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$[PtMe(^iPr_3P)_2]^+$: a Pt(II) complex with an agostic interaction that undergoes C–H activation†

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The T-shaped Pt(II) complex $[PtMe(^iPr_3P)_2][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$, which is stabilised by an agostic interaction, undergoes acid-catalysed intramolecular C–H activation in the presence of THF to afford cyclometallated $[Pt(THF)(^iPr_3P)(^iPr_2PCHMeCH_2)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$.

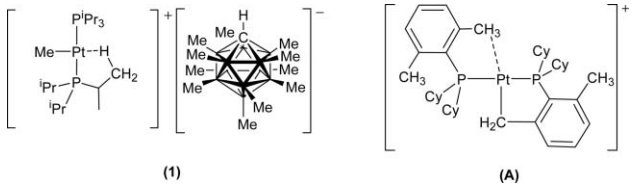
Coordinatively unsaturated platinum(II) complexes, such as $[PtMeL_2]^+$ (L = 2-electron donor), are of significant interest due to their central role in alkane C–H activation,[1,2] or as models of intermediates in late transition metal catalysed olefin polymerisation.[3,4] These complexes are usually transient, being generated *in situ* by ligand dissociation, with the resulting unsaturation being relieved by coordination of an anion (*e.g.* triflate), solvent (*e.g.* nitrile) or by agostic interactions. For these latter complexes only a handful of examples of Pt(II) have been reported. Spencer has described $[Pt(R)(P\text{–}P)]^+$ complexes (P–P = chelating ligand, R = norbornyl, ethyl) that show β-agostic C–H interactions.[4,5] More recently Baratta and Stoccoro prepared a Pt(II) centre supported by a δ-agostic interaction from the bulky phosphine $PCy_2(2,6\text{-}Me_2C_6H_3)$, complex **A** (Scheme 1).[6] Related complexes of isoelectronic Rh(I) and Pd(II) have also been described.[7] In principle these Pt(II) agostic complexes can be thought of as arrested intermediates in intramolecular C–H activation, and thus as models for intermolecular alkane activation by Pt(II) complexes.[1] We report here the synthesis and characterisation of a new Pt(II) agostic complex and its facile, acid-catalysed, C–H activation to form a cyclometallated compound.

Treatment of *cis*-$[PtMe_2(^iPr_3P)_2]$ with one equivalent of the neutral radical [1-H-*closo*-$CB_{11}Me_{11}$]$^\bullet$[8] in CH_2Cl_2 or fluorobenzene solution results in the immediate and quantitative formation of the new compound *trans*-$[PtMe(^iPr_3P)_2][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$, **1**. Methane ($\delta^1$H 0.20) is also observed, consistent with a one-electron homolysis reaction mechanism.[9] Methide abstraction using $B(C_6F_5)_3$ or $[CPh_3][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$ also results in the clean formation of **1**, along with $[MeB(C_6F_5)_3]^-$ and $MeCPh_3$ respectively. Complex **1** was fully characterised by multinuclear NMR spectroscopy‡ and X-ray crystallography§, and shown to be a "14-electron" T-shaped platinum(II) complex stabilised by a γ-agostic interaction.

In the solid-state (Fig. 1), complex **1** is a cationic platinum(II) centre in a pseudo square-planar environment (sum of angles around Pt = 360.0°), coordinated to two *trans* phosphines and a methyl ligand. The anion is remote to the metal centre. The fourth coordination site is taken up by a rather long γ-agostic interaction [C(31)–Pt(1) 2.859(7) Å] showing one relatively close Pt–hydrogen distance [Pt–H 2.24(4) Å]. The Pt–σ–methyl distance [Pt(1)–C(13) 2.026(5) Å] is relatively short,[10] consistent with a weakly bound *trans* ligand. DFT calculations on **1** (see ESI†) are in accord with the single close Pt···H contact. Structurally, **1** is similar to $[Pt\{PCy_2(2,6\text{-}Me_2C_6H_3)\}\{PCy_2(2\text{-Me-6-}CH_2\text{-}C_6H_3)\}][BAr^f_4]$ **A**,[6] in which one phosphine ligand is cyclometallated while the other partakes in an agostic interaction with the metal centre. In this complex, the agostic interaction is somewhat stronger [Pt–C 2.432(6) Å] than in **1**.

^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy show that, at room temperature, compound **1** has C_{2v} symmetry, presumably due to rapid intramolecular exchange of the isopropyl CH_3 groups on both phosphines at the metal centre. This process is facile, as cooling to 190 K resulted in no significant change in the spectra. This is in contrast to **A**, in which exchange of methyl groups can be frozen out at 178 K, consistent with the presence of a stronger Pt···H_3C interaction. Kubas has reported that the closely related compound $[PtH(^iPr_3P)_2][BAr^f_4]$ forms a solvent (CH_2Cl_2) complex in the solid-state and in solution rather than an agostic interaction.[11] Even though the Pt···H_3C interaction in **1** is relatively long, we see no evidence for its displacement by CD_2Cl_2: when **1** is prepared in fluorobenzene, identical NMR chemical shifts and *J*(PtP) or *J*(PtH) coupling constants are observed compared to those found in CD_2Cl_2, suggesting a similar structure in which the agostic interaction is retained. The value of *J*(PtCH_3) for the methyl *trans* to the agostic interaction [106 Hz] is also higher than that expected for a compound with a strongly coordinating *trans* ligand {*e.g.* 83 Hz for $[PtMeCl(^iPr_3P)_2]$}.[12] Unfortunately infrared spectroscopy on complex **1** did not provide evidence for either an agostic interaction or a CH_2Cl_2 complex.[11]

The agostic interaction in **1** can be displaced by stronger Lewis bases than CD_2Cl_2. Addition of H_2 to **1** in CD_2Cl_2 yields *trans*-$[PtH(^iPr_3P)_2(\eta^2\text{-}H_2)][BAr^f_4]$[11] and methane, presumably through a



Scheme 1

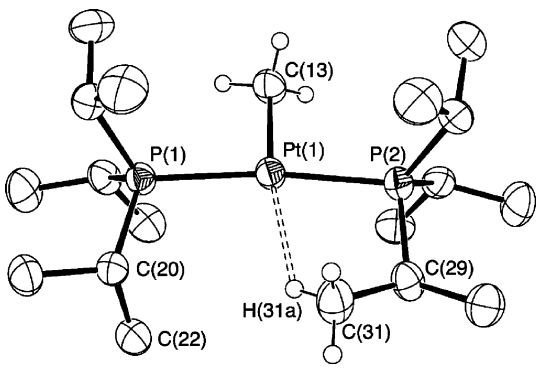


Fig. 1 Cationic portion of complex **1**. Hydrogen atoms, apart from those associated with C(13) and C(31), are omitted. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Pt(1)–C(13) 2.026(5); Pt(1)–P(1) 2.3161(12); Pt(1)–P(2) 2.3024(12); Pt(1)–C(31) 2.859(7); Pt(1)–H(31A) 2.24(4) Å. Selected bond angles (°) P(2)–Pt(1)–P(1) 171.80(4); C(13)–Pt(1)–P(1) 93.36(15); C(13)–Pt(1)–P(2) 94.81(15); C(31)–C(29)–P(2) 108.2(4); C(22)–C(20)–P(1) 111.9(3).

† Electronic supplementary information (ESI) available: experimental data, DFT calculations and proposed mechanism for the formation of **3**. See http://www.rsc.org/suppdata/cc/b4/b410846a/

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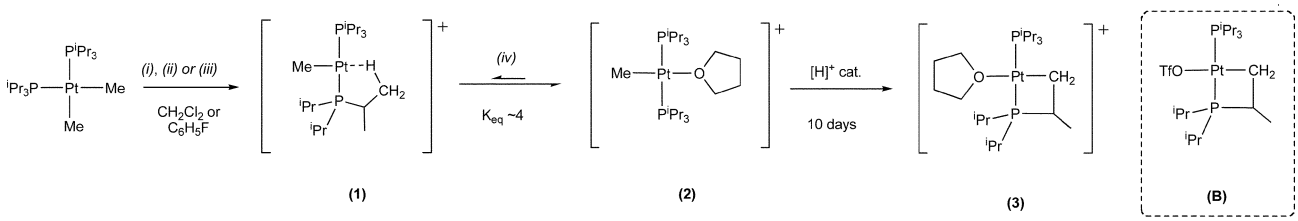

Scheme 2 *(i)* [1-H-*closo*-$CB_{11}Me_{11}$]; *(ii)* [1-H-*closo*-$CB_{11}Me_{11}$][CPh_3]; *(iii)* $B(C_6F_5)_3$; *(iv)* 5 equivalents THF in CD_2Cl_2.

dihydrogen platinum methyl intermediate. Use of D_2 results in *trans*-[Pt(D)(^{i}Pr$_3$P)$_2$(η^2-D$_2$)][BAr^f_4] and CH_3D. Addition of THF to a CD_2Cl_2 solution of **1** rapidly affords the adduct species *trans*-[PtMe(^{i}Pr$_3$P)$_2$(THF)][1-H-*closo*-$CB_{11}Me_{11}$] **2**, which was characterised by multinuclear NMR spectroscopy by comparison with [PtH(^{i}Pr$_3$P)$_2$(THF)][BAr^f_4].[11] Cooling a solution of **2** to 230 K resulted in an equilibrium distribution between the agostic complex **1** and the THF adduct **2** in a 1 : 4 ratio (Scheme 2). At this temperature the bound THF molecule appears at δ 3.90 and δ 1.90 in the ^{1}H NMR spectrum, shifted downfield from free THF [δ^1H: 3.68, 1.82].

Unexpectedly, when left at room temperature for 10 days the THF adduct **2** slowly but cleanly converts to a new product, which has been characterised by NMR and mass spectroscopy as the cyclometallated Pt(II) compound *cis*-[Pt(^{i}Pr$_3$P)(^{i}Pr$_2$PC(H)MeCH$_2$)-(THF)][1-H-*closo*-$CB_{11}Me_{11}$] **3** (Scheme 2), by comparison with the previously reported complex *cis*-[Pt(OTf)(^{i}Pr$_3$P)-(^{i}Pr$_2$PC(H)MeCH$_2$)], **B**.[12] Complex **3** represents the formal intramolecular C–H activation product of complex **1** with concomitant elimination of methane (as observed by ^{1}H NMR spectroscopy). THF is strongly implicated in the reaction pathway (see ESI†), as **1** remains unchanged on heating in CD_2Cl_2 (40 °C, 7 days), but addition of THF (5–10 equivalents) induces cyclometallation to form **3**. Cyclometallation of ^{i}Pr$_3$P ligands on Pt(II) is not without precedent, and has been suggested to proceed by an acid-catalysed mechanism. For example the formation of complex **B** (Scheme 2) from [Pt(Me)OTf(^{i}Pr$_3$P)$_2$][12] requires traces of acid. For **2** this is also the case. Addition of *ca.* 10 mol% of HCl to **1** in CD_2Cl_2–THF results in the accelerated formation of **3** as the major product [$PtCl_2$(^{i}Pr$_3$P)$_2$ is identified by ^{31}P{^{1}H} NMR spectroscopy as the minor product]. Also consistent with the involvement of acid in the reaction pathway is that addition of the hindered base 2,6-di-*tert*-butylpyridine to **2** leaves it unchanged (by ^{1}H and ^{31}P NMR spectroscopy) with no cyclometalled product observed after 4 days in CD_2Cl_2–THF. The source of acid is, however, not known. Likely, though, is that it is adventitious water, as coordination of H_2O to a cationic {Pt(II)}$^+$ fragment would enhance its acidity. Aqua complexes such as [PtMe(PR_3)$_2$(OH_2)]$^+$ are well-known.[13]

Finally, compound **3** reacts rapidly with H_2 in CD_2Cl_2 solution to open the Pt(II) metallacycle and afford [PtH(^{i}Pr$_3$P)$_2$(THF)][1-H-*closo*-$CB_{11}Me_{11}$] (Scheme 3), which has previously been characterised by Kubas as the [BAr^f_4]$^-$ salt.[11]

Complex **1** is a rare example[4] of a well characterised "14-electron" Pt(II) agostic complex that subsequently undergoes intramolecular C–H activation (albeit acid catalysed). That such complexes are often implicated in cyclometallation reactions of Pt(II),[14] coupled with the ease of preparation of **1**, suggests that these systems may be attractive precursors for developing the chemistry of cationic unsaturated d^8 metals.

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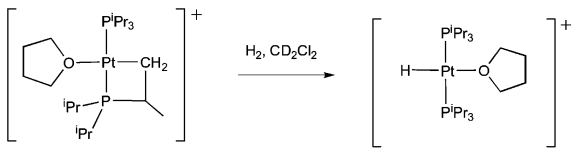

Scheme 3

Notes and references

‡ *Spectroscopic data:* Complex **1** (all at 298K, CD_2Cl_2): δ ^{1}H: 2.56 (m, 6H, ^{i}PrCH), 1.69 (t, 3H, Pt–Me, ^2J(PtH) 106, ^3J(PH) 5.6), 1.34 (dd, 36H, ^{i}PrCH$_3$, ^3J(PH) 14.8 ^3J(HH) 7.6), 1.15 (s, 1H CH_{cage}), −0.18 (s, 15H, B–CH_3(2–6)), −0.43 (s, 15H, B–CH_3(7–11)), −0.55 (s, 3H, B–CH_3(12)). δ ^{31}P{^{1}H}: 47.1 (^1J(PtP) 2757). δ ^{11}B: −0.51 (s, 1B), −8.60 (s, 5B), −11.90 (s, 5B). δ ^{13}C{^{1}H}: 60.19 (s, cage C), 23.24 (t, ^1J(PC) 14, ^{i}Pr$_3$P C–H), 18.82 (s, ^{i}Pr$_3$P CH_3), −3.82 (br s, B–CH_3), −14.11 (s, ^1J(PtC) 755, Pt–CH_3). *HRMS (ES+):* Theoretical for $C_{19}H_{45}P_2Pt_1$ = 530.2639 *m/z*. Observed = 530.2637 *m/z*. Yield: 79%. *Complex* **3** (at 220K in CD_2Cl_2 unless noted): δ ^{1}H{^{31}P}: 3.92 (m, 4H, THF O(CH_2CH$_2$)$_2$), 2.97 (1H, m, PtCH$_2$CHMeP), 2.58 (2H, m, PtCH_2CHMeP(CHMe$_2$)$_2$), 2.21 (3H, m, Pt–P(CHMe$_2$)$_3$, 1.92 (6H, m, O(CH$_2$CH_2) THF and PtCH_2CHMeP), 1.41–1.05 (34H, 7 sets of d, PtCH$_2$CH*Me*P, Pt–P(CH*Me*$_2$)$_3$, PtCH$_2$CHMeP(CH*Me*$_2$)$_2$ and cage C–H): 1.41 (d, ^3J(HH) 7), 1.38 (d, ^3J(HH) 7), 1.29, (d, ^3J(HH) 7), 1.24 (d, ^3J(HH) 7), 1.15 (d, ^3J(HH) 7), 1.12 (d, ^3J(HH) 7) and 1.05 (d, ^3J(HH) 7)], −0.21 (s, 15H, B–CH_3(2–6)), −0.46 (s, 15H, B–CH_3(7–11)), −0.59 (s, 3H, B–CH_3(12)). δ ^{31}P{^{1}H} 41.8 (d, ^2J(PP) 358 ^1J(PtP) 3010), −15.8 (d, ^2J(PP) 358, ^1J(PtP) 2124). δ ^{11}B (298K, CD_2Cl_2): −0.60 (s, 1B), −8.75 (s, 5B), −12.08 (s, 5B). δ ^{13}C{^{1}H}: 75.25 (s, THF), 59.79 (s, cage C), 34.19 (d, J(PC) 31), 29.99 to 17.46 (complex overlapping isopropyl signals and the remaining THF signal), −3.20 (br s, B–CH_3), −17.40 (d, ^2J(PC) 22, ^1J(PtC) not observed, Pt–CH_2). *HRMS (ES+):* Theoretical for $C_{18}H_{41}P_2Pt_1$ ([M] − THF) = 514.2331 *m/z*. Observed = 514.23312 *m/z*.

§ *Crystallographic data.* Intensity data were collected at 150 K on a Nonius Kappa CCD, using graphite monochromated MoKα radiation (λ = 0.71073 Å). **1**: $C_{31}H_{79}B_{11}P_2Pt$, M = 827.88, $P\bar{1}$, a = 9.2420(4) Å, b = 12.9830(5) Å, c = 18.3320(7) Å, α = 87.486(1)°, β = 86.543(2)°, γ = 86.672(2)°, V = 2190.13(15) Å^3, Z = 2, μ = 3.296 mm^{-1}, unique reflections = 8719 [R(int) = 0.0515], R_1 = 0.0374, $wR2$ = 0.0832 [$I > 2\sigma(I)$]. CCDC 245432. See http://www.rsc.org/suppdata/cc/b4/b410846a/ for crystallographic data in .cif or other electronic format.

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