A neutral, acyclic, borataalkene-like ligand for group 11 metals: L- and Z-type ligands side by side†‡

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The overall neutral α-borylated phosphorus ylide Ph3PC(Me)BÆt2 behaves like a polar borataalkene and can act as acyclic, ambiphilic π-type ligand with L- and Z-type functionalities side by side. In the complexes [MX(μ-Ph3PC(Me)BÆt2)] (M = Cu, Ag, Au; X = Cl, NTF2), the bonding is dominated by the highly nucleophilic ylidic carbon atom (L-type ligand). The Lewis acidic boron atom furnishes nonetheless a small but significant bonding contribution (Z-type ligand).

Boron-based ligands for transition metal complexes have received considerable attention for many years.1 Among others, one focus of interest refers to ambiphilic chelate ligands featuring an L-type donor entity and a Z-type acceptor unit suitable to stabilize metal–boron interactions.2 Boron-based π-ligands have also been studied, most often cyclic structures.3 Acyclic boron-based π-ligands,4 however, are relatively scarce and only a few transition metal complexes have been described.5 Interests in these types of ligands are rooted in their isoelectronic relationship to olefin ligands (Scheme 1),6 which have been studied in great detail during the past decades and are important intermediates in catalytic processes or serve as leaving groups in starting materials and as steering ligands in homogeneous catalysis, for instance.7 An inherent feature of anionic borataalkenes8 is their flexibility to potentially act as a “classical” π-ligand according to the well-known Dewar–Chatt–Duncanson (DCD) model6–7 or as ambiphilic L-/Z-type ligand (Scheme 1).9

Piers and co-workers presented in 1999 the first example of an electron-poor, “early” Ta(0) complex featuring an anionic, C6F5-borataalkene ligand (I in Scheme 1), which was synthesized by converting a Ta-bound alkylidene into the η2-coordinated [H2C–B(C6F5)2]− ligand.10 Quantum chemical calculations predicted that the latter species readily converts to boryl-substituted methyl ligand, most likely due to steric congestion. In 2020, Erker succeeded in isolating complexes of “late”, i.e. electron-rich metals bearing an anionic P/C=–B chelate ligand (II).11 Neutral heteroelement analogs of η2-bound olefins are, however, very rare. To the best of our knowledge, only one example has been described in the literature. Amgoune and Bourissou described the synthesis and full characterization of the platinum complexes [[Ph3P]2Pt(μ3-P–B(C6F5)3)] (III; R = ‘Bu, Cy) and performed an in-depth quantum-chemical analysis.12 Although the BP-based π-ligand is bound symmetrically, the polar electronic profile of the ligand is also reflected in its partially asymmetric bonding mode featuring characteristics of both a DCD-type π-ligand and an ambiphilic L-/Z-type ligand.

In this context, we recently reported on a highly polarized π-bond consisting of a ylide carbon atom and a boron atom within the η2-borylated phosphorus ylide Ph3PC(Me)BÆt2.
(L1, Scheme 2). As exemplified in small molecules activation, the competition for the lone-pair of electrons between the boryl (BR3) and phosphoryl (PR3) substituents results in electronic frustration within this overall neutral, highly polarized borataalkene-like molecule. We now hypothesized that species L1 would be a promising candidate to act as an acyclic, ambiphilic π-type ligand with L- and Z-type functionalities side by side. Note that a cyclic analog possessing the 9-borataphenanthrene anion has been recently published by Martin and co-workers. Reported herein is the successful 1

Treatment of L1 with various group 11 precursors to furnish the complexes 1–5.

