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Structure and protonation of the bis-ethylene adduct $[Pt(\mu\text{-}PBu^t_2)(\eta^2\text{-}CH_2{=}CH_2)]_2$. Pt–H–P agostic interaction and proton scrambling†

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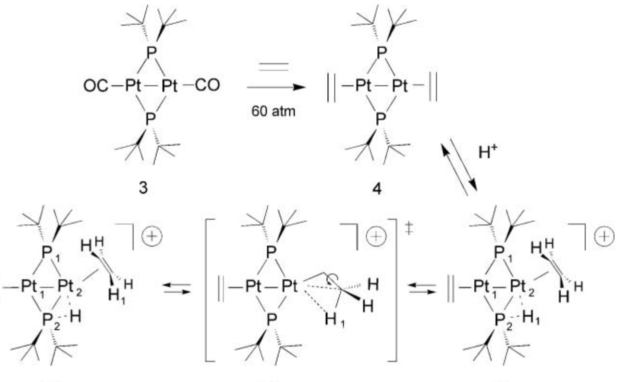
The bis-ethylene derivative $[Pt(\mu\text{-}PBu^t_2)(\eta^2\text{-}CH_2{=}CH_2)]_2$ was prepared and characterized by X-ray diffraction; its protonation affords $[Pt_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(\eta^2\text{-}CH_2{=}CH_2)_2](CF_3SO_3)$, with a rarely observed P–H–M agostic proton in rapid exchange with those of the adjacent ethylene molecule.

Different, extremely rare, bridging coordination modes have been reported for the ubiquitous phosphine donors, which almost invariably act as terminal ligands.[1,2] One of these, exploiting a P–H–Pd agostic interaction, was discovered in the secondary phosphine complexes $[Pd_2(\mu\text{-}PR'_2)(\mu\text{-}PR'_2H)(PR_3)_2](CF_3SO_3)$ [(**1a–f**); R′ = Bu^t, R = Me, Et, Ph, C_6H_4OMe-2, PR_3 = PBu^t_2H; R′ = Cy, PR_3 = $PEtCy_2$],[2] which were mainly obtained by protonation of the corresponding bis-phosphido bridged neutral derivatives or by substitution of the terminal PBu^t_2H ligands in $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)_2](CF_3SO_3)$ (**1e**). Although other E–H–M interactions have been observed quite frequently,[3] no other example of P–H–M interaction has been unambiguously[4] stated so far, probably due to the easy oxidative addition of the relatively weak P–H bond.[5] Recalling that, at variance with the formation of the palladium derivatives **1a–f**, the protonation of the platinum derivatives $[Pt_2(\mu\text{-}PBu^t_2)_2(L)(L')]$ gave the classical hydrides $[Pt_2(\mu\text{-}PBu^t_2)_2(H)(L)(L')](CF_3SO_3)$ [(**2**); L = L′ = PBu^t_2H; L = PBu^t_2H, L′ = CO],[4b,6] we now report the synthesis of the bis-ethylene derivative $[Pt(\mu\text{-}PBu^t_2)(\eta^2\text{-}CH_2{=}CH_2)]_2$, (**4**), and its reaction with CF_3SO_3H, giving the P–H–Pt bridged $[Pt_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(\eta^2\text{-}CH_2{=}CH_2)_2](CF_3SO_3)$, (**5**).

Complex **4** is one of the few structurally characterized bis-ethylene complexes containing at least two metal–metal bonded transition metal centres[7] and has been prepared in nearly quantitative yield by dissolving the dicarbonyl $[Pt(\mu\text{-}PBu^t_2)(CO)]_2$ (**3**) in toluene under 60 atm of ethylene (Scheme 1). Fig. 1 shows an ORTEP view of complex **4**,‡ which exhibits an approximately D_{2h} symmetry, with a nearly planar, metal–metal bonded, $[(\eta^2\text{-}C_2)Pt]_2(\mu\text{-}P)_2$ core [max dev. C(2), 0.03(1) Å, Pt–Pt′ = 2.6230(8) Å], and the C(1)–C(2) distance [1.41(2) Å] significantly longer than in free ethylene (1.337 Å).[8] These features are reminiscent of those found in trigonal planar $Pt(PR_3)_2(\eta^2\text{-}C_2H_4)$ complexes,[9] and differ from those shown by square planar Pt(II) analogues,[10] thus suggesting a significant π-basicity of the $Pt_2(\mu\text{-}P)_2$ core of **4**. The symmetric solid state structure of **4** is preserved in solution, as may be argued by the NMR spectra, showing equivalent Pt (δ_{Pt} = −5925 ppm), P (δ_P = 292.7 ppm) nuclei and *t*-butyl groups (δ_H = 1.23 ppm; δ_C = 32.2 (CH_3), 40.1 (CCH_3) ppm), and symmetrically coordinated ethylene ligands (δ_H = 2.57 ppm; δ_C = 26.7 ppm). Complex **4** reacts with an equimolar amount of triflic acid to give **5** in 85% yield. Significant ^{31}P and ^{195}Pt NMR spectroscopic data for **5** and the proposed solution molecular structure are reported in Scheme 1.

