SUPPORTING INFORMATION

EXPERIMENTAL

General Methods. All manipulations were performed under an inert atmosphere of argon, using standard Schlenk-line and glove box techniques. Glassware was dried in an oven at 130°C overnight and flamed with a blowtorch, under vacuum, three times before use. CH_2Cl_2, pentane was distilled from CaH_2, C_6H_5F was distilled from P_2O_5 under vacuum and CD_2Cl_2 was distilled under vacuum from CaH_2. ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Advance 300 MHz or a Bruker Advance 400 MHz FT-NMR spectrometers. Residual protio solvent was used as reference for ^{1}H NMR spectra (CD_2Cl_2: $\delta = 5.33$) and ^{13}C NMR spectra (CD_2Cl_2: $\delta = 53.8$). ^{11}B and ^{31}P NMR spectra were referenced against $BF_3.OEt_2$ (external) and 85% H_3PO_4 (external) respectively. Infrared spectra were recorded on a Nicolet NEXUS FT-IR spectrometer. Solution spectra were recorded using a 0.1mm solution cell. Microanalysis of all the new compounds was consistently low in %C, even though performed on crystalline material pure by NMR spectroscopy (>99%).

$(^{i}Pr_3P)_2PtMe_2$,[1] $[CPh_3][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$[2] and $[1\text{-H-}closo\text{-}CB_{11}Me_{11}]^{\bullet}$[3] were synthesised using literature procedures or modifications thereof. The compounds $B(C_6F_5)_3$ and 2,6 –di-^{t}butylpyridine were used as purchased.

$[(^{i}Pr_3P)_2Pt(Me)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$: A Young's ampoule was charged with equimolar quantities of $[(^{i}Pr_3P)_2PtMe_2]$ (0.020g) and $[1\text{-H-}closo\text{-}CB_{11}Me_{11}]^{\bullet}$ (0.011g) (or alternatively 0.020g of $CPh_3[1\text{-H-}closo\text{-}CB_{11}Me_{11}]$ and then dissolved in 5ml of C_6H_5F, resulting in the formation of a yellow solution. Yellow crystals were obtained (0.024g) by the slow diffusion of pentane at -20ºC.

Yield: 79%

$\delta^{1}H$ (298K, CD_2Cl_2): 2.56 (m, 6H, ^{i}Pr CH), 1.69 (t, 3H, Pt-Me, ^{2}J(PtH) 106, ^{3}J(PH) 5.6), 1.34 (dd, 42H, ^{i}Pr CH_3, ^{3}J(PH) 14.8 ^{3}J(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)).

$\delta^{31}P\{^{1}H\}$ (298K, CD_2Cl_2): 47.1 (^{1}J(PtP) 2757)

$\delta^{11}B$ (298K, CD_2Cl_2): -0.51 (s, 1B), -8.60 (s, 5B), -11.90 (s, 5B).

$\delta^{13}C\{^{1}H\}$(298K, CD_2Cl_2): 60.19 (s, Cage C), 23.24 (t, ^{1}J(PC) 14, $^{i}Pr_3P$ C-H), 18.82 (s, $^{i}Pr_3P$ CH_3), -3.82 (br s, B-CH_3), -14.11 (s, ^{1}J(PtC) 755, Pt-CH_3).

Accurate Mass Spec (ES+): Theoretical for $C_{19}H_{45}P_2Pt_1$ = 530.2639m/z. Experimentally Observed = 530.2637m/z

[*trans*-$(^{i}Pr_3P)_2Pt(Me)(THF)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$: To a solution of $[(^{i}Pr_3P)_2Pt(Me)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$ (made *in-situ*) in CD_2Cl_2 was added via syringe 5 equivalents of THF (20μl). The room temperature NMR spectra are fluxional, with only one sets of broadened signals visible in the $^{31}P\{^{1}H\}$ NMR, the trans to the fluxional site Me is also significantly broadened. At 230K the fluxionaility is frozen out and two sets of signals are visible – one is the agostic complex $[(^{i}Pr_3P)_2Pt(Me)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$. The other is assigned as [*trans*-$(^{i}Pr_3P)_2Pt(Me)(THF)][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$, also present in the ^{1}H NMR spectra are the signals for free THF.

