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Oxidative addition of ether *O*-methyl bonds at a Pt(0) centre†‡

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Naseralla A. Jasim, Robin N. Perutz,* Barbara Procacci and Adrian C. Whitwood

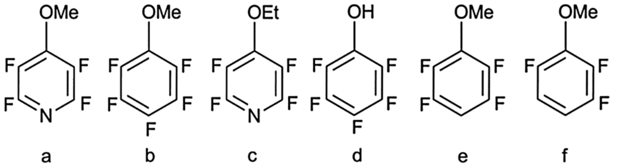
$Pt(PCyp_3)_2$ (Cyp = cyclopentyl) undergoes C–O oxidative addition with 2,3,5,6-tetrafluoro-4-methoxypyridine, pentafluoroanisole, 2,3,5,6-tetrafluoroanisole and 2,3,6-trifluoroanisole yielding platinum methyl derivatives. The reactions occur in preference to C–H or C–F activation.

We have shown that $Pd^0(PR_3)_2$ and $Pt^0(PR_3)_2$ complexes can undergo C–F oxidative addition, and the resulting square-planar Pt(II) complexes are stable to C–F reductive elimination.[1–3] However, C–F reductive elimination is possible from 3-coordinate Pd(II)[4] and from the metal aryl fluoride complexes in oxidation state IV.[5–8] The related oxidative addition of ether C–O bonds appears to be missing from the literature although examples of C–O reductive elimination of ethers from Pd(II) are known.[9,10] In contrast, C–O (ester) oxidative addition at Pt(0) has recently been described[11] and reductive elimination of ester C–O bonds from Pd(IV) and Pt(IV) is well known.[12–14] We demonstrate the importance of electron withdrawing aryl groups for achieving oxidative addition of methyl aryl ethers at Pt(0) and probe the mechanism of C–O activation.

Activation of C–O bonds of ethers at transition metals, first described many years ago,[15–17] has been rejuvenated by the work of Carmona, Paneque[18,19] and Goldman[20,21] who investigated the reactivity of iridium tris(pyrazolyl)borate and iridium pincer complexes, respectively. In both cases, the C–O activation was associated with initial methyl C–H bond activation (see Scheme S1 in ESI‡). Carmona and Paneque used methylated anisoles and demonstrated rearrangement to Ir–O metallacycles containing Ir═carbene linkages. Goldman used fluorinated anisoles and isolated the products of "simple" *O*-methyl oxidative addition. Following the initial C–H cleavage, aryloxy migration and 1,2-hydride migration generated the product. Cross-coupling reactions involving unsupported aryl methyl ether C–O bonds have been described at nickel.[22,23] In contrast to the iridium reactions, the cross-coupling results in cleavage of the aryl C–O bond although this bond is stronger than the O–CH_3 bond.

Here we report the reactions of $Pt^0(PCyp_3)_2$ **1** (Cyp = cyclopentyl) with 2,3,5,6-tetrafluoro-4-methoxypyridine, pentafluoroanisole, 2,3,5,6-tetrafluoroanisole and 2,3,6-trifluoroanisole and show that $Ar^FO–CH_3$ oxidative addition occurs in preference to C–H or C–F oxidative addition. We also compare reactions with pentafluorophenol and 2,3,5,6-tetrafluoro-4-ethoxypyridine (Scheme 1). These reactions offer competition between C–F, C–H, C–O and O–H activation.

The thermal reaction of **1** in the presence of tetrafluoromethoxypyridine **a** (1 equiv., hexane, 60 °C, 2 days) generated one product quantitatively (Scheme 2). The colourless crystalline material was characterised by multinuclear NMR spectroscopy, LIFDI mass spectrometry[24] and X-ray crystallography. The ^1H NMR spectrum shows a triplet resonance at δ 0.89 with ^{195}Pt satellites (J_{PH} = 6.3, J_{PtH} = 83.8 Hz) with integration 3H relative to cyclopentyl protons and no signals to higher field. The ^{195}Pt-^1H HMQC spectrum shows that this resonance correlates with a platinum triplet at δ −4060. The ^1H peaks of the tricyclopentylphosphine also show cross-peaks to the platinum resonance. The $^{31}P\{^1H\}$ NMR spectrum gives a singlet at δ 22.3 with Pt



Scheme 1 Substrates.

