Activation of a non-strained C–C bond with platinum(II)

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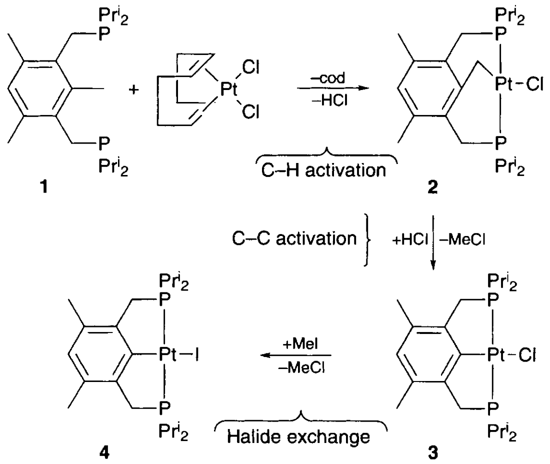
The aromatic phosphine 1 reacts with (cod)PtCl$_2$ to yield the C–H activation product 2; treatment of 2 with HCl results in overall selective functionalization of the strong Ar–Me bond to generate MeCl and the Ar–Pt complex 3.

The development of soluble transition-metal complexes capable of the selective activation and functionalization of carbon–carbon bonds under mild conditions is a highly desirable goal and a subject of considerable interest.[1] Recently, we reported the cleavage of an unstrained and unactivated carbon–carbon bond by a rhodium(I) complex under mild conditions,[2a] which led to selective methylene transfer into non-polar Si–H, Si–Si and C–H bonds.[2b] Direct C–C oxidative addition to rhodium(I) was also observed.[2c] We report here on the competitive activation of C–H and C–C bonds with platinum(II) leading to selective functionalization of the carbon–carbon bond using a polar substrate (HCl) with no overall change in the metal oxidation state.

Reaction of the bisphosphine 1,3-bis(diisopropylphosphinomethylene)mesitylene (**1**; dippmH)[2b] with a stoichiometric amount of (cod)PtCl$_2$ (cod = cycloocta-1,5-diene) in thf at room temperature leads to the formation of (dippm)PtCl **2**,‡ possessing a methylene group bridging between the aromatic ring and the metal centre (Scheme 1). Remarkably, heating of the thermally stable **2** in a benzene–dioxane solution at 82 °C with a tenfold excess of HCl for 45 min results in the formation of methyl chloride and the Ar–Pt complex **3**.[3] Methyl chloride was detected by NMR and by GC. Complexes **2** and **3** have been characterized spectroscopically by various NMR techniques and by FDMS.§ $^{31}P\{^1H\}$ NMR follow-up of the reaction of complex **2** with HCl shows the formation of a new species (presumably **D**) giving rise to a singlet at δ 35.23 flanked by platinum satellites ($^1J_{PtP}$ = 1919.3 Hz) which is in equilibrium with **2** (Fig. 1).¶ The relatively small platinum–phosphorus coupling constant might suggest a Pt^{IV} oxidation state,[4] although further identification is hampered by the low concentration and instability of the intermediate. The overall process (**2** → **3**) is first order in **2** with k_{obs} = 1.43 × 10^{-3} s^{-1} at 82 °C (Fig. 1).

Mechanistically, coordination of **1** to the Pt^{II} centre, leading to the formation of *cis*-(dippmH)PtCl$_2$ **A**, is likely to precede the selective C–H activation step (Scheme 2).|| Activation of C–H bonds by Pt^{II} phosphine complexes is postulated to involve three-coordinate 14-electron species.[5,6] The reaction may proceed by dissociation of a chloride to generate a 14-electron T-shaped intermediate **B**[7] which is in equilibrium with the sterically more favourable **C**.[8] Subsequently C–H activation gives the alkylhydride Pt^{IV} complex **D** and reductive elimination affords **2** and HCl, which is a reversible process.¶[9] Hence, treating **2** with an excess of HCl shifts the equilibrium of the kinetically favourable C–H activation process towards **C**, which is likely to be a common intermediate for the C–H and C–C activation processes. **C** can undergo electrophilic attack by the metal on the *ipso* carbon of the aromatic ring resulting in an arenonium complex **E**, which might undergo a reversible 1,2-methyl shift affording the Pt^{IV} complex **F**,[10] regenerating the aromatic π system. Alternatively, complex **F** can be formed directly from **C** by a concerted oxidative addition process. Oxidative addition of strained carbon–carbon bonds to Pt^{II} is known,[11] although here a non-strained, strong C–C bond is involved. Reductive elimination from **F** can give **3** and MeCl.[12] Treating the thermally stable **3** in benzene with an excess of MeI results in halide exchange to afford **4**, suggesting the existence of an equilibrium between **F** and **3**.[12,13] The observation of **D** shows that the rate-determining step is not protonation of the metal complex, but probably involves a later step such as the formation of a 14-electron complex **C** or the C–C activation itself.

