Dalton Transactions

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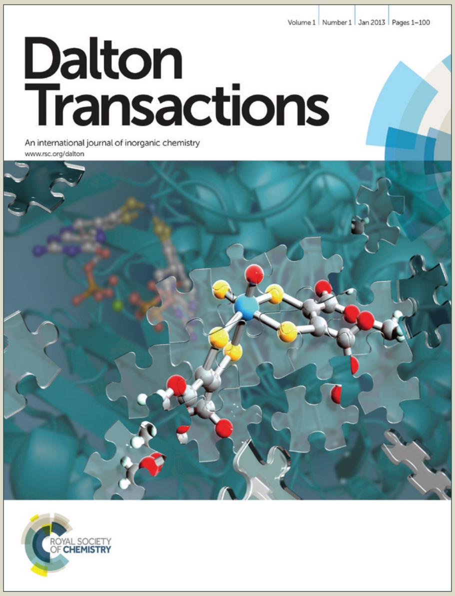

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Silver ion enhanced C-H activation in Pt(II) hydroxo complexes†

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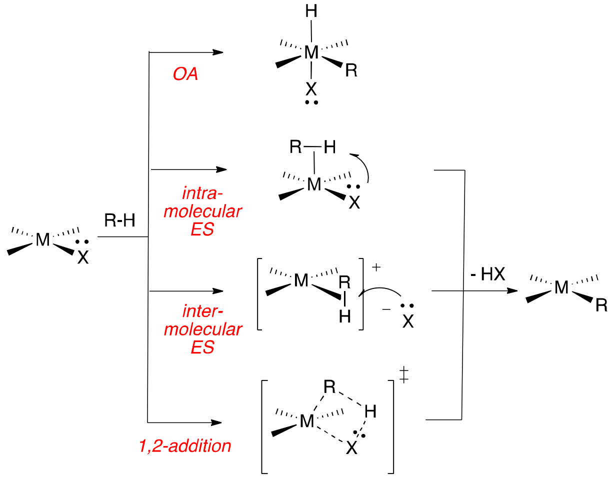
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Reacting neutral Pt(II) hydroxo compounds (NN)Pt(R)(OH) (R = OH, Ph, and Me, NN = bulky terphenyl diimine) with silver bis(trifluromethanesulfonyl)imide produces new hydroxo complexes with the silver binding through the Pt-OH bonds as determined by ^{195}Pt NMR and X-ray analysis (R = OH). These complexes were found to activate the aromatic C-D bonds of C_6D_6 at significantly enhanced rates relative to the silver free hydroxo complexes. Mechanistic studies for R = Ph are consistent with a homogeneous pathway that is bimolecular ($\Delta H^{\ddagger} = 17(2)$ kcalmol^{-1} and $\Delta S^{\ddagger} = -25(6)$ e.u. and $\Delta G^{\ddagger}_{295} = 10(2)$ kcal mol^{-1}), first order in [Pt] and substrate.

Introduction

The activation of C-H bonds mediated by late transition metal centres has long been an important area of research in organometallic chemistry.[1, 2] It is now appreciated that, in addition to the textbook mechanism of direct oxidative addition (OA), variants of electrophilic substitution (ES) mechanisms are also viable pathways for cleavage of C-H bonds (Scheme 1).[3] One such flavour of ES is the direct 1,2-addition of a C-H bond across an M-X bond[4, 5] (X = anionic N or O-based ligand) where the X ligand lone pair is intimately involved[6] in R-H cleavage and X-H bond formation. For X = OH or OR, additions of examples of 1,2-addition reactions for H_2[7-9] and unfunctionalized C-H[5, 10-14] bonds have been reported, but instances of group 10 metal hydroxos or alkoxos engaging in this reactivity are relatively scarce.[15, 16]



Scheme 1. Mechanisms of C-H activation.