$\delta^{1}H$ (298K, CD_2Cl_2): 2.56 (m, 6H, ^{i}Pr CH), 1.58 (br s, 3H, Pt-Me, ^{2}J(PtH) 98), 1.33 (dd, 42H, ^{i}Pr CH_3, ^{3}J(PH) 14.8 ^{3}J(HH) 7.2), 1.14 (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)).
$\delta^{31}P\{^1H\}$ (298K, CD_2Cl_2): 46.1 (br s ^1J(PtP) 2771)

Low Temperature Data:
δ^1H (230K, CD_2Cl_2): 3.90 (m, 4H, THF), 2.33 (m, 6H, ^{i}Pr CH), 1.90 (m, 4H THF), 1.28 (vt, 42H, ^{i}Pr CH_3, ^3J(PH) 13.4 ^3J(HH) 6.7), 1.11 (s, 1H CH_{cage}), 0.76 (t, 3H, Pt-Me ^2J(PtH) 86Hz, ^3J (PtP) 5.2)-0.25 (s, 15H, B-CH_3(2-6)), -0.54 (s, 15H, B-CH_3(7-11)), -0.67 (s, 3H, B-CH_3(12)).
$\delta^{31}P\{^1H\}$ (230K, CD_2Cl_2): 40.3 (^1J(PtP) 2820)

[(^{i}Pr$_3$P)(THF)Pt{κ^2-P(^{i}Pr$_2$)(CH(CH_3)CH_2)}][1-H-*closo*-$CB_{11}Me_{11}$] {(tri-isopropyl phosphine)(THF)(2,2-diisopropyl-3-methyl-1-platina-2-phosphacyclobutane)}: 5 equivalent of THF is added via a syringe to 20mgs of [*trans*-(^{i}Pr$_3$P)$_2$Pt(Me)][1-H-*closo*-$CB_{11}Me_{11}$] dissolved in CD_2Cl_2. On standing the solution gradually lightened in colour from yellow to colourless over the course of ten days (periodically monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy until only one complex is present) to quantitatively (by $^1H\{^{31}P\}$, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy) produce [(^{i}Pr$_3$P)(THF)Pt{κ^2-P(^{i}Pr$_2$)(CH(CH_3)CH_2)}][1-H-*closo*-$CB_{11}Me_{11}$]. Solid material was unobtainable despite repeated attempts. Facile loss of the coordinated THF molecule prevented satisfactory microanalysis.
Yield: Quantitative by NMR Spectroscopy
$\delta^1H\{^{31}P\}$ (220K, CD_2Cl_2): 3.92 (m. 4H, THF O(C**H**$_2$CH$_2$)$_2$)*, 2.97 (1H, m, PtCH$_2$C**H**MeP) 2.58 (2H, m, PtCH$_2$CHMeP(C**H**Me$_2$)$_2$), 2.21 (3H, m , Pt-P(C**H**Me$_2$)$_3$, 1.92 (6H, m, O(CH$_2$C**H**$_2$) THF and PtC**H**$_2$CHMeP), 1.41 – 1.05 (34H, 7 sets of d, PtCH$_2$CH**Me**P, Pt-P(CH**Me**$_2$)$_3$ and PtCH$_2$CHMeP(CH**Me**$_2$)$_2$ and an obscured 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)).
*At temperatures below 260K signals for free (3.68 and 1.86) and coordinated THF (3.92 and 1.92) above 270K only one signal visible (3.76 and 1.89).
$\delta^{31}P\{^1H\}$ (220K, CD_2Cl_2): 41.8 (d, ^2J (PtP) 358 ^1J(PtP) 3010), -15.8 (d, ^2J(PtP) 358, ^1J(PtP) 2124)
$\delta^{11}B$ (298K, CD_2Cl_2): -0.60 (s, 1B), -8.75 (s, 5B), -12.08 (s, 5B).
$\delta^{13}C\{^1H\}$(220K, CD_2Cl_2): 75.25 (s, THF), 59.79 (s, Cage C), 34.19 (d, 31 J(PC)), 29.99 to 17.46 (complex overlapping isopropyl signals and remaining THF signal), -3.20 (br s, B-CH_3), -17.40 (d, ^2J(PC) 22, ^1J(PtC) not observed, Pt-CH_2).
Accurate Mass Spec (ES+): Theoretical for $C_{18}H_{41}P_2Pt_1$ ($[M]^+$ - THF) = 514.2331m/z. Experimentally Observed = 514.23312m/z

