Unprecedented reversible coupling of alkynyl and phosphide ligands on a dinuclear platinum framework†

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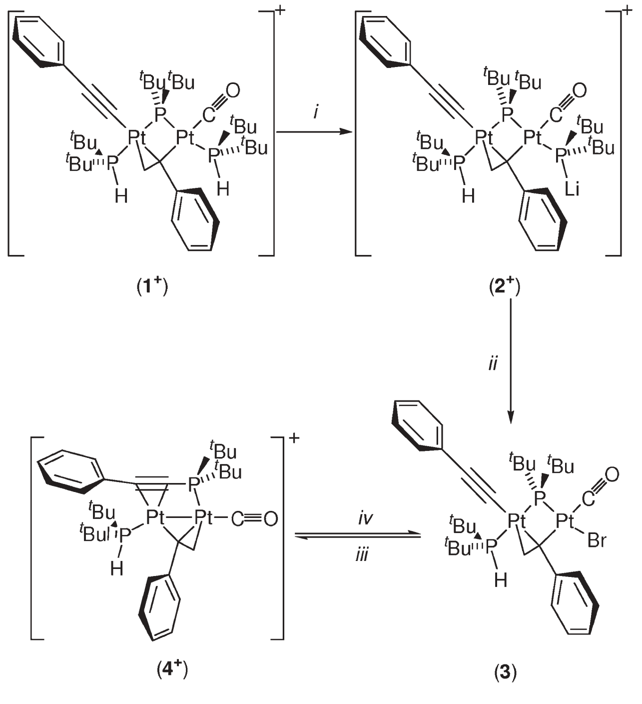
The reductive coupling of the bridging phosphide and the adjacent σ-alkynyl moieties in $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)(Br)]$ is promoted by bromide abstraction and is reversed by adding N^nBu_4Br.

The coordination chemistry of alkynylphosphines has been widely explored so far, including: (i) coordination to metal centre(s) by phosphorus and/or the C≡C moiety;[1] (ii) activation of the P–C bond, yielding phosphide and alkynide fragments;[2] (iii) intramolecular coupling of the C≡C bonds of two coordinated alkynylphosphines;[3] and (iv) insertion of alkynylphosphines into reactive M–H or M–C bonds.[3a,4]

Here we report on the unprecedented reversible coupling between a bridging phosphide and a σ-alkynyl moiety in $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)(Br)]$ (**3**) according to Scheme 1. The reaction of the parent complex $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)_2]^+$ ($\mathbf{1}^+$)[5] (as $\mathbf{1}[CF_3SO_3]$) with PhLi (1 : 1 molar ratio) yields quantitatively the lithium derivative $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2Li)]^+$ ($\mathbf{2}^+$),‡ which, in turn, reacts with benzylbromide yielding the bromo derivative $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)(Br)]$ (**3**) (85% yield), the tertiary phosphine P^tBu_2Bz and $LiCF_3SO_3$.§



i: +PhLi, -PhH; *ii:* +BzBr, -Li$^+$, -P^tBu_2Bz; *iii:* +$TlPF_6$, -TlBr; *iv:* +N^nBu_4Br

Scheme 1

The molecular structure of **3**¶ shows the dinuclear framework supported by the nearly symmetrically-bridged phosphide and the $\mu,\eta^1:\eta^2$-alkenyl fragment. The geometry around each Pt centre is approximately square planar while the immediate coordination sphere consists of the phosphine and the σ-alkynyl moiety (for Pt1), and the bromide and CO (for Pt2) (Fig. 1).

