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A metal and a metalloid Lewis acid bridged by a μ_2-phosphinidene†

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Dinuclear phosphinidene complexes bridging two transition metal centres are now well established. However, a phosphinidene bridging a metal centre and a main group Lewis acid has not yet been reported. Herein, we describe the generation of a highly reactive phosphinidene complex bridging a tungsten and a boron centre. Furthermore, the synthesis and dyotropic rearrangement of a P-borane adduct of an *N*-methylimidazole-stabilized neutral, electrophilic terminal phosphinidene complex is reported.

In 1975, Huttner reported on the synthesis of the first μ_2-phosphinidene-bridged dinuclear complex[1] and subsequently, μ_3- and μ_4-phosphinidene complexes.[2,3] Dinuclear complexes are commonly prepared *via* salt metathesis starting from dihalophosphanes,[4] metallophosphanes[5,6] or anionic phosphinidene complexes.[7] Additionally, syntheses *via* deprotonation of phosphanyl ligands,[6,8] dehydrohalogenation[9] or elimination reactions[10] are possible.

Complexes have either a trigonal pyramidal geometry at phosphorus, which can be regarded as doubly metallated phosphanes **I** (Fig. 1), *e.g.* $[Pt_2(dippe)_2(\mu_2\text{-}PPh)]$[11] or $[Fe_2Cp_2(\mu_2\text{-}PMes^*)(\mu_2\text{-}CO)\text{-}(CO)_2]$,[12] or a trigonal planar geometry (**II**) representing a μ_2-bridged phosphinidene complex, *e.g.*, $[W_2(\mu_2\text{-}PCp^*)(CO)_{10}]$[13] or $[W_2Cp_2(\mu_2\text{-}PMes^*)(CO)_4]$.[7] However, complexes **II** could be better described by a 3c,4e π-bond as confirmed by short metal–phosphorus distances.[14,15] Examples with slightly longer bond distances[13,16] can be explained by steric repulsion of the metal fragments and the *P*-substituent, however, they are still shorter than a typical single dative bond as in $[W(CO)_5(PMe_3)]$.[17]

Trigonal planar complexes **II** with an M–P–M π-bonding have small HOMO–LUMO gaps, thus allowing for an admixture of excited states to the electronic ground state configuration (paramagnetic contribution). Therefore, phosphorus nuclei reveal ^{31}P NMR chemical shifts at a very low field (593–1077 ppm).[2,18,19] A broad range of synthetic applications are known for symmetric (M = M) dinuclear phosphinidene complexes **II**, including reactions with nucleophiles, electrophiles, E–H bonds (E = B and P), unsaturated organic molecules and p-block elements, as well as addition of metal fragments, thermolysis and photolysis reactions.[2] While mixed metal μ-phosphinidene complexes have been reported,[15,20] phosphinidenes bridging a metal and a main group Lewis acid are not known.

We recently reported on the synthesis of the donor-stabilised, neutral, electrophilic, terminal phosphinidene complex adduct **1**[21] and we showed that the phosphorus centre in N-donor adducts can be protonated by Brønsted–Lowry acids, but only in the case of superacids were N-donor adducts of P–H phosphenium complexes formed.[22]

Herein, we describe the reactions of an *N*-MeIm donor adduct **1** of a terminal phosphinidene complex with a transition metal and a main group Lewis acid leading to homo- and hetero-dinuclear-bridged phosphinidene complexes, and report on a unique case of a dyotropic rearrangement.

To probe the Lewis basicity and kinetic availability of the P-centre of complex **1**, it was first treated with the labile tungsten(0) complexes $[W(CO)_5(NCMe)]$ and $[W(CO)_5(thf)]$ (Scheme 1). Addition of $[W(CO)_5(MeCN)]$ to **1** in benzene-d_6

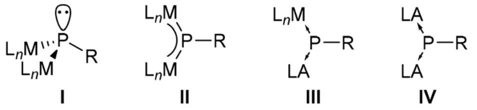

Fig. 1 General structures of a dimetallophosphane (I) and μ_2-phosphinidene bridging two metal fragments (ML_n) (II), a metal and a main group Lewis acid (LA) (III), and two main group Lewis acids (IV).

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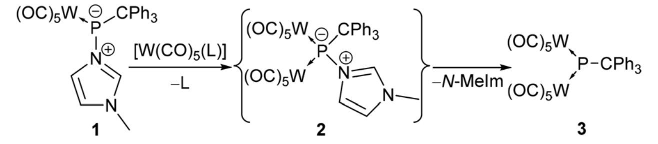
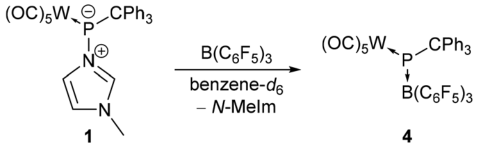


Scheme 1 Proposed formation of the N-donor adduct of dinuclear phosphinidene complex **2** and its conversion into **3**.