DFT Calculations on (1)

Gas-phase geometry optimization of the structure was carried out with the B3LYP//LANL2DZ level using the Gaussian 03 package of programs. The LANL2DZ basis set is specialized for dealing with high atomic atoms (beyond the third row).The structure was characterized by harmonic frequency calculations and was shown to be a minima.

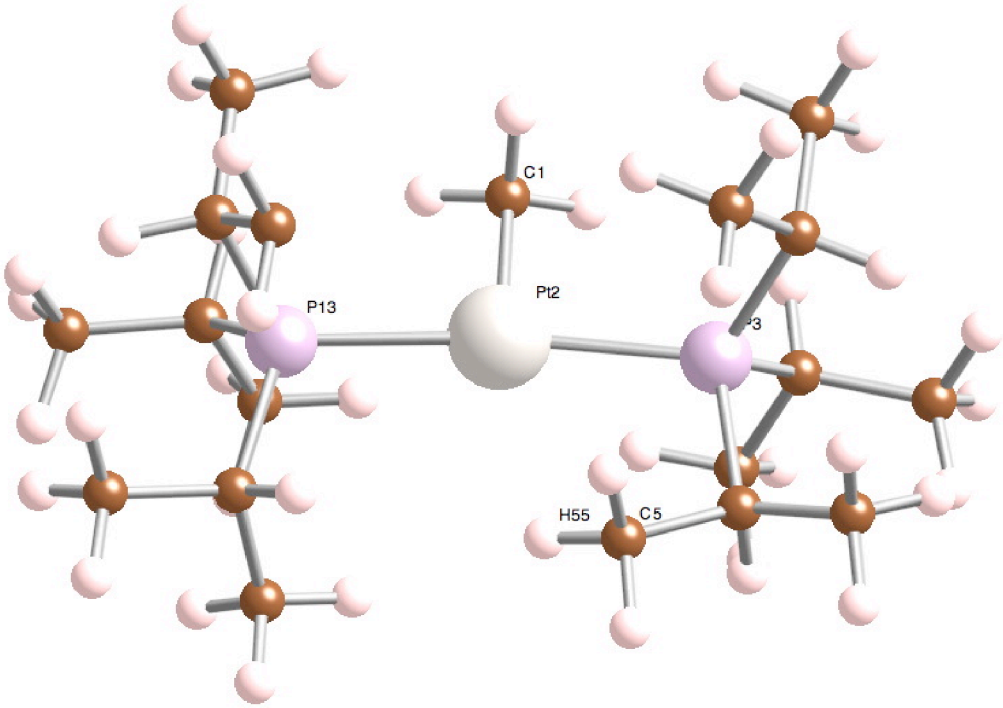
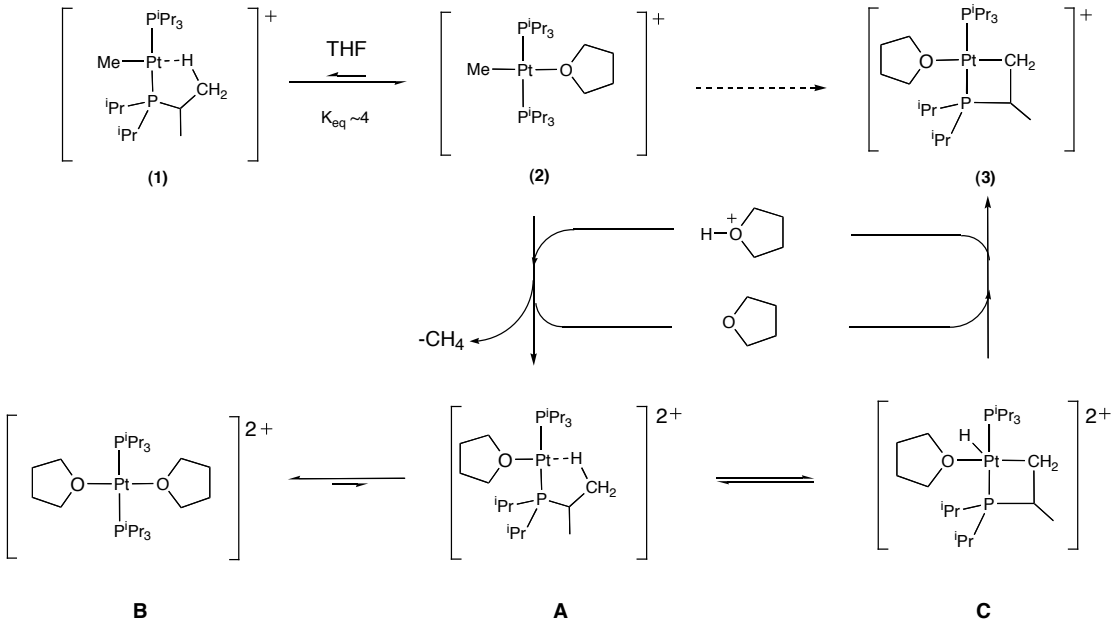