The bromide abstraction from **3**, operated by an excess of $TlPF_6$, promotes the unprecedented reductive|| coupling of the bridging phosphide and the σ-alkynyl ligand, affording the platinum(I) dinuclear cation $[Pt_2(\mu\text{-}\kappa P:\eta^2\text{-}P^tBu_2\text{–}C{\equiv}C\text{–}Ph)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(CO)(P^tBu_2H)]^+$ ($\mathbf{4}^+$) isolated as the hexafluorophosphate salt $(\mathbf{4})[PF_6]$ (96% yield).** As shown in Fig. 2, the cation $\mathbf{4}^+$ contains a Pt1–Pt2 bond [2.6282(2) Å] supported by the $\mu,\eta^1:\eta^2$ -alkenyl fragment and the $\mu\text{-}\kappa P:\eta^2$-alkynylphosphine,

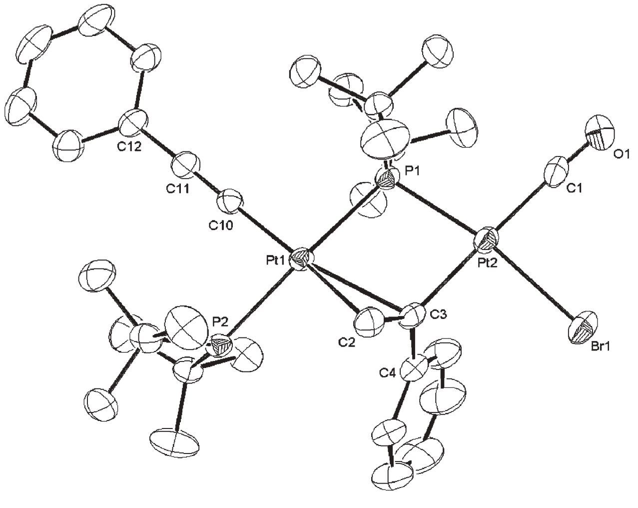


Fig. 1 ORTEP view of $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1:\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)(Br)]$ (**3**) as **3**·THF (thermal ellipsoids at 50% probability level). Selected bond distances (Å) and angles (°): Pt(1)–Pt(2) 3.550(1); Pt(1)–C(10) 1.970(4); Pt(1)–P(2) 2.3372(9); Pt(1)–P(1) 2.3383(9); Pt(1)–C(2) 2.234(4); Pt(1)–C(3) 2.402(4); Pt(2)–P(1), 2.2943(9); Pt(2)–C(1) 1.903(4); Pt(2)–C(3) 2.066(4); Pt(2)–Br(1) 2.5222(4); C(1)–O(1) 1.138(5); C10–C(11) 1.214(5); C(11)–C(12) 1.439(5); C(2)–C(3) 1.381(5); C(3)–C(4) 1.494(6); Pt(1)–C(10)–C(11) 174.1(4); Pt(2)–P(1)–Pt(1) 100.05(3).¶

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† Electronic supplementary information (ESI) available: NMR data. See http://www.rsc.org/suppdata/cc/b4/b418893d/
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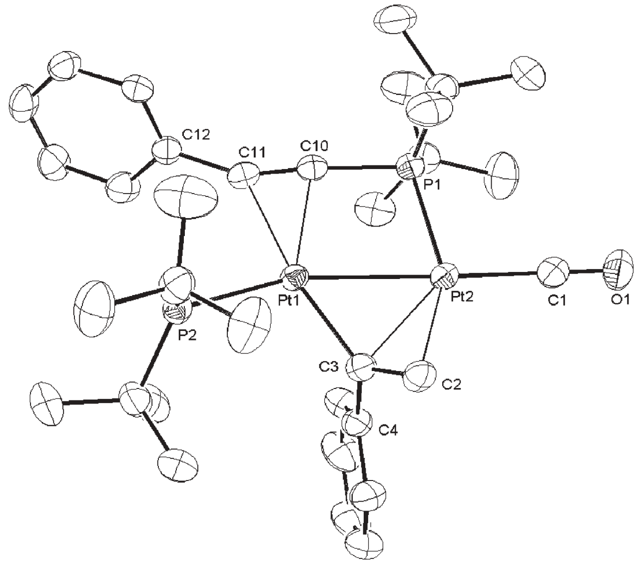