Scheme 2 Formation of complex **4** as a μ$_2$-phosphinidene bridging a tungsten and a boron centre.

led to a deep violet solution within a few minutes but the ^{31}P{^{1}H} NMR spectrum revealed only a marginal conversion of **1** under ambient conditions (4% *via* ^{31}P{^{1}H} NMR integration). However, reaction of **1** with [W(CO)$_5$(thf)] revealed an improved outcome. The main product **3** showed a signal at 791.4 ppm ($^1J_{W,P}$ = 185.2 Hz) but the maximum content was only about 46%. Besides the homo-dinuclear μ$_2$-phosphinidene complex **2**, other products were observed in the ^{31}P{^{1}H} NMR spectrum at 247.0 ppm (2%), 182.2 ppm ($^1J_{W,P}$ = 193.9 Hz) (6%), 150.4 ppm ($^1J_{W,P}$ = 192.3 Hz) (6%) and 69.9 ppm ($^1J_{P,H}$ = 371.9 Hz, $^1J_{W,P}$ = 274.7 Hz) (5%). We assumed that the broad signal at 150.4 ppm ($^1J_{W,P}$ = 191.6 Hz) can be assigned to the primarily formed compound **2** (Scheme 1) which converts into **3** *via* loss of the N-donor. Unfortunately, no ^{31}P NMR data of N-donor adducts of homo-dinuclear μ$_2$-phosphinidene complexes were reported by Huttner, but the colour change from blue to yellow was described to be indicative.[19,23]

An *in situ* UV/vis spectrum of the reaction mixture of complex **1** with [W(CO)$_5$(MeCN)] in THF containing **3** shows a characteristic absorption at 540 nm which is assigned to a transition in the W–P–W π-system. Similar homo-dinuclear μ$_2$-phosphinidene complexes were described earlier by Huttner, Jutzi and Kuchen; the ^{31}P NMR parameters and UV/vis data are compiled in Table 1.[19,24–26]

Going from a transition metal to a main group Lewis acid, namely tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$), addition of a slight excess (1.1 eq.) of B(C$_6$F$_5$)$_3$ to complex **1** in benzene-d_6 under ambient conditions resulted in a colour change from yellow to deep turquoise-blue within 20 minutes and the formation of hetero-dinuclear complex **4** (Scheme 2). Formation of the diradical ion pair *via* a single electron transfer (SET) from the HOMO of complex **1** (−6.07 eV) to the LUMO of B(C$_6$F$_5$)$_3$ (−2.31 eV) seems to be unlikely, as demonstrated by the high computed value of ΔG_{SET} = +47.8 kcal mol^{-1} for the separated ion pair. Indeed, an *in situ* UV/vis spectrum of the reaction mixture reveals an absorption at 578 nm which is in accordance with the observed colour, and significantly differs from that of the reported tris(pentafluorophenyl)borane radical anion ($\lambda_{\max}$ = 603 nm).[27]

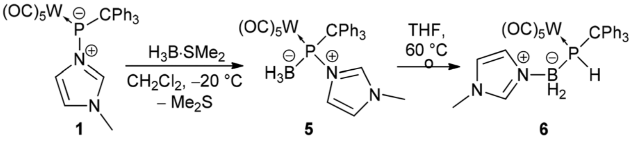
Table 1 ^{31}P{^{1}H} NMR and UV data of dinuclear μ$_2$-phosphinidene complexes [M$_2$(CO)$_{10}$(PR)][19,24,25]

M	R	δ(^{31}P)/ppm	$^1J_{W,P}$/Hz	λ_1/nm (UV/vis)	Lit.
W	CPh$_3$	791.4	185.2	540	This work
Cr	Mes	1216	—	584	24
W	Mes	961	176.4	557	24
W	Bis	—	—	—	24
Cr	Cp*	1331	—	605	25
W	Cp*	1074	177	575	25
Cr	^{t}Bu	1362	—	617	19
W	Methyl	1041	168	564	26
Cr	Methyl	1300	—	598	26

The ^{31}P{^{1}H} NMR spectrum of the reaction mixture (after 1.5 h) showed a strongly deshielded ^{31}P resonance at 1040.3 ppm ($^1J_{W,P}$ = 180.1 Hz) and hence, it is assigned to the hetero-dinuclear complex **4**. The ^{31}P chemical shift of this molecular species is in rather good agreement with the computed value of 974.3 ppm (see the ESI†). To improve the formation of complex **4**, various changes were examined but the best outcome was obtained when **1** was fully consumed (3.4 eq. of B(C$_6$F$_5$)$_3$, stirring for 6.5 hours at rt) and only a 24% content of **4** was determined (*via* integration). Unfortunately, complex **4** converted rather rapidly into a main product (δ(^{31}P{^{1}H}) = −132.8 ppm, $^1J_{W,P}$ = 260.3 Hz) which could not be isolated.