Department of Chemistry, University of York, York, UK YO10 5DD. E-mail: robin.perutz@york.ac.uk

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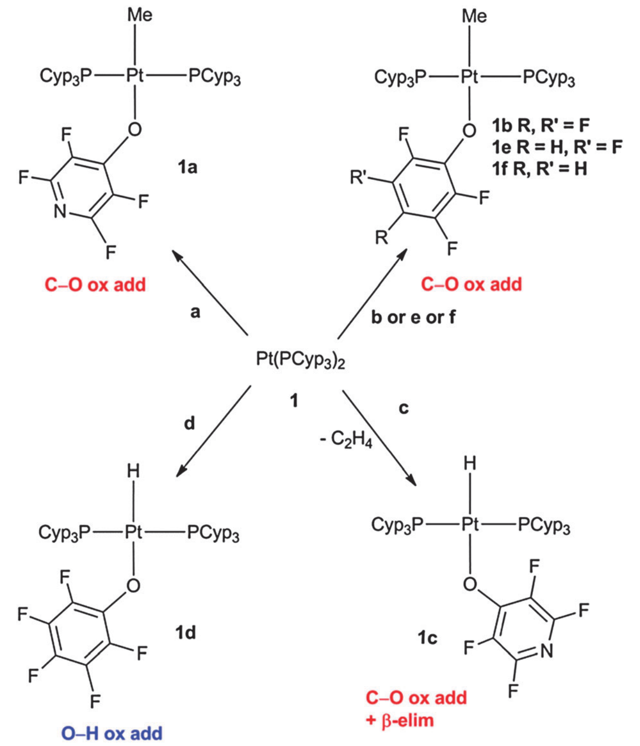
‡ Electronic supplementary information (ESI) available: Scheme of reactions of ethers at iridium, general procedures, syntheses, HSQC of **1a** and **1c**, the kinetic isotope effect including spectra, *in situ* monitoring of formation of **1b**, the kinetic plot and spectra of intermediates, NMR data, crystallographic methods and data for **1a**, **1b**, **1e** and **1f**. CCDC 966767, 966768, 983216 and 983215. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00853g



Scheme 2 Reactivity of **1**.

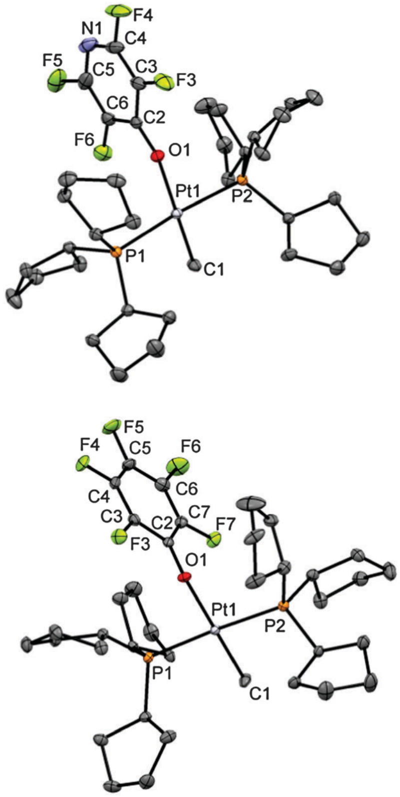


Fig. 1 Molecular structure of **1a** (above) and **1b** (below). H atoms omitted. Anisotropic displacement parameters shown as 50% ellipsoids.