The postulated mechanism involving an arenonium intermediate is well precented by the work of van Koten and co-workers.[12–14] in which it was shown that a NCN-type Pt^{II} complex, similar to **3**, reacts reversibly with MeI to yield an arenonium complex analogous to **E**. This process was proven to proceed *via* a Pt^{IV} intermediate, similar to **F**.[12] A theoretical study[10] predicted that a 1,2-methyl shift between the *ipso* carbon of the aromatic group and the metal centre is an allowed process. The reported C–C cleavage of the arenonium



Scheme 1 C–H and C–C activation

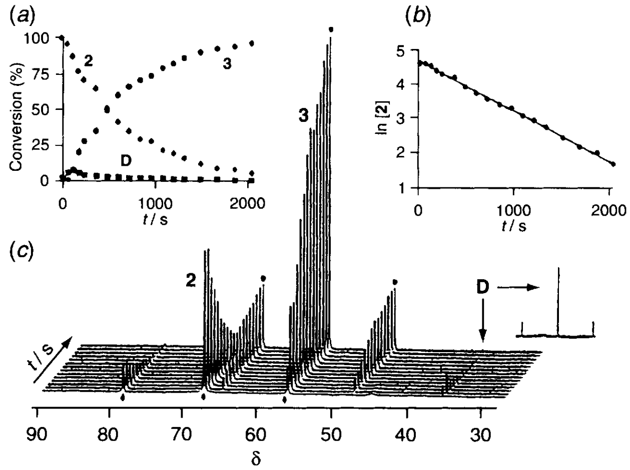


Fig. 1 $^{31}P\{^1H\}$ NMR progress of the reaction of complex **2** with HCl

cation[12–14] is undoubtedly driven by the generation of the aromatic system.

Complex **3** was recovered unchanged when treated with an excess of MeCl, indicating that the C–C activation generating MeCl is thermodynamically more favourable than the competing C–H activation process which generates HCl, while the latter is kinetically prefered. Although the Me–Cl bond (E_{BD} = 84 kcal mol^{-1}; 1 cal = 4.184 J) is weaker than H–Cl (103 kcal mol^{-1})[15] and Ar–Me is stronger than $ArCH_2$–H (*e.g* Ph–Me 102 kcal mol^{-1}, $PhCH_2$–H 88 kcal mol^{-1}), [16] the C–C activation thermodynamics are more than compensated by the formed H–CH_2Cl bonds (E_{BD} = 100.9 kcal mol^{-1}). Moreover, the Ar–M bond is expected to be much stronger than the $ArCH_2$–M bond.[17]

This study shows that it is possible to achieve selective activation of an unstrained C–C bond. The overall process involves functionalization of a strong Ar–Me bond with $PtCl_2$ to generate Ar–PtCl and Me–Cl. Formally, the transformation from **2** to **3** can be viewed as a new entry into the 'methylene transfer' chemistry,[2b] in which a methylene group is transferred to HCl. The system that we reported previously involves rhodium(I) and non-polar substrates. Our results indicate that platinum(II) complexes may be designed to thermodynamically prefer C–C over C–H activation with overall retention of the metal oxidation state and functionalization of the carbon–carbon single bond by polar substrates.