Relevant to the structural elucidation is that: i) δ_{P1} and δ_{P2} differ by *ca.* 100 ppm, suggesting remarkably different chemical environments for the two nuclei;[11] ii) J_{P1Pt1} and J_{P1Pt2} are very similar, while markedly different J_{PPt} coupling constants are associated with P2; and iii) J_{H1P2} is large and J_{H1Pt2} and J_{H1P1} are small compared with the corresponding parameters of the hydride cations 2^+.[2d,4b,12] The whole set of data rules out a hydride (type **2**) structure, as well as a fast (at 200 K)[13] equilibrium between a type **2** hydride and its phosphine (P–H, non agostic) tautomer, and points to a P2–H1–Pt2 (static) agostic interaction as shown in **5a**. The hypothesis is further confirmed by the ^1H–^{195}Pt and ^1H–^{31}P HMQC spectra (200 K, see Supporting Information), which respectively show correlation peaks between the resonance of H1 in **5a** and the ^{195}Pt signal at −6494.8 ppm (Pt2) and the ^{31}P one at 303.1 ppm (P2). Finally, the ^1H NMR spectrum of **5** indicates that the structure is fluxional. Indeed, i) the resonances due to H1 and to the protons of the adjacent ethylene molecule appear severely



δ (ppm)	J (Hz)
P_1 = 402.2	P_1,Pt_1 = 2346
P_2 = 303.1	P_1,Pt_2 = 2440
Pt_1 = -5962	P_2,Pt_1 = 2505
Pt_2 = -6495	P_2,Pt_2 = 345
H_1 = -2.06	H_1P_1 = 29
	H_1P_2 = 86
	H_1Pt_2 = 363

Scheme 1

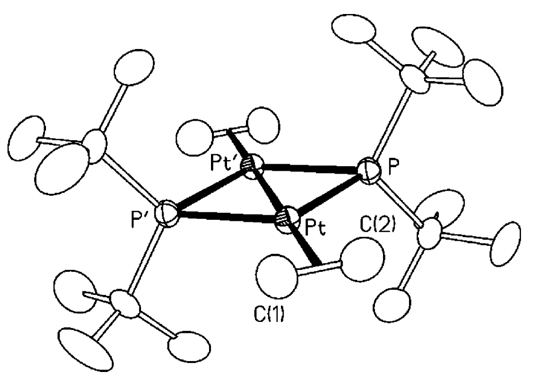


Fig. 1 View of the molecular structure of **4**. Ellipsoids are at 30% probability level. Selected bond lengths [Å] and angles [°]: Pt–Pt′ 2.6230(8), Pt–C(1) 2.086(8), Pt–C(2) 2.098(9), Pt–Eth 1.969(9), Pt–P 2.290(2), Pt–P′ 2.293(2), C(1)–C(2) 1.41(2), P–Pt–P′ 110.17(6), P–Pt–Pt′ 55.15(5), P′–Pt–Pt′ 55.03(6), Eth–Pt–P 124.2(3), Eth–Pt–P′ 125.6(3), Eth–Pt–Pt′ 179.3(3), Pt–P–Pt′ 69.83(6). Eth is the centroid of the C(1)–C(2) bond. ′ = 1 − *x*, 1 − *y*, 1 − *z*.

