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ARTICLE TYPE

A sterically congested 1,2–diphosphino–1'–boryl–ferrocene: synthesis, characterization and coordination to platinum

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A new class of tritopic ferrocene-based ambiphilic compound has been prepared by assembling diphosphino- and boryl-substituted cyclopentadienides at iron. The presence of five sterically demanding substituents on the ferrocene platform induces conformation constraints, as apparent from XRD and NMR data, but does not prevent chelating coordination to platinum. The Lewis acid moiety is pendant in both the free ligand and the platinum complex.

Ambiphilic compounds combine Lewis acids and Lewis bases on a common platform.[1] When strong donor-acceptor interaction between these antagonist moieties is prevented sterically and/or geometrically, their juxtaposition opens great opportunities in small molecule activation and ultimately metal-free catalysis (so-called frustrated Lewis Pair –FLP– catalysis),[2] as well as in coordination chemistry and metal/Lewis acid cooperativity.[3]

Various scaffolds have been used to build ambiphilic compounds. In particular, C2 spacers have attracted great interest due to the proximity they impart to the antagonist sites, while enabling to tailor rigidity (*cf.* *ortho*-C_6H_4, CH=CH, CH_2–CH_2 bridges). Due to its unique and versatile properties, the ferrocene platform is also very appealing and over the years, an increasing variety of ferrocene-based ambiphilic compounds have been described (Figure 1). Most studies have focused to date on monophosphine-boranes, in which the relative position of the phosphorus and boron atoms have been varied (see compounds **A-D**).[4-8] A few tritopic compounds have also been reported. Landis and co-workers studied early on compounds **E** in which a pendant benzoxaborolidine moiety was appended to a 1,1'-diphosphino-ferrocene scaffold.[9] Later on, the ferrocene and *ortho*-phenylene spacers were combined by Emslie *et al.* to prepare the diphosphine-borane **F**. The structure and reactivity of ensuing platinum complexes were investigated, providing nice examples of metal–Lewis acid cooperativity.[10]

To take advantage of possible cooperativity between neighbouring sites we became interested in ambiphilic compounds featuring three or more functional groups directly bonded to the ferrocene platform. To our knowledge, only one such compound was reported to date: the 1-phosphino-1',3'-diboryl ferrocene **G** that was prepared by Clark and co-workers *via* direct iridium-catalysed C–H borylation of (diphenylphosphino)ferrocene.[11] The stepwise introduction of phosphino and boryl groups on ferrocene is tedious and inherently complicated by compatibility/selectivity issues. Reacting pre-functionalized cyclopentadienides with iron dichloride is more convergent and might be synthetically attractive. This assembling methodology proved to be very efficient for the preparation of polyphosphines such as the 1,2,1'-triphosphino-ferrocenes **H**.[12] In such tritopic compounds the two bulky *t*-Bu groups exert conformational control and maintain the phosphorus atoms in close proximity, resulting in unique coordinating properties towards transition metals, as well as rare "through-space" nuclear spin-spin couplings.[13] Recently, we extended this assembling strategy to the preparation of 1,1'-diboryl ferrocenes **I** (and related cobaltocenes) from boryl-substituted cyclopentadienides.[14,15] These advances prompted us to test the same approach for the preparation of hitherto unknown 1,2–diphosphino–1'–boryl–ferrocenes.

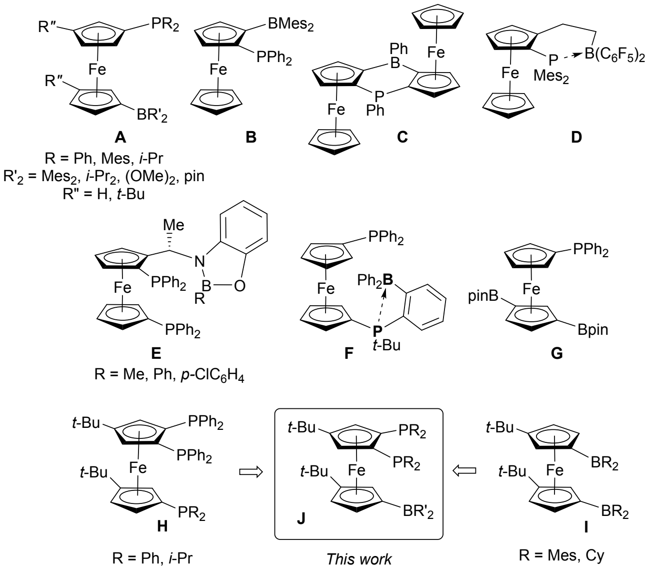

Fig. 1 Selected ferrocene-based (di)phosphine-boranes, poly-phosphines and poly-boranes.