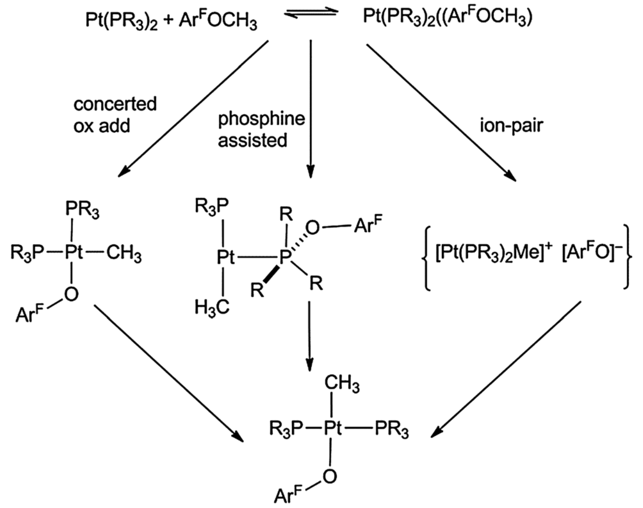
satellites (J_{PtP} 2962 Hz). The ^{19}F NMR spectrum shows two sets of inequivalent fluorines at δ −168.3 (m, F *meta* to N) and at δ −99.0 (m, F *ortho* to N) in a 1 : 1 integration ratio. ^{13}C{^{1}H} NMR spectroscopy reveals a triplet at δ −34.3 with ^{195}Pt satellites (J_{PC} = 7 Hz, J_{PtC} = 695 Hz) which correlates with the ^{1}H NMR resonance at δ 0.89. This pair of correlated resonances is consistent with a methyl group bound to platinum (a methoxy group would be expected at lower field with small couplings to Pt). Compound **1a** was therefore assigned as *trans*-$\mathrm{Pt(PCyp_3)_2(CH_3)(OC_5F_4N)}$. Colourless crystals were grown by slow diffusion of hexane into a concentrated benzene solution. The crystal structure was determined and the nature of **1a** (Fig. 1) was confirmed demonstrating conclusively that the $\mathrm{Ar^FO{-}CH_3}$ bond of the ether undergoes selective oxidative addition at the Pt(0) centre (Scheme 2).

The reaction of **1** with pentafluoroanisole **b** proceeded analogously to that with tetrafluoromethoxypyridine generating **1b** as the only product (Scheme 2). The product **1b** exhibits similar spectroscopic features to those for **1a** and was therefore assigned as *trans*-$\mathrm{Pt(PCyp_3)_2(CH_3)(OC_6F_5)}$. A crystal structure of **1b** (crystals grown from hexane) confirmed its identity (Fig. 1). The Pt–O and Pt–C bond lengths for **1a** are 2.1586(15) and 2.044(2) Å, respectively. The Pt–O–C angle is 130.10(15)° and the torsional angle of the ring C(3)–C(2)–O(1)–Pt is 21.2(3)°. The corresponding Pt–O and Pt–C bond lengths for **1b** are 2.1306(15) and 2.047(2) Å, while the Pt–O–C angle is 126.78(14)° and the torsional angle is 27.3(3)°.

Goldman showed that the kinetic isotope effect (KIE) for oxidative addition of pentafluoroanisole $(k_{\mathrm{OCH_3}})/(k_{\mathrm{OCD_3}})$ to the iridium pincer complexes is 4.3 ± 0.3 providing strong support for initial C–H bond activation.[20,21] We synthesised **a**-d_3 and investigated the reaction of **1** with a mixture of **a** and **a**-d_3 in hexane. The reaction was performed with a 10-fold excess of each substrate with the consequence that no heating was required to generate a mixture of **1a** and **1a**-d_3. The ^{31}P NMR spectrum and the ^{195}Pt NMR spectrum showed clear isotopic shifts to low field of 0.17 ppm (35.3 Hz) and 14.2 ppm (1527 Hz), respectively. Determination of the initial substrate ratio by mass spectrometry and the product ratio by quantitative ^{31}P{^{1}H} NMR spectroscopy yielded a kinetic isotope effect $k_{\mathrm{H}}/k_{\mathrm{D}}$ of 1.11 ± 10%.

The progress of the reaction of **1** with two equiv. **b** at 50 °C was monitored *in situ* by ^{31}P NMR spectroscopy in protio solvents. The half-life of **1** proved to be *ca.* 3 times shorter in THF than in hexane ($t_{1/2}$ 200 and 620 min, respectively). An intermediate was detected in the early stages of reaction in both solvents which declined with time. It exhibited a ^{31}P resonance with J_{PtP} = 3956 Hz characteristic of Pt(0) (δ 26.9, s, in THF) and five distinct ^{19}F resonances, consistent with a provisional assignment as $\mathrm{Pt(PCyp_3)_2(\eta^2\text{-}C{=}C\text{-}C_6F_5OMe)}$ (see ESI‡).

Complex **1**, dissolved in hexane, also reacted with tetrafluoroethoxypyridine **c** (1.1 equiv., 60 °C), but the ^{1}H NMR spectrum showed this time that the principal product is a platinum hydride (δ −24.6, t J_{PH} 13.1 Hz, J_{HPt} 1234 Hz). The ^{31}P{^{1}H} NMR spectrum shows a singlet resonance at δ 46.2 (J_{PtP} = 2940 Hz). The complex exhibits a ^{195}Pt resonance as a triplet of doublets at δ −4704 with the corresponding coupling constants. The ^{195}Pt-^{1}H HSQC spectrum links the hydride and the cyclopentyl resonances at δ 1.85 to the ^{195}Pt resonance



Scheme 3 Proposed mechanisms of C–O oxidative addition.

at δ −4704. The ^{19}F NMR spectrum shows two multiplets at δ −99.3 (m, F *ortho* to N) and −169.8 (m, F *meta* to N). Evidence for free C_2H_4 was obtained when the reaction was performed in C_6D_6 and monitored *in situ* by its ^1H NMR resonance at δ 5.2. Complex **1c** was assigned as *trans*-$Pt(PCyp_3)_2(H)(OC_5NF_4)$, in keeping with the similar results obtained by Goldman.[20,21] The X-ray structure of a crystal of **1c** was consistent with the formulation but suffered from disorder both in the cyclopentyl rings and the OC_6F_5 group.

The formation of platinum aryloxy hydrides can also be achieved by reaction with the corresponding phenol, as shown by reaction of **1** with pentafluorophenol **d** (300 K, 1.1 equiv. in hexane) yielding **1d** as the only product which was identified as the O–H oxidative addition product $Pt(PCyp_3)_2(H)(OC_6F_5)$. The hydride resonated at δ −24.3 (t, J_{PH} 13.4, J_{PtH} 1178 Hz) while the ^{195}Pt resonance appeared at δ −4696 (td, J_{PtP} 2964, J_{PtH} 1176 Hz).

We also investigated the importance of the number of fluorine substituents in the reactivity of **1** with methylarylethers and potential competition with C–H activation. The reaction of **1** with 2,3,5,6-tetrafluoroanisole **e** proceeds more slowly than that with **b** but yields an analogous product, *trans*-$Pt(PCyp_3)_2(CH_3)(OC_6HF_4)$ **1e**. The reaction between **1** and 2,3,6-trifluoroanisole, **f**, required excess **1f** to proceed and yielded *trans*-$Pt(PCyp_3)_2(CH_3)(OC_6H_2F_3)$, **1f**. The rates of reaction decreased in the order **b** > **e** > **f**, as the number of fluorine substituents was reduced. There was no reaction between **1** and anisole even with excess substrate. The crystal structures of **1e** and **1f** (Fig. S3, ESI‡) are similar to those of **1a** and **1b**. However, **1e** exhibits a contact between Pt and F(7) (2.972(1) Å), shorter than the sum of the van der Waals radii (3.22 Å), and a torsion angle C(3)–C(2)–O(1)–Pt of −1.00(14)°.

Our results provide some guidance on the mechanism of reaction, even though a definitive conclusion is not yet possible. The C–H activation route appears to be very unlikely for $Pt(PCyp_3)_2$ because of the low KIE, the difficulty of forming a carbene at Pt, and the accessibility of cyclometalated products by C–H activation as observed for $CpRh(PMe_3)$.[25,26] Three alternative routes are consistent with a low KIE: direct oxidative addition, phosphine-assisted reaction[2,3] and an ion-pair route[9] (Scheme 3). In each case, initial coordination of the substrate would occur, consistent with detection of the Pt(0) intermediate in the reaction with **b**. Direct oxidative addition reaction represents the reverse of the reductive elimination reactions observed by Buchwald.[10,27] The selectivity for breaking the O–CH_3 bond can be understood in the phosphine-assisted route because of the preference to put the electronegative O–Ar^F group on the metallophosphorane.[2,28,29] The ion-pair route generates $[Pt(PCyp_3)_2Me]^+$ with the ethers and $[Pt(PCyp_3)_2H]^+$ with pentafluorophenol[30,31] in parallel to recent C–O reductive elimination mechanisms.[9] The increased rate in the more polar solvent, THF, lends support to the ion-pair route.

These results demonstrate selective C–O oxidative addition at fluorinated aromatic methyl ethers. The selectivity for the O–CH_3 bond in **b**, **e** and **f** in preference to the O–Ar bond matches Goldman's observations (also with fluorinated arenes). With unfluorinated Ar–O–CH_3 substrates, Paneque again observed O–CH_3 cleavage[19] but Milstein observed Ar–O cleavage at Rh(PCP).[17] The reaction of **a** at $Pt(PCyp_3)_2$ contrasts with the C–F oxidative addition observed with the same substrate at $Ni(PEt_3)_2$ and with the cyclometallation product formed by C–H and C–F activation at $CpRh(PMe_3)$.[24–26]

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