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† Electronic supplementary information (ESI) available: experimental procedures and characterization data. See http://www.rsc.org/suppdata/cc/b4/b408081e/

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broadened at room temperature, while at 200 K the signals sharpen in a doublet of doublets at −2.06 ppm (P–H–Pt), and a singlet at 4.02 ppm (C_2H_4) (these signals are correlated by an exchange peak in the ^{1}H EXSY spectrum), and ii) the other ethylene molecule gives a sharp singlet at 3.18 ppm in the whole temperature range. Therefore both ethylene molecules should freely rotate even at 200 K, and a dynamic process exchanging H1 with the four protons of the adjacent olefin is operative. With reference to the mechanism, the low temperature ^{1}H and ^{31}P NMR spectra contain only resonances assignable to complex **5**, and are thus uninformative about possible intermediates. However, it seems reasonable that exchange occurs through the bis-phosphido-ethyl derivative **5b** (as a true intermediate or a transition state) shown in Scheme 1. The proposed C–H–Pt agostic interaction may help to stabilize the otherwise unsaturated (28-e$^-$) intermediate. We recall that a closely related reaction occurs in mononuclear *cis*-ethylene–hydride phosphine derivatives of Pd(II)[14*a*] or Pt(II),[14*b*] which are known to be in equilibrium with the agostic ethyl tautomer. Alternative mechanisms *via*: a) insertion of the ethylene molecule into the agostic P–H–Pt bond, with formation of the tertiary phosphine $PEtBu^t_2$ (which could also be formed by reductive elimination from **5b**), or b) oxidative addition of vinylic CH bonds, require multistep sequences with major skeletal rearrangements, and seem therefore less probable. It is worth noting that ethylene–hydride/ethyl equilibria, of paramount relevance in transition metal catalysis,[15] have not yet been definitely recognized in polynuclear systems, although they have been reasonably suggested also in a few other reports.[16]

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Notes and references

‡ Crystal data for **4**: $C_{20}H_{44}P_2Pt_2$, crystal dimensions 0.50 × 0.42 × 0.10 mm, $M = 736.67$, $T = 293(2)$ K, space group $P\bar{1}$ (No. 2), $a = 8.250(2)$, $b = 8.406(1)$, $c = 9.973(1)$ Å, $\alpha = 95.41(2)$, $\beta = 99.22(2)$, $\gamma = 111.03(2)^\circ$, $V = 628.6(2)$ Å^3, $Z = 1$, $D_c = 1.946$ g cm^{-3}, μ(Mo-K$_\alpha$) = 11.244 mm^{-3}, F (000) = 350, $\lambda_{MoK\alpha} = 0.71073$ Å, $R(Fo) = 0.0375$. CCDC 236901. See http://www.rsc.org/suppdata/cc/b4/b408081e/ for crystallographic data in .cif or other electronic format.

Synthesis of 4. An orange solution of $[Pt(\mu\text{-}PBu^t_2)(CO)]_2$ (100 mg, 0.136 mmol) in toluene (5 ml) was saturated with ethylene (60 atm) and stirred for 4 hours at room temperature. The resulting yellow solution was evaporated and the yellow residue identified as $[Pt(\mu\text{-}PBu^t_2)(\eta^2\text{-}CH_2CH_2)]_2$ (92 mg; 92% yield). Calcd for $C_{20}H_{44}P_2Pt_2$: C 32.6; H 6.02. Found: C 32.4; H 6.35%.

Synthesis of 5. Triflic acid (17 μl; $d = 1.69$ g ml^{-1}; 0.19 mmol) was added to a CH_2Cl_2 solution (3 ml) of $[Pt(\mu\text{-}PBu^t_2)(\eta^2\text{-}CH_2CH_2)]_2$ (140 mg, 0.190 mmol). The solution was concentrated and Et_2O (1 ml) was added, yielding a yellow precipitate, which was filtered off, dried *in vacuo* and identified as $[Pt_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(\eta^2\text{-}CH_2CH_2)_2](CF_3SO_3)$ (143 mg, 85% yield). Calcd for $C_{21}H_{45}F_3O_3P_2Pt_2S$: C 28.4; H 5.11. Found: C 28.2; H 5.35%.

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12 The reverse assignment of δ_{P1} and δ_{P2} (P2 *trans* to H1) results in a meaninglessly small value of the coupling constant associated with the PtP bond *trans* to H1 ($^1J_{P2Pt2} = 345$ Hz).

13 The values of δ_{H1} (−2.06 ppm) and δ_{P2} (303.1 ppm) rule out the presence of any significant amount of the P–H (terminally bonded) tautomer. Moreover, sharp and well defined ^{1}H and ^{31}P NMR signals (including the ^{195}Pt satellites), which varied their position and intensity only marginally, were observed in the range 253–180 K.

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