In this context, we report here the preparation and full characterization of a sterically congested compound **J** featuring five bulky substituents on a ferrocene. Coordination of this diphosphine-borane to platinum is described. The conformations of the free (P, P, B)-ambiphilic ligand (Figure 2) and of its platinum complex are discussed based on X-ray crystallographic data, along with their multi-nuclear NMR properties, in particular with respect to “through-space” nuclear spin-spin couplings.

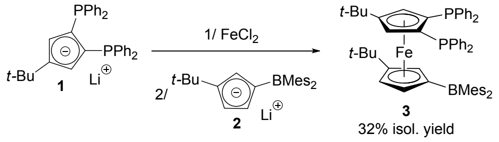

Fig. 2 Synthesis of the 1,2-diphosphino-1'-boryl-ferrocene **3** by direct assembling of functionalized cyclopentadienides at iron.

Solutions of the 4-*tert*-butyl-1,2-bis(diphenylphosphino)-cyclopentadienide lithium salt **1** (a well-known and useful precursor for polyphosphino-ferrocenes such as **H**)[12] and 3-*tert*-butyl-1-dimesitylborylcyclopentadienide lithium salt **2** (used to prepare 1,1'-diboryl-metallocenes **I**)[14,15] in tetrahydrofuran were successively added to $FeCl_2$ at –50°C (Fig. 2). Conditions were varied, but a mixture of ferrocenes was systematically formed.† Nevertheless, this route gave direct access to the targeted 1,2-diphosphino-1'-boryl-ferrocene **3** ferrocene in a reasonable 32% isolated yield. Simple work-up followed by crystallization afforded **3** as a purple air-stable crystalline powder. The structure of **3** was analysed by X-ray diffraction (Figure 3, racemate, centrosymmetric space group P21/n).

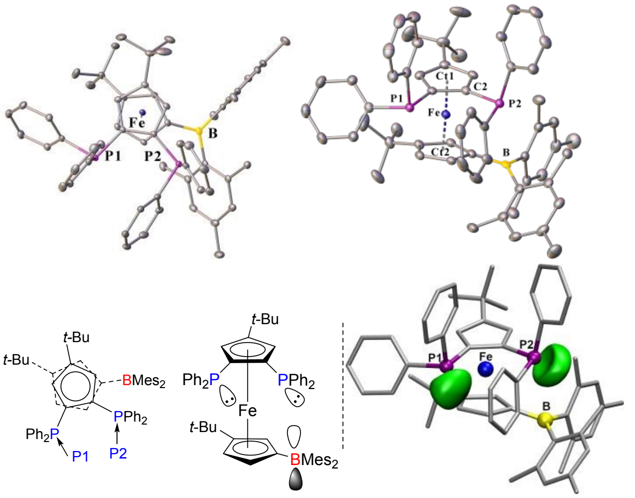

Fig. 3 Molecular views of the 1,2-diphosphino-1'-boryl-ferrocene **3** (top and side views, thermal ellipsoids at 50% probability, Ct1 = C1-C2-C3-C4-C5 and Ct2 = C6-C7-C8-C9-C10 centroids). Hydrogen atoms omitted for clarity. Selected bond length (Å) and angles, torsions (°): Fe-Ct1 = 1.6645(10); Fe-Ct2 = 1.6816(10); P1-C1 = 1.827(2); P2-C2 = 1.824(2); B-C6 = 1.545(3); Ct1-Fe-Ct2 = 173.87(5); P1-C1-Ct1 = 179.46(15); P2-C2-Ct1 = 168.56(16); B-C6-Ct2 = 166.42(19); P1-Ct1-Ct2-B = –120.62(6); P2-<Ct1-Ct2-B = –41.76(6); B···P1 = 6.132(2); B···P2 = 4.239(2). Bottom right: P-lone pairs (green) visualized by ELF analysis.

The diphosphine-borane **3**, bearing five bulky groups on the ferrocene backbone, is among the most hindered polyfunctionalized ferrocenes reported to date.[5,12,16] To optimize the spatial distribution of the substituents, sterically hindered ferrocenes classically adopt a staggered[12a,c,d] or an eclipsed[12b] conformation. In compound **3**, the two cyclopentadienyl (Cp) rings are about eclipsed with a cisoid arrangement of the two *tert*-butyl groups. Steric congestion also induces some tilting of the two Cp rings that are not exactly parallel [tilt ang. = 10.21(13) °].

With this conformation, the three heteroatoms are oriented in the same direction, opposite to the *tert*-butyl groups. The two phosphorus atoms are in quite different environments, the one referred as P2 sitting closer to boron. The P2-C2-Ct1 bond angle deviates from linearity by *ca.* 11° (Fig. 3 and Fig. S1)[17] but this distortion does not result in intramolecular P→B interaction. The boron atom is in trigonal planar environment [sum of bond angles of 359.1(2) °], and the P2…B is long at 4.239(2) Å. This value falls in the low range of those observed in related monophosphino-boryl-ferrocenes [P…B distances ranging from 4.106(3) to 6.731(3) Å].[4,5] It is also noteworthy that the orientation of the lone pairs at P1 and P2 differs from that usually encountered in sterically congested 1,2-diphosphino-ferrocenes.[12] Indeed, the P lone pairs typically point to each other in a conformation prone to the chelating coordination of transition metals, and to the existence of strong through-space J_{PP} coupling ($^{TS}J_{PP}$, see below).[13] In the diphosphino-boryl-ferrocene **3**, the lone pair at P1 points towards P2, while the P2 lone pair is oriented outwards making an angle of 45° with the P2-B axis.

Given this conformation and the steric congestion of the ferrocene backbone, we were intrigued about the coordination properties of the diphosphino-boryl-ferrocene **3**. Are the two phosphorus atoms accessible enough and does the framework retains enough conformational freedom for **3** to behave as a chelating ligand? To address these questions, **3** was reacted with $PtCl_2$(COD). The platinum complex **4** was thereby obtained in quantitative yield (Figure 4). Despite the conformational restrictions imposed by the five sterically demanding substituents, compound **3** preserves enough conformational flexibility to enable rotation around the Cp-P2 bond, allowing the chelating coordination of phosphorus P1/P2 to platinum. The two Cp rings are quasi perfectly eclipsed in **4** [the dihedral angle P2…Ct1…Ct2…B = –72.14(18) °]. The boron center shifts further away from P2 [P2…B = 5.294(7) Å] and sits far from the Pt coordination sphere. The Lewis acid moiety does not interact with the metal center, as observed in previously reported diphosphine-borane Pt complexes,[10,18] but remains pendant.

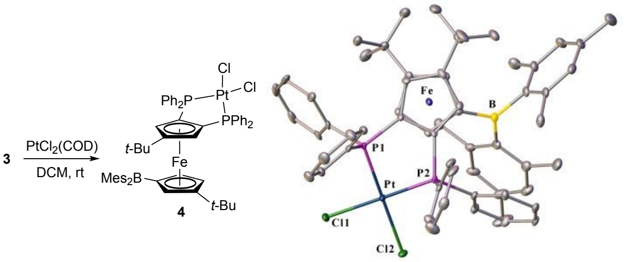

Fig. 4 Synthesis and molecular structure of the 1,2-diphosphino-1'-boryl-ferrocene platinum dichloride complex **4**. Thermal ellipsoids at 50% probability, same numbering as for **3**. Hydrogen atoms and dichloromethane molecules omitted for clarity. Selected bond length (Å) and angles, torsions (°): Fe-Ct1 = 1.670(3); Fe-Ct2 = 1.689(3); P1-C1 = 1.802(6); P2-C2 = 1.783(6); B-C6=1.562(9); P1-Pt = 2.2185(15) ; P2-Pt = 2.2406(15) ; Pt-Cl1 = 2.3587(15); Pt-Cl2 = 2.3387(14); Ct1-Fe-Ct2 = 177.71(14); P1-C1-Ct1 = 170.6(5); P2-C2-Ct1 = 168.8(5); B-C6-Ct2 = 155.9(6); Cl2-Pt-Cl1 = 88.60(5); Cl1-Pt-P1 = 92.41(5); P1-Pt-P2 = 85.47(5); P2-Pt-Cl2 = 93.21(5); P1-Ct1-Ct2-B = –132.64(18); P2-Ct1-Ct2-B = –72.14(18); B···P1 = 6.555(7); B···P2 = 5.294(7).

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The difference in energy between the conformations of 1,2–diphosphino–1'–boryl–ferrocene in the free ligand **3** and in the Pt complex **4** was assessed by DFT.† Accordingly, rotating the P2 lone pair to enable chelation of platinum (conformation **3***, see ESI) was found to cost in energy about 2.6 kcal mol^{-1}.

Polyphosphino-ferrocenes featuring proximal phosphorus atoms such as triphosphine **H** (Fig. 2) display rather strong nuclear spin couplings operating "through-space" (TS).[12,13] This non-classical coupling prompted us to have a closer look at the NMR features of the diphosphine-borane **3** and of its platinum complex **4**. The ^{31}P NMR spectrum of diphosphine-borane **3** in CDCl$_3$ solution exhibits two signals, consistent with two inequivalent phosphorus atoms, but in a puzzling pattern. As depicted in Figure 5, an apparent doublet is found at –23.8 ppm (*J* = 60 Hz), which is attributed to the phosphorus atom P1 by comparison with analogous trifunctionalized polyphosphino-ferrocenes.[12] The second phosphorus P2 is characterized by a broad signal at –18.2 ppm with a width at half-height of 167 Hz. To confirm the existence of spin coupling, the ^{31}P NMR spectrum was recorded at various frequencies (243, 202 and 121 MHz). The same value of *J* = 60 Hz was retained for P1. The signal for P2 remained broad but the 60 Hz coupling became distinguishable at low frequency (Fig. 5, bottom).

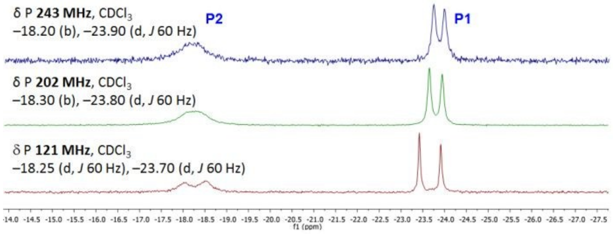

Fig. 5. ^{31}P NMR of the diphosphino-boryl-ferrocene **3** in CDCl$_3$ at 243, 202 and 121 MHz (CDCl$_3$, 300 K).

The magnitude of the J_{P1P2} coupling is clearly very strong for a covalent "through-bond" (TB) ^3J coupling, suggesting some "through-space" (TS) spin coupling, in line with the relatively short internuclear distance d(P1…P2) = 3.871(2) Å observed in the XRD of **3**.[19] The contribution of a *J* "through-space" component was further supported by the solvent-dependence of the J_{P1P2} coupling noticed when replacing chloroform for toluene (from 60 to 44 Hz, see Fig. S2). TS couplings have been authenticated in various types of constrained molecules,[13,20] including functionalized ferrocenes, and the pathways for such spin-spin couplings have been analysed theoretically.[21] The J_{P1P2} coupling displayed by **3** falls in the lower range of those reported for polyphosphino-ferrocenes,[12c] where couplings as high as 98 Hz have been found,[12b] while values up to 180 Hz have been predicted for model compounds such as *cis*-(H$_2$P)CH=CH(PH$_2$).[21a]

The origin of the P2 signal broadness was intriguing, and ^{31}P NMR analysis of **3** in the range 325–220 K (Fig. S3) did not evidence major changes of the two ^{31}P NMR signals in terms of chemical shift and $^{TS}J_{P1P2}$ coupling (60 ± 3 Hz). The coupling became apparent at P2 below 260 K, but the signal remained broad ($\Delta_{\upsilon 1/2}$ = 80–170 Hz). This variable-temperature analysis ruled out the hypothesis of an equilibrium between *open* and *closed* forms as the result of an intramolecular P→B interaction. Such a dynamic phenomenon was reported by Erker *et al.* for the 1-PMes$_2$-2-(CH$_2$)$_2$B(C$_6$F$_5$)$_2$]-ferrocene **D**.[8a] In compound **D**, the *closed* form dominated at low temperature with a ^{31}P NMR signal shifted downfield by *ca.* 40 ppm compared to the *open* form.

Steric congestion and conformational restraints are likely to contribute to the broadness of the P2 NMR signal. Indeed, hindered rotation around the Fc–B bond of **3** was apparent from the inequivalence of the mesityl groups at boron in the ^{1}H NMR spectrum (Fig. S4). Comparison with a less sterically congested diphosphino-boryl-ferrocene **3'** (Fig. 2) featuring a B(*i*-Pr)$_2$ instead of BMes$_2$ group, corroborated this view. In this case, a sharp ^{31}P NMR signal was conversely observed for P2.†

Since the lone pair of P2 points towards the vicinity of the boron atom, we wondered about the existence of non-bonding ^{31}P-^{11}B nuclear spin coupling which might also contribute to broaden the P2 NMR signal.[22] In the absence of visible ^{11}B signal,[23] a series of ^{31}P{^{1}H, ^{11}B} spectra were recorded by varying the ^{11}B decoupling frequency from +100 to –100 ppm (Fig. S5). These decoupling experiments did not result in any sharpening of the P2 NMR signal, discarding the hypothesis of TS ^{31}P-^{11}B spin coupling in **3**.

Also noteworthy is the modification of the ^{31}P NMR spectrum upon coordination of **3** to platinum (Figure 6). Consistent with the crystallographic structure of **4**, the eclipsed conformation of the ferrocene backbone together with the *cis*-chelation of the two PPh$_2$ groups to platinum places the BMes$_2$ moiety further away from P2. Accordingly, complex **4** displays two well-resolved ^{31}P NMR signals at close chemical shifts (22.0 and 21.6 ppm). The J_{P1P2} spin-spin coupling constant is very much decreased (12.0 Hz for **4**), as expected from the quaternization of the phosphorus atoms that no longer allows lone pair-conveyed spin-spin interaction.[13]

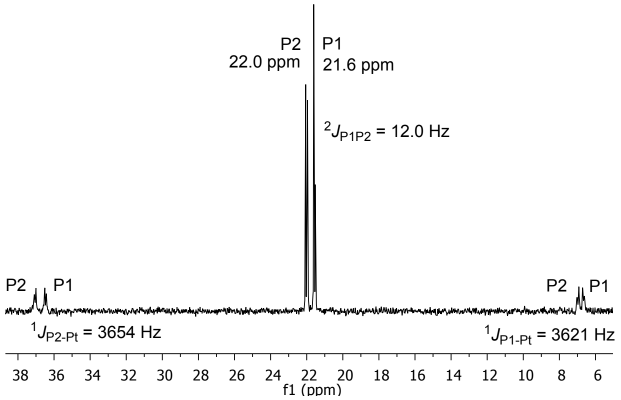

Fig. 6. ^{31}P NMR of the diphosphino-boryl-ferrocene platinum complex **4** in CD$_2$Cl$_2$ (121 MHz, 300 K). Note that the large $^1J_{PPt}$ couplings of 3621 Hz (P1) and 3654 Hz (P2) are typical of a square-planar PtCl$_2$ complex in *cis* geometry.[24]

In conclusion, the diphosphine-borane **3**, a new type of tritopic ferrocene, was prepared by reacting functionalized cyclopentadienides with FeCl$_2$. The presence of five sterically demanding substituents, including a BMes$_2$ moiety, on the ferrocene core induces conformational constraints, but does not prevent chelating coordination of the two phosphorus atoms to platinum to give complex **4**. The presence of "through-space" spin nuclear couplings in these (P, P', B)-functionalized ferrocenes has been analysed. Future work will seek to generalize this assembling approach to other densely functionalized ferrocene-based ambiphilic compounds with the ultimate goal of triggering reactivity and ligand behaviour thanks to the redox-properties of the ferrocene moiety.[4b,25]

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Notes and References

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†Electronic Supplementary Information (ESI) available: Experimental details and analytical data, NMR data and X-ray crystallographic data. CCDC 1902394 (**3**) and 1902395 (**4**). Computational details, ELF and AIM analysis, relative energy for conformers **3** and **3*** (Figs. S6-S8). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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A unique tritopic (P, P, B)-ferrocene ambiphile with antagonist functions directly attached to the metallocene backbone is described.