Scheme 2

Fig. 1 Molecular structure of 2, thermal ellipsoids drawn at the 30% probability level. (structural parameters of the second molecule in the asymmetric unit are given in square brackets). Selected bond lengths (pm) and angles (°): Au1–C1 211.3(6), Au1–B1 239.4(8) [241.8(8)], Au1–Cl1 227.7(4), P1–C1 178.2(7), C1–B1 155.2(11), C1–C2 155.2(10); P1–C1–Au1 109.0(3), B1–C1–Au1 80.0(4), C1–Au–Cl1 178.2(2) [176.5(2)].

is no longer available for both π-interactions with σ*(PC) or p(B) orbitals. The gold atom is coordinated in a linear fashion by the ylidic carbon atom and the chloride ligands (C1–Au1–Cl1 = 178.2°). The C1–Au1–Cl1 axis is slightly tilted towards the boron atom (C1–B1–C1–Au1 = 80.0°) indicating bonding interaction between the boron center and the gold atom. The short B–Au distance of 239.4 pm found in the solid-state is a strong indication for a Au–B interaction. The distance is in the same region found for gold complexes of polydentate B/P ligands.

The 1H NMR spectra of 1 and 2 in d8-toluene display line broadening at room temperature due to dynamic processes, in particular for the ethyl groups bound to boron. Variable temperature NMR investigations revealed energy barriers of ~16 (for 1) and ~15 (for 2) kcal mol−1 (for further details, see section S5, ESI†). We assumed that this dynamic process is associated with the rotation around the Cylide–B bond. Indeed, density functional theory (DFT) calculations at the dispersion-corrected BP86-D3/def2-TZVPP level (ESI†) indicate that the activation barrier associated with the Cylide–B rotation in 1 and 2 is 17.5 and 17.8 kcal mol−1, respectively. Both values agree reasonably well with the experimental ones (Fig. S1, ESI†).

Interestingly, the rotation along the Cylide–B bond has a dramatic impact on the bonding situation in the corresponding transition state TS. As depicted in Fig. S1 (ESI†), the relatively short B–Au distance of 241.4 pm in 2 is significantly longer in TS (314.3 pm), thus indicating that the Au⋯B interaction in the latter saddle-point can be considered as negligible.

Furthermore, the 11B NMR signal of 2 at a chemical shift of δ(11B) = 53.6 ppm shifted upfield compared to the free pro-ligand L1 (δ(11B) = 56.5 ppm). This is reminiscent of the 11B highfield shift of the boron–gold complexes featuring Au→B interactions (Chart S1, ESI†).

To check the accessibility of other group 11 complexes, we also prepared the whole series of {M(NTf2)} complexes 3–5 (M = Cu, Ag, Au; Scheme 2). It turned out, however, that only highly sensitive, oily products are formed. Due to this, a full characterisation was not possible. We have nevertheless performed comprehensive NMR studies and the results are convincing (e.g. 19B NMR chemical shifts of δ(19B) = 53.3 ppm for 3, 58.5 ppm for 4, 53.8 ppm for 5, respectively, and δ(11B) = 31.3 ppm (d, 1JAgB = 27.8 Hz) for 4 in d8-toluene).

Again, line broadening at room temperature was observed for all complexes due to the dynamic process associated with the rotation around the Cylide–B bond. Variable temperature NMR investigations on 3–5 revealed slightly lower energy barriers of ~15 (for 3 and 4) and ~14 (for 5) kcal mol−1.

To further investigate the bonding situation in the newly prepared complexes, we first explored the electronic structure of the pro-ligand L1 with the help of DFT calculations. From the computational studies it becomes clear that pro-ligand L1 is best described by the zwitieronic resonance structure (Fig. S2, ESI†) with a negative charge on the carbon atom (i.e. ylide) and only to a lesser extent by the borataalkene structure. This is confirmed by comparing the charges and Wiberg Bond Indices of related species (see Table S1, ESI†). Indeed, the computed HOMO can be viewed as a lone-pair at the carbon atom, which
is slightly delocalized into the adjacent vacant \( p_z \) atomic orbital of boron (see below). The latter finding is reflected in the computed C–B Wiberg bond index of 1.24, which suggests a partial, highly polarized C–B bond.

More quantitative insight into the bonding situation of the \([\text{MCl}]\) complexes (\( M = \text{Cu}, \text{Ag}, \text{Au} \)) can be gained by means of the energy decomposition analysis (EDA) method computed at the relativistic ZORA-BP86-D3/TZ2P/BP86-D3/def2-TZVP level. From the data in Table 1, columns 2–4, it becomes evident that the main contribution to the bonding between \( \text{L1} \) and \([\text{MCl}]\) comes from the electrostatic interactions (measured by the \( \Delta V_{\text{elstat}} \) term), which contribute ca. 65% to the total interaction (\( \Delta E_{\text{int}} \)). This is consistent with the zwitterionic nature of pro-ligand \( \text{L1} \) commented above. Despite that, the orbital interactions (\( \Delta E_{\text{orb}} \)) are also significant, albeit to a lesser extent (ca. 30%). In contrast, interactions coming from dispersion forces (\( \Delta E_{\text{disp}} \)) are much less important in the \( \text{L1} \cdots[\text{MCl}] \) interaction (ca. 5%).

The natural orbital for chemical valence (NOCV) extension of the EDA method was applied next to further partitioning the orbital term into its main pair-wise interactions. According to the EDA-NOCV, two main orbital interactions dominate the total \( \Delta E_{\text{orb}} \) term, namely the donation from the lone-pair at the carbon atom to the \( \sigma^*(\text{M–Cl}) \) and the \( \pi \)-backdonation from a doubly-occupied \( d \) atomic orbital at the transition metal to the vacant \( p_z \) atomic orbital of the boron atom, denoted as \( \rho_1 \) and \( \rho_2 \), respectively (see Fig. 2). The \( \sigma \)-donation \( \text{LP}(\text{C}) \rightarrow \sigma^*(\text{M–Cl}) (\rho_1) \) is significantly stronger than the \( \pi \)-backdonation (\( \rho_2 \)). When inspecting the influence of the coordinated group 11 metal, it becomes clear that \( M = \text{Au} \) leads to stronger interactions in all contributions and that the (hypothetical) silver complexes exhibit the lowest values when compared to Au or Cu complexes. This, however, is consistent with recent computations of Bayat et al.$^{192}$ on phosphorus ylide complexes of group 11 metals and recent bonding analyses of related \( \text{Au(i)} \) complexes. This also correlates with the highest promotion energy for \( \text{Ag(i)} \) in the series \( \text{Cu(i)} \) (8.25 eV) \( < \text{Ag(i)} \) (9.94 eV) \( > \text{Au(i)} \) (7.83 eV) and the lowest electron affinity in the series \( \text{Cu(i)} \) (7.72 eV) \( > \text{Ag(i)} \) (7.59 eV) \( < \text{Au(i)} \) (9.22 eV). Moreover, the \( \text{Au} \rightarrow \text{p}_{\pi}(\text{B}) \) backdonation is comparable to that found in those complexes having a single anchor boron ligand (Chart S1, ES1), which were confirmed to exhibit a significant \( \text{Au} \rightarrow \text{B} \) interaction.$^{20}$ This backdonation is also validated by the NBO method, which provides a noticeable \( \text{Au} \rightarrow \text{B} \) WBI of 0.25 and locates a significant stabilizing delocalization from the doubly-occupied \( d \)-atomic orbital of gold to the \( p_z \)-atomic orbital of boron (associated \( \Delta E_{\text{WBI}} = -14.2 \) kcal mol$^{-1}$). Therefore, our EDA-NOCV analysis indicates that the orbital interactions in 2 can be described as two donor–acceptor interactions involving the highly nucleophilic ylidic carbon atom as the dominant ligating atom (L-type ligand) and the Lewis acidic boron atom, which furnishes a weaker yet noticeable bonding contribution as a Z-type ligand. Results above suggest that the \( \text{Au} \rightarrow \text{p}_{\pi}(\text{B}) \) backdonation can be efficiently modulated by modifying either the geometry or the Lewis acidity of the \( \text{BR}_2 \) moiety. For instance, in the rotated TS (Fig. S1, ES1), the \( \text{Au–B} \) bond distance is significantly longer than in that in 2 as a consequence of the position of the \( p_z \) atomic orbital of boron, which is much less available to accept electron density from the gold atom. As a result, this saddle-point becomes destabilized with respect to 2 and exhibits an almost negligible \( \text{Au} \rightarrow \text{p}_{\pi}(\text{B}) \) \( \pi \)-backdonation (\( \Delta E_{\text{orb}}(\rho_2) < -1 \) kcal mol$^{-1}$).

![Fig. 2](image-url)
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To check the influence of the Lewis acidity of the Br₂
atom, we attached both a strong electron- withdrawing
(CF₃) and electron-donor (OMe) groups directly to the boron
atom. From the data in Table 1, columns 7 and 8, the replace- ment of the ethyl groups by CF₃ significantly enhances the
Au→p(B) π-backdonation, which becomes almost twice as
strong as that in the parent 2 (ΔEorb(ρ₂) = −25.3 kcal mol⁻¹).
This is reflected in a markedly shorter Au–B bond (225.8 pm).
At variance, the presence of the donor methoxy groups pro-
vokes the opposite effect and the Au→p(B) π-backdonation
becomes weaker (ΔEorb(ρ₂) = −9.9 kcal mol⁻¹) whereas the
corresponding Au–B is much longer (258.9 ppm). We also studied the effect of the M-bound anion and compared {MCl} with {M(NTf₂)} (cf. Table 1, columns 5–7). When changing X = Cl⁻ to {NTf₂}, the interaction between the {MX} and the ligand L₁ becomes clearly stronger. This is mainly due to a significant increase in the orbital interactions (the electrostatic term also increases albeit to a lesser extent). In particular, the LP(C)→σ*(M–X) (ρ₁) interaction becomes stronger because the {NTf₂} fragment is a much better acceptor as compared to [MCl].²⁹ For this reason, the Au→p(B) π-backdonation is slightly weaker.

In summary, this case study clearly depicts that the polar π-
bond of the z-borylated phosphorous ylide differs significantly
from a C–C π-bond and is even more polar than the phosphino-
boranate published by Angoume and Bourissou.¹² In the {MCl}
complexes 1 and 2, the highly nucleophilic ylidic carbon atom is
the dominant ligating atom (L-type ligand). The Lewis acidic
boron atom furnishes a small but significant bonding contribu-
tion as a Z-type ligand. Thus, the bonding is asymmetric from
both the geometric and the electronic perspectives. The overall
neutral, acyclic pro-ligand L₁ indeed behaves like a polar
borataalkene ligand, which is induced by the competition for
the lone-pair of electrons. Quantum chemical calculations pre-
dict that the strength of the Au–B interaction can be increased
by introducing electron-withdrawing groups and decreased by π-
donating substituents on boron. We also provided experimental
and computational evidence that the L-type ligand contribution
can be increased upon moving from X = Cl⁻ to {NTf₂}. Thus, it
appears that the whole continuum between ambiphilic L- and Z-type
coordination and DCD-type π-coordination can be covered by
fully exploring the coordination chemistry of variously substi-
tuted z-borylated phosphorous ylides. Investigations in this
direction are currently performed in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 Selected reviews: (a) J. T. Goettel and H. Braunschweig, Coord. Chem. Rev., 2019, 380, 184; (b) H. Braunschweig, R. D. Dewhurst and
2 Selected reviews: (a) G. Bouhadir and D. Bourissou, Chem. Soc. Rev., 2015, 44, 1065; (b) A. Angoume and D. Bourissou, Chem. Commun.,
5 Early work on π-complexes of amino-9-fluorenylideneborane:
15 To a degree, the boron containing allyl type ligands can be seen as neighboring L- and Z-type ligands: (a) M. D. Wroder and J. C. Peters, Dalton Trans., 2018, 47, 3733; (b) F. Jiang, P. J. Shapiro, F. Fahs and B. Twanmley, Angew. Chem., Int. Ed., 2003, 42, 2631; (c) K. B. Kolpin and D. J. H. Emslie, Angew. Chem., Int. Ed., 2010, 49, 2716.
18 This should not be the case, because upon coordination, the ylidic carbon atom possesses less electron density and the signal should be shifted downfield: (a) H. Nöh and B. Wrackmeyer, Chem. Ber., 1981, 114, 1150; (b) B. Wrackmeyer, Z. Naturforsch., B: J. Chem. Sci., 2015, 70, 421.