Figure S1. DFT calculated structure for 1. Selected bond lengths and angles: Pt2-C1 2.053 Å, Pt2-P3 2.430 Å, Pt2-P13 2.436 Å, Pt2-C5 3.245 Å, Pt2-H55 2.610 Å. P-Pt-P 171.55°

Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

Proposed Mechanism for the formation of 3



Scheme S1

Based on earlier studies of C-H activation in mono and di-cationic Pt(II) systems we propose the following mechanism for the formation of **3** from **1** (Scheme S1).[4-7]

Complex **1** is in equilibrium with the THF adduct **2** (as shown by NMR spectroscopy). Complex **1** does not undergo protonolysis while **2** does – presumably because the metal centre is more electron rich in **2**. A similar observation has been made by Thorn, who showed that [($^{i}Pr_3P)_2PtCl(Me)$] undergoes protonolysis whereas [($^{i}Pr_3P)_2Pt(OTf)(Me)$] does not.[7] The protonation of **2** from traces of acid to form **A** would be expected to be slow (as well as being irreversible) and may be the rate determining step as it is well documented that monocationic Pt(II)-alkyls are relatively stable to protonolysis.[6] Intramolecular C-H activation of **A** would form a dicationic alkyl hydride **C**, which could then be deprotonated by THF to afford **3**. Protonated THF completes the cycle by delivering $[H]^+$ to **2**. Intermediates such as **A** – **C** have been proposed by Labinger and Bercaw in the mechanism of intramolecular C-H activation in the presence of base by Pt(II) dications bearing α-diimine ligands.[5]

Support for this mechanism comes from:

- THF (acting both as a Brønsted base and a Lewis base in the mechanism) is needed for the reaction to proceed – complex **1** does not cyclometallate in CD_2Cl_2 alone.

- Addition of hindered base stops the reaction (i.e. protonolysis is halted) and does not coordinate to **2** (no change in $^{31}P\{^{1}H\}$ NMR spectrum).

- No intermediates are observed – **2** converts smoothly to **3** over 10 days, suggesting that the irreversible **2** to **B** protonolysis is the rate determining step.

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