The limited success of achieving the formation of a stable borane adduct led us to conclude that the steric demand of the system and the borane used were the origin of the instability. Therefore, complex **1** was treated with the borane adduct H$_3$B·SMe$_2$ which underwent the reaction smoothly and selectively formed the hetero-dinuclear phosphinidene complex **5** having *N*-methylimidazole still bound to phosphorus (Scheme 3). This product was also thermally unstable but could be isolated *via* precipitation at −20 °C, and a low solubility in common organic solvents was beneficial. ^{31}P NMR spectra (dichloromethane-d_2) showed a broad resonance signal of **5** at 163.5 ppm which was corroborated by a calculated value of 133.0 ppm (see the ESI†) for the model complex **5′** (prime numbering indicates *P*-^{t}Bu substitution).

Due to the adduct formation, rotation about the P–C bond is hindered and the *ortho*-C*H* protons of all phenyl groups differ significantly. The B*H*$_3$ protons were determined as a very broad doublet between 1.24 ppm and 1.52 ppm. The ^{11}B NMR spectrum showed a resonance at −24.9 ppm as a very broad singlet. The ATR FTIR spectrum of complex **5** showed an



Scheme 3 Synthesis of the *N*-methylimidazole-to-phosphinidene complex borane P-adduct **5** and its thermal rearrangement to **6**.

absorption at 2402 cm^{-1} attributed to the B–H valence vibration. HRMS experiments (APCI method) confirmed the elemental composition of the molecular ion (*m*/*z* 693.0944). The final confirmation of the molecular structure of the borane P-adduct **5** came from X-ray diffraction analysis. The molecular structure (Fig. 2, left) discloses a slightly elongated P–CPh_3 bond of 1.9540(19) Å and an angular sum at phosphorus of 313.76(3)°, being slightly smaller than expected for a tetrahedral geometry.

When a solution of complex **5** in THF was heated to 60 °C, formation of a P–H containing compound was observed while the *N*-MeIm donor had shifted to the boron centre (Scheme 4).

The conversion of **5** into **6** came with a strong highfield-shifted signal in the ^{31}P NMR spectrum at −42.6 ppm ($^{1}J_{P,H}$ = 289.3 Hz, $^{1}J_{P,B}$ = 49.2 Hz), which is in good agreement with a computed value of −30.9 ppm for the *P*-^{t}Bu model complex (**6′**), revealing also the presence of the *N*-methylimidazole unit. It is noteworthy that the diminished steric congestion allowed for free rotation about the P–C bonds at ambient temperature. Complex **6** was further confirmed by APCI-HRMS and single-crystal X-ray diffraction analysis (Fig. 2, right). Similar base-stabilised phosphanylborane complexes have been reported by Scheer, *e.g.* $[W(CO)_5P(H)_2B(H)_2NMe_3]$ (δ^{31}P = −184.2 ppm, $^{1}J_{P,B}$ = 63 Hz), although the route is different.[28]

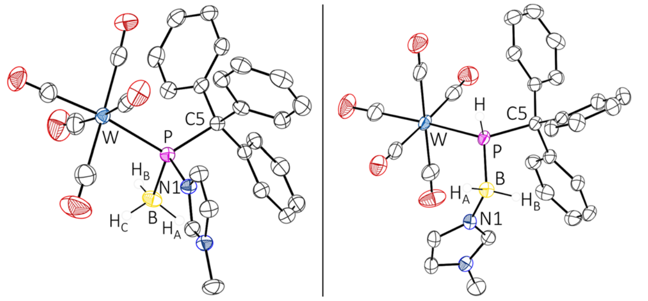


Fig. 2 Molecular structures of **5** (left) and **6** (right). Thermal ellipsoids are set at 50% probability, and solvent molecules and hydrogen atoms are omitted for clarity, except for those bound to boron and phosphorus atoms. The selected bond lengths/Å and bond angles/°: **5**: W–P 2.5688 (5), P–C5 1.9540(19), P–N1 1.8138(16), P–B 1.959(2), N1–P–W 107.17(5), N1–P–C5 101.73(8), N1–P–B 100.26(9), C5–P–W 121.14(16), C5–P–B 111.77(9), B–P–W 111.89(7); **6**: W–P 2.5650(4), P–C5 1.9179(14), P–B 1.9904(16), N1–B 1.5586(19), C5–P–W 123.10(4), C5–P–B 107.48(6), B–P–W 118.20(5), N1–B–P 111.31(9).