Fig. 2 ORTEP view of $[Pt_2(\mu\text{-}\kappa P{:}\eta^2\text{-}P^tBu_2\text{–}C{\equiv}C\text{–}Ph)\{\mu,\eta^1{:}\eta^2\text{-}C(Ph)CH_2\}(CO)(P^tBu_2H)]^+$ ($\mathbf{4}^+$) in (**4**)$[PF_6]\cdot$DME (thermal ellipsoids at 50% probability level). Selected bond distances (Å) and angles (°): Pt(1)–Pt(2) 2.6282(2); Pt(1)–P(2) 2.286(1); Pt(1)–C(3) 2.023(4); Pt(1)–C(10) 2.195(4); Pt(1)–C(11) 2.216(4); Pt(2)–P(1) 2.288(1); Pt(2)–C(1) 1.896(5); Pt(2)–C(2) 2.227(4); Pt(2)–C(3) 2.230(4); Pt(1)–C(10) 1.759(4); C(2)–C(3) 1.398(6); C(3)–C(4) 1.503(6); C(10)–C(11) 1.232(6); C(11)–C(12) 1.468(6); P(1)–C(10)–Pt(1) 100.7(2); C(10)–P(1)–Pt(2) 101.2(1); O(1)–C(1)–Pt(2) 178.6(4); C(11)–C(10)–P(1) 174.3(4); C(2)–C(3)–C(4) 117.7(4). CCDC 254341.

thus appearing as the first structurally characterised complex with the P–C≡C moiety μ-κ*P*:η^2-coordinated to a bimetallic core with a metal–metal bond.

It is worth noticing the structural differences observed in the coordinated alkenyl fragment in $\mathbf{4}^+$ and **3**, *i.e.*: the Pt1–C3–Pt2 angle is 105.0(2)° in **3** and 76.2(1)° in $\mathbf{4}^+$; the methylene moiety coordinates Pt1 in **3** and Pt2 in $\mathbf{4}^+$. These differences may be related to the reductive coupling (Scheme 1, *iii*) and to the resulting metal–metal bond.

The reaction of the bromide ion (as N^nBu_4Br) with $\mathbf{4}^+$ easily and cleanly yields **3** (Scheme 1, *iv*),†† thus being the first chemically promoted oxidative P–C cleavage, compared with the thermal P–C activation reported so far.[2]

As far as the solution molecular structures of **3** and $\mathbf{4}^+$ are concerned, the following NMR data (see ESI†) indicate that the solid state molecular structure of both compounds is preserved in solution: (i) two non-equivalent platinum centres (^{195}Pt) are present both in **3** (δ −4187.5, −4255.5 ppm) and $\mathbf{4}^+$ (δ −5444.1, −5427.4 ppm); (ii) four non-equivalent *tert*-butyl groups (^{1}H) are observed as a consequence of the oblique arrangement of the alkenyl C≡C bond with respect to the Pt1–Pt2 both in **3** (δ 0.79, 1.34, 1.43, 1.56 ppm) and $\mathbf{4}^+$ (δ 0.85, 1.07, 1.36, 1.49 ppm); (iii) the J_{PPt} coupling constants (2347, 2107 Hz) of the bridging phosphorous in **3** are indicative of a substantially symmetrical arrangement of the phosphide ligand with respect to the $[Pt_2]$ core; (iv) the ^{31}P signal of the alkynylphosphine indicates a strong scalar coupling with only one of the two platinum centres, and a weaker one with the other (2915, 228 Hz), in agreement with the μ-κ*P*:η^2 hapticipy.

In summary, we have synthesised and fully characterised the phosphido-bridged alkynyl derivative **3** and the alkynylphosphine derivative **4**$[PF_6]$ showing that bromide abstraction from **3** promotes the reductive coupling of the phosphide and σ-alkynyl fragments yielding the cation $\mathbf{4}^+$. Moreover, the alkynylphosphine in $\mathbf{4}^+$ undergoes easy and clean cleavage of the P–C bond producing quantitatively **3** upon the addition of bromide.

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Notes and references

‡ The solution structure of $\mathbf{2}^+$ has been elucidated by ^{31}P NMR. Indeed, after the reaction of $\mathbf{1}^+$ (δ_P = 72.7, 43.6, −52.0 ppm, *cf.* ref. 5) with PhLi (1 : 1 molar ratio) the $^{31}P\{^1H\}$ NMR spectrum shows three resonances at 72.1, 42.6, −61.1 ppm, and the ^{1}H-coupled ^{31}P NMR spectrum shows the resonance of the phosphine adjacent to the CO ligand as a singlet (72.1 ppm) while the resonance at 42.6 ppm appears as a doublet ($^1J_{HP}$ = 313 Hz), clearly indicating the regioselectivity of the deprotonation.

§ Synthesis of $[Pt_2(\mu\text{-}P^tBu_2)\{\mu,\eta^1{:}\eta^2\text{-}C(Ph)CH_2\}(C{\equiv}C\text{–}Ph)(CO)(P^tBu_2H)(Br)]$ (**3**): A THF solution (20 ml) of **1**$[CF_3SO_3]$ (100 mg, 82.7 μmol) was treated with phenyllithium (THF solution, 1.8 M, 50 μl, 90 μmol) and, after 30 min stirring, benzylbromide (39.5 μl, d = 1.44 g ml^{-1}, 0.333 mmol) was added. The resulting mixture was stirred for 4 h and finally evaporated *in vacuo*. The residue was extracted with benzene yielding P^tBu_2Bz and $LiCF_3SO_3$ as a colourless solid and a yellow solution of **3**, which was finally obtained as a microcrystalline powder (70 mg, 85% yield) after removing all the volatiles *in vacuo*.

¶ Crystal Data: **3**·THF. $C_{37}H_{57}BrO_2P_2Pt_2$, M = 1065.86, monoclinic, a = 15.9215(2), b = 11.2562(2), c = 22.8096(3) Å, β = 104.380(1)°, U = 3959.8(1) Å^3, T = 200(2) K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo–Kα) = 8.177 mm^{-1}, 39906 reflections measured, 9069 unique (R_{av} = 0.0339) which were used for solution and refinement. Final $R1$ and R_{w2} indices [7694 reflections, $I \geqslant 2\sigma(I)$] were 0.0232 and 0.0530 respectively. CCDC 254340. **4**$[PF_6]\cdot$DME. $C_{37}H_{59}F_6O_3P_3Pt_2$, M = 1148.93, orthorombic, a = 16.7547(1), b = 11.2562(2), c = 25.9733(3) Å, U = 8742.1(1) Å^3, T = 200(2) K, space group $Pbca$ (no. 61), Z = 8, μ(Mo–Kα) = 6.561 mm^{-1}, 86396 reflections measured, 9947 unique (R_{av} = 0.0518) which were used for solution and refinement. Final $R1$ and R_{w2} indices [7783 reflections, $I \geqslant 2\sigma(I)$] were 0.0258 and 0.0548 respectively. CCDC 254341. See http://www.rsc.org/suppdata/cc/b4/b418893d/ for crystallographic data in .cif or other electronic format.

|| To the best of our knowledge, the only related reaction is the addition of the coordinated diphenylphosphide fragment to C_β or C_γ of the butadiynyl fragment in $[Fe_2(CO)_6(\mu\text{–}PPh_2)]_2(\mu\text{–}C{\equiv}C\text{–}C{\equiv}C)$ upon reaction with $P(OMe)_3$ or $NHEt_2$, respectively.[6]

** Synthesis of $[Pt_2(\mu\text{-}\kappa P{:}\eta^2\text{-}P^tBu_2\text{–}C{\equiv}C\text{–}Ph)\{\mu,\eta^1{:}\eta^2\text{-}C(Ph)CH_2\}(CO)(P^tBu_2H)][PF_6]$, (**4**$[PF_6]$): A CH_2Cl_2 solution (10 ml) of the complex **3** (102 mg, 0.103 mmol) was treated with $TlPF_6$ (50 mg, 0.143 mmol). After 1 h stirring, the suspension was filtered, and the resulting solution partially evaporated and diethylether was added yielding **4**$[PF_6]$ as a pale yellow solid (104 mg, 96% yield).

†† The reaction of $\mathbf{4}^+$ with N^nBu_4Br gives quantitatively the product **3** (by NMR spectroscopy), finally isolated with a 95% yield.

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