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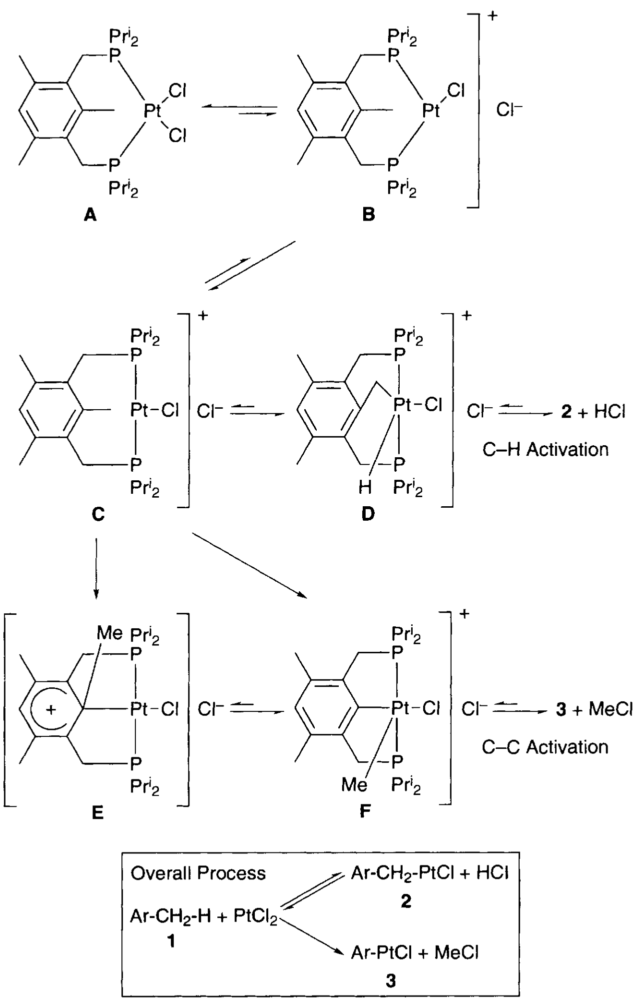

Scheme 2 Postulated mechanism

Footnotes

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‡ An analogous complex, (dippm)PtI, having similar spectroscopic properties has been characterized by X-ray analysis; FDMS: M^+ 701.

§ *Spectral data* for **2**:‡ ^{1}H NMR (C_6D_6, 400.1 MHz): δ 6.51 (s, 1 H, *p*-H of C_6HPt), 2.91 [dt, ^2J(H,H) 14.9, ^2J(H,P) 3.4, ^3J(H,Pt) 54.6 Hz, 2 H, CH_2P, left part of AB quarter], 2.53 [d, ^2J(H,H) 14.9 Hz, 2 H, CH_2P, right part of AB quarter], 2.32 [t, ^3J(H,P) 9.9, ^2J(H,Pt) 92.0 Hz, 2 H, $ArCH_2Pt$], 2.27 (m, 2 H, C*H*Me_2), 2.18 (s, 6 H, Me_2C_6HPt), 1.89 (m, 2 H; C*H*Me_2), 1.20 [dd, ^3J(H,H) 7.8, ^3J(H,P) 15.2 Hz, 12 H, $CHMe_2$], 1.05 [dd, ^3J(H,H) 7.2, ^3J(H,P) 15.0 Hz, 6 H, $CHMe_2$], 0.84 [dd, ^3J(H,H) 7.2, ^3J(H,P) 13.3 Hz, 6 H, $CHMe_2$]. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): δ 69.05 [s, ^1J(P,Pt) 3599 Hz]. Elemental analysis for $C_{23}H_{41}Cl_1P_2Pt·0.5thf$: calc: C, 46.47; H, 7.02. Found: C, 46.52; H, 6.81%. FDMS: M^+ 610.

Spectral data for **3**: ^{1}H NMR (400.1, C_6D_6): δ 6.75 (s, 1 H, *p*-H of C_6HPt), 2.72 [vt, *J*(H,P) 4.2, *J*(H,Pt) 18.5 Hz, 4 H, CH_2P], 2.26 (m, 4 H, C*H*Me_2), 2.19 (s, 6 H, Me_2C_6HPt), 1.39 [dd, *J*(H,H) 7.2, *J*(H,P) 16.4 Hz, 12 H, $CHMe_2$], 0.91 [dd, *J*(H,H) 7.1, *J*(H,P) 14.7 Hz, 12 H, $CHMe_2$]. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): δ 56.37 [s, ^1J(P,Pt) 2857 Hz]. FDMS: M^+ 596.

¶ Addition of bases such as $H_2N(CH_2)_3OH$ results in disappearance of **D** and an increase of **2**.

‖ A study of the coordination chemistry of diphosphines to Pd^{II} and Pt^{II} will be published elsewhere.

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