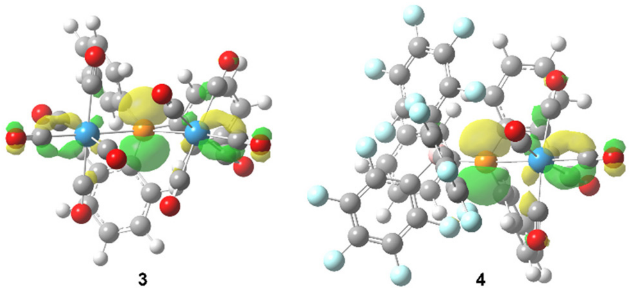
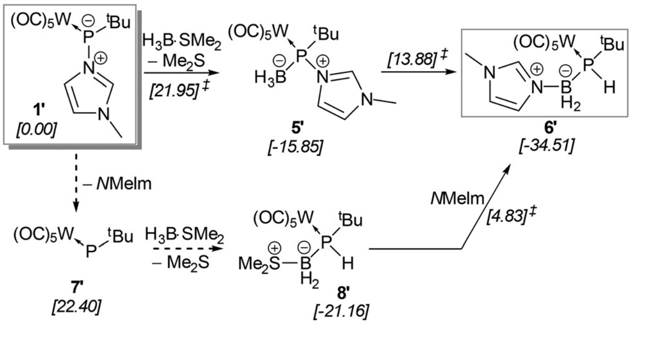


Fig. 3 Computed (B3LYP-D3/def2-TZVP(ecp)) Kohn–Sham LUMO isosurfaces (0.05 au) for **3** and **4** viewed from the P–CPh_3 axis.



Scheme 4 Proposed mechanism for the formation of the rearranged model product **6′** from phosphinidene adduct complex **1′**. The computed [$CPCM_{THF}$/PWPB95-D3/def2-QZVPP//$CPCM_{THF}$/PBEh-3c] relative Gibbs free energies (kcal mol^{-1}) are given in square brackets for ground and transition states (the latter indicated by the ‡ superscript). The dashed arrows indicate barrierless processes.

Quantum chemical calculations (see computational details) reveal the expected trigonal planar geometry at P for both **3** ($\sum$<P = 359.6°) and **4** ($\sum$<P = 359.0°) confirming the sp^2 hybridisation. As expected, the vacant p atomic orbital at P constitutes the LUMO (Fig. 3), showing very low energy values for **3** and **4** (−2.69 and −3.32 eV, respectively), in line with a high positive natural charge at P (1.15 and 0.59 e, for **3** and **4**, respectively), thus indicating the highly electrophilic character of these bridging phosphinidene species compared to adduct complex **1** (the LUMO is mostly located at the metal fragment, with ε_{LUMO} = 1.33 eV, q^n(P) = 0.42 e). Carbonyl ligands intertwining in **3** are favoured by a non-covalent interaction between the different metal fragments (Fig. S113†). A significant shortening of the P–W bond distance in **3** (2.48 and 2.46 Å) and **4** (2.42 Å), in the same range as similar complexes,[13,15,16] is due to the partial double bond character (WBI = 0.735/0.774 and 1.263, respectively) compared to **1** (*d* = 2.63 Å; WBI 0.457). The P–CPh_3 distances in **3** (1.95 Å) and **4** (1.96 Å) fall in the normal range, but steric crowding at P remarkably elongates the P–$B(C_6H_5)_3$ distance in **4** (2.07 Å; compared to 1.93 Å for $H_3P–BH_3$ at the same level).

The mechanism of the formation of the P-borane adduct **5** and its rearrangement to **6** was investigated starting from the *tert*-butyl (instead of trityl)-substituted model compound **1′** (Scheme 4). A thorough analysis of the potential energy surface (see Fig. S114† for a full description) reveals that the lowest energy path proceeds over an exergonic low barrier addition of borane to phosphorus (**5′**), followed by the moderate barrier ($\Delta\Delta G^‡$ = 29.73 kcal mol^{-1}) of the rate-determining formal type I dyotropic migration[29] of hydride and *N*-MeIm between B and P giving (model) complex **6′**, in sum, a remarkable case.

Author contributions

DB, AEF and RS wrote the manuscript and the ESI.

Conflicts of interest

There are no conflicts to declare.

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