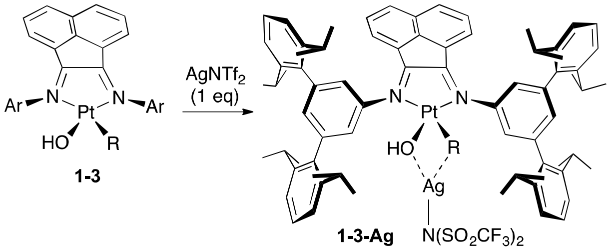
A previous report from our group detailed the double benzene C-H addition across a terminal *bis*-hydroxo moiety in a Pt(II) diimine complex.[17] Higher temperatures (> 80°C) and prolonged reaction times were required to facilitate the double C-H bond addition, and a detailed study revealed the production of catalytically active nanoparticles[9] resulting from decomposition of the *bis*-hydroxo (**1**) accelerated the formation of the C-H activation products by catalysing the reaction,[17] providing an alternate path to the higher barrier homogeneous route.

We hypothesized that increasing the electrophilicity of the metal centre might prevent deposition of Pt(0) and steer the C-H activation through the homogeneous path.[18] One means of doing this is to treat the Pt(II) compounds with Ag(I) salts; it has been known for some time that d^8 square planar diimine Pt(II) species readily form complexes with Ag(I) salts either via metallophilic bonds[19-22] or interactions with the two hydrocarbyl ligands.[22] Furthermore, one electron oxidations can generate transient Pt(III) derivatives that disproportionate into Pt(IV)/Pt(II) and provide a path for double C-H activation reactions in (NN)PtMe$_2$ derivatives[22, 23] via more electrophilic Pt(IV) species. We thus explored the reactivity of the monomeric *bis*-hydroxo complex **1** and the hydroxo methyl and phenyl derivatives **2** and **3**, respectively, with silver bis(trifluromethane-sulfonyl)imide (AgNTf$_2$) to determine what effect this might have on the C-H activation chemistry of these compounds. In this contribution, we discuss the nature of these Pt(II)-Ag(I) complexes and demonstrate enhanced rates of C-H activation via homogeneous pathways.

Results and Discussion

Synthesis and Characterization

The monomeric hydroxo complexes **1**, **2**, and **3** have been previously reported[24, 25] and feature the very bulky terphenyl substituted diimine ligand shown in Scheme 2. While preventing dimerization in these Pt hydroxo derivatives, the ligand provides ample open space about the metal centre for reactivity and so we anticipated facile Pt-Ag bond formation.[22] Indeed, upon reaction of each hydroxo species with 1 equivalent of $AgNTf_2$ in either tetrahydrofuran (THF) or bromobenzene (C_6D_5Br) at room temperature a rapid reaction was observed, based on visible colour changes. The products were isolated as microcrystalline powders in good yield based on expected mass balance. Spectroscopically, new species were indicated by shifts in the resonances for the ligand in the ^{1}H NMR spectra, and the NTf_2 anion was present as evidenced by appropriate resonances in the ^{19}F NMR traces. However, analysis of the ^{195}Pt NMR spectral data[26, 27] suggested the silver ion was not interacting with the Pt centre as expected. Typically, the ^{195}Pt NMR chemical shift moves ≈ 200 ppm downfield upon formation of a Pt→Ag bond;[21, 28] instead, we recorded substantial *upfield* shifts of 700-900 ppm in the products **1-Ag**, **2-Ag**, and **3-Ag** relative to the shifts observed in the starting compounds **1-3** (Scheme 2). We also note a substantial upfield shift for the hydroxo protons in **2-Ag** (0.39 ppm) and **3-Ag** (0.50 ppm), relative to those found in the uncomplexed starting materials **2** (1.89 ppm) and 3 (1.45 ppm). In the methyl complex **3-Ag**, the resonance for the methyl protons at 1.49 ppm is unchanged from that observed for **3** (1.45 ppm), and we are unable to assign any Pt-H coupling constant with any confidence for the silver adduct. These data indicate that the silver ion is complexed to the platinum starting materials via a different bonding mode than ligation directly to the metal, so we endeavoured to determine the structure of one of them to probe this issue further. Accordingly, the structure of **1-Ag** was determined via an X-ray crystallographic determination.



	^{195}Pt NMR **1-3**	Δ(PPM)	^{195}Pt NMR **1-3-Ag**
1: R = OH	- 547	730	-1276
2: R = C_6H_5	- 1485	757	-2242
3: R = CH_3	- 1272	893	-2167

Scheme 2. Reactions of hydroxos with $AgN(SO_2CF_3)_2$.

The molecular structure of **1-Ag** is shown in Figure 1 along with selected metrical data. As can be seen, the silver cation is ligated by the two hydroxo oxygen atoms and a molecule of benzene, with a weak contact with the nitrogen atom of the NTf_2 counteranion—and not the Pt centre.[29] The silver cation is not quite equidistant from each hydroxo moiety (Ag1-O1 = 2.436(5) and Ag1-O2 = 2.276(5) Å) and is located 15.1(3)° above the O1-Pt1-O2 plane. The Ag1-N3 distance is 2.443(8) Å, while the closest contact with the proximal benzene moiety is with C75 at 2.446(12) Å; the other carbons are between 2.8 and 3.8 Å away from Ag(1). This result corroborates the ^{195}Pt NMR data and is in line with findings by Sharp and co-workers who reported that gold and silver cations bond preferentially to oxygen moieties rather than platinum in dimeric compounds with bridging oxo ligands.[30, 31] Based on the ^{195}Pt NMR data, we presume the structures of **2-Ag** and **3-Ag** exhibit similar complexation of Ag(I) to the hydroxo ligand; for **2-Ag**, there may also be a π interaction between the Ag moiety and the platinum phenyl group as observed by Moret and Chen in a related *bis*-phenyl Pt(II) diimine complex.[22] We base this on the fact that the upfield shift in the ^{195}Pt resonance in **2-Ag** is similar in magnitude to that of **1-Ag**. The much larger perturbation in the chemical shift of the methyl hydroxo complex **3-Ag** in comparison may indicate a stronger association with the single –OH ligand in the absence of a second group capable of donating to the Ag(I) Lewis acid. However, in the absence of structural data and conclusive NMR evidence, it must be admitted that any interaction between the silver ion and the Ph or CH_3 groups in **2-Ag** or **3-Ag** are rather ill defined in these complexes.

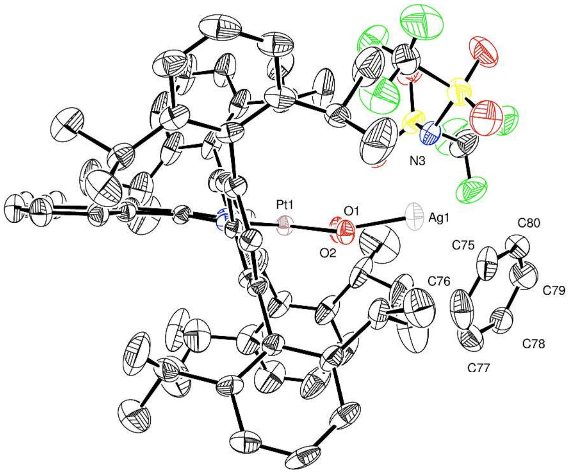


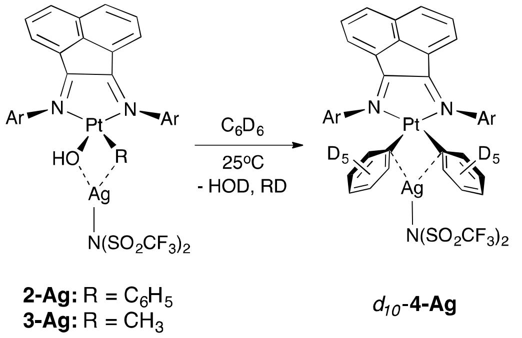
Figure 1. X-ray molecular structure of **1-Ag** (hydrogen atoms and three molecules of benzene are not shown for clarity). Thermal Ellipsoids are at 30% probability. Selected metrical bond lengths (Å) angles and torsions (°): Pt1-O1, 1.989(5); Pt1-O2, 1.981(5); O1-Ag1, 2.436(5); O2-Ag1, 2.276(5); Ag1-N3, 2.443(8), Ag-C75: 2.446(12); O1-Pt1-O2, 83.2(2); O1-Ag1-O2, 67.91(18).

C-H Activation Chemistry

While acquiring the full complement of NMR data on compounds **1-3-Ag**, it was observed that adducts **2-Ag** and **3-Ag** slowly reacted with solvent C_6D_5Br at room temperature to eliminate water and benzene or methane, respectively. Concomitant formation of a mixture of new Pt diimine complexes (the same in both cases) was observed. *Bis*-hydroxo compound **1-Ag** underwent similar reactivity, but required slightly elevated temperatures (> 323K) to react. We surmised that these were C-H activation reactions involving the solvent; the observation was significant in that the reactions were occurring in a much milder temperature regime than was observed for the silver free systems **1-3**, which required heating to > 363K in order to induce C-H activation with benzene.[17] It thus appears that the presence of the silver ion serves to enhance the rate of C-H activation in these systems, and so we sought to study the somewhat simpler reaction of these compounds with benzene.

Both **2-Ag** and **3-Ag** react slowly with C_6D_6 at room temperature over the course of 2-3 days to give the Ag supported *bis*-phenyl complex *d_{10}*-**4-Ag** (Scheme 3). The identity of *d_{10}*-**4-Ag** was confirmed through its synthesis of its perproteo isotopomer via reaction of the previously reported neutral *bis*-phenyl complex **4** and 1 equivalent of $AgNTf_2$. The ^{195}Pt NMR spectrum of **4-Ag** exhibits an upfield chemical shift of 300 ppm with respect to **4**, suggesting that the Ag cation is interacting with both phenyl rings in this complex[22, 23] as depicted, rather than the Pt centre directly, but this has not been confirmed structurally due to difficulties in growing suitable crystals for X-ray analysis.

Speciation plots for the conversion of methyl hydroxo compound **3-Ag** to *d_{10}*-**4-Ag** over time were complex and provided evidence for the presence of both **2-Ag** and the putative silver adduct of the phenyl-methyl species expected upon 1,2 C-D addition to the hydroxo group in **3-Ag** (Figure S1). These intermediates appeared at competitive rates, suggesting that the C-H activation processes leading to elimination of HOD and DCH_3 have similar barriers under these conditions. Eventual conversion to *d_{10}*-**4-Ag** was clean and complete, but kinetic analysis of this complex process was difficult due to the multiple intermediates. We thus focused on the simpler system involving conversion of the phenyl hydroxo complex **2-Ag** to **4-Ag**; since elimination of DC_6H_5 leads only to the *d_5* isotopomer of **2-Ag**, the NMR analysis is less complicated and kinetic analysis can be carried out relatively easily.



Scheme 3. 1,2-addition of *d_6*-benzene.

The kinetic progress of the conversion of **2-Ag** to *d_{10}*-**4-Ag** was monitored by ^{1}H NMR spectroscopy in water saturated C_6D_6 using integration relative to an internal standard of hexamethylbenzene to determine the concentration of each species at a given time. Because the reaction rate is inhibited by free water[7, 8, 17] (see Figure S2), the excess free water is necessary to engender pseudo-first order kinetics in [**2-Ag**] (Figure 2, top); in the presence of excess water, the reaction to form *d_{10}*-**4-Ag** proceeds with an observed rate constant of 4.91(4) x 10^{-6} s^{-1} at 295K. Monitoring the rate at three different initial concentrations of [**2-Ag**] confirmed the first order dependence on **2-Ag** (Figure 2, middle). Finally, evaluation of the rate constant at different temperatures gave values of 1.97(4) x 10^{-5} s^{-1} (308K), 4.9(2) x 10^{-5} s^{-1} (318K) and 1.13(7) x 10^{-4} s^{-1} (329K) and allowed for the determination of activation parameters using an Erying plot (Figure 2, bottom). The reaction from **2-Ag** to **4-Ag** gives activation parameters of $\Delta H^\ddagger$ = 17(2) kcal mol^{-1} and $\Delta S^\ddagger$ = 25(6) e.u. Therefore, at 295K, $\Delta G^\ddagger$ is 10(2) kcal mol^{-1}, this value is similar to the $\Delta G^\ddagger$ value calculated by Gunnoe and co-workers (ΔG_{298} = 9.1 kcal mol^{-1}) for the benzene C-H bond addition across a Ru-OH bond.[11]

The silver-free phenyl hydroxo compound **2** does not undergo reaction with C_6D_6 at room temperature, either to produce *d_{10}*-**4** or *d_5*-**2** (Figure S3) and so it is clear that the presence of the silver ion enhances the rate of C-H bond activation involving both the Pt-OH and the Pt-C_6H_5 groups. It also appears that these lower temperature processes are homogeneous, in contrast to the heterogeneous, Pt(0) catalysed reactions that dominate in the silver free systems at higher temperature.[17] Unfortunately, use of the mercury test[32, 33] for

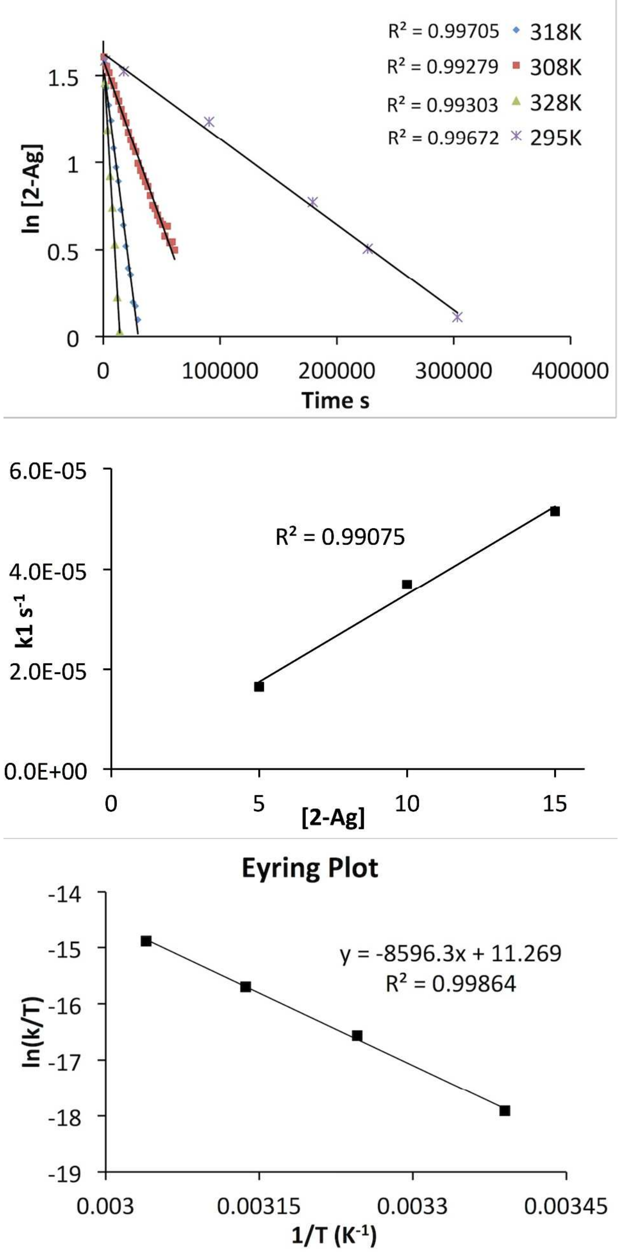
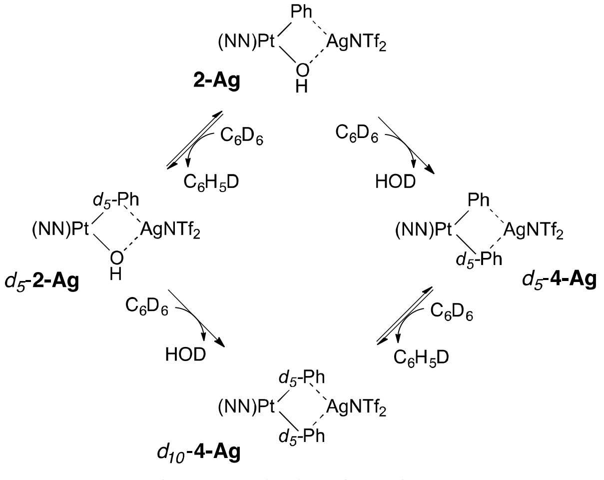


Figure 2. Rates between the reaction of **2-Ag** to **4-Ag**. Top: 1st order plots for the conversion of **2-Ag** to **4-Ag** at different temperatures in wet C_6D_6 (≈30 mM/L H_2O). Starting [**2-Ag**]: 5.05 mM/L; Middle: Plot of varying [**2-Ag**]$_0$ vs k_{obs} at 308 K; Bottom: Erying plot using k_{obs} at different temperatures.

heterogeneously catalysed pathways was precluded by the fact that the silver adducts reacted with elemental mercury to give a mixture of products. Nonetheless,the clean first order behaