol) and <sup>*i*</sup>Bu<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)OH (119.2 mg, 0.5 mmol) were mixed in hexane and stirred for 10 min, resulting in the precipitation of purple microcrystals of **6**. The solution was allowed to stand at -20 °C overnight to induce further precipitation. The supernatant was removed *via* cannula and the solids dried *in vacuo*. Yield: 127.8 mg, 0.305 mmol, 61%. <sup>1</sup>H NMR (300 Hz, benzene-d<sub>6</sub>): No aromatic (including C<sub>5</sub>H<sub>5</sub>) signals could be unambiguously assigned due to paramagnetic line broadening.  $\delta$  1.48 (br. S, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 Hz, benzene-d<sub>6</sub>):  $\delta$  12.8 (s). ESI-MS: 415.17 [M]. Elemental analysis: calc. C, 69.90; H, 7.77; found. C, 69.91; H, 7.78.

Crystallographic details for **5** and **6** can be found in Table 3.

## Representative procedure for the catalytic dehydrocoupling of Me<sub>2</sub>NHBH<sub>3</sub>

Compound 2 or 6 and Me<sub>2</sub>NHBH<sub>3</sub> (10–50 eq.) were each weighed into an NMR tube as finely ground powders. The NMR tube was connected to a Schlenk line and evacuated. The tube was immersed in liquid nitrogen to a depth of 5 cm and 0.7 mL PhF (2) or benzene-d<sub>6</sub> (6) was added from a calibrated bulb *via* vacuum transfer from CaH<sub>2</sub>. The tube was sealed and immediately placed in a dry ice/acetone bath and stored until required. Immediately prior to loading into an NMR spectrometer (300 MHz), the sample was inverted and thawed so that the solids were not in contact with the solvent. The solvent was allowed to warm to ambient then the tube inverted and shaken

Table 3 Crystallographic details for 5 and 6

Compound	5	6
Chemical formula	C48H33BF20OPTi	C <sub>24</sub> H <sub>32</sub> OPTi
Formula mass	1095.42	415.37
Crystal system	Orthorhombic	Monoclinic
a/Å	18.5031(8)	9.599(2)
b/Å	17.8620(8)	10.528(3)
c/Å	27.4342(11)	10.456(3)
$\alpha/^{\circ}$	90.00	90.00
$\beta^{\circ}$	90.00	96.260(6)
$\gamma/^{\circ}$	90.00	90.00
Unit cell volume/Å <sup>3</sup>	9067.1(7)	1050.4(4)
Temperature/K	100(2)	100(2)
Space group	Pbca	P21
No. of formula units per unit cell, $Z$	8	2
No. of reflections measured	153 693	12 230
No. of independent reflections	10 740	3587
R <sub>int</sub>	0.1055	0.0432
Final $R_1$ values $(I > 2\sigma(I))$	0.0436	0.0377
Final w $R(F^2)$ values $(I > 2\sigma(I))$	0.0933	0.1000
Final $R_1$ values (all data)	0.0766	0.0380
Final $wR(F^2)$ values (all data)	0.1092	0.1004
Flack parameter	—	0.005(5)

thoroughly to insure dissolution of all of the solids. The tube was quickly loaded into the NMR spectrometer and an appropriate series of  ${}^{11}B{}^{1}H{}NMR$  spectra acquired until complete conversion was achieved.

#### Conclusions

We have synthesised titanium-phosphorus frustrated Lewis pairs based on titanocene–phosphinoaryloxide complexes. The facile reduction of the cation titanium(IV) complex  $[Cp_2TiOC_6H_4P-('Bu)_2][B(C_6F_5)_4]$  with hydrogen led us to synthesise the titanium(III)-phosphorus FLP  $[Cp_2TiOC_6H_4P('Bu)_2]$ . Both of these complexes catalyse the dehydrogenation of Me<sub>2</sub>HN·BH<sub>3</sub>, albeit with lower activity than their zirconium(IV) or hafnium(IV) counterparts. The facile reduction of these titanium(IV) species by hydrogen suggests possibilities in replacing more expensive stoichiometric reducing agents in catalytic cycles where such one electron processes depend on this oxidation state manifold.<sup>42</sup> We also believe the isolation of reduced d<sup>1</sup> metal-containing frustrated Lewis pairs may open yet new possibilities for small molecule activation in cases where metal backbonding is important for substrate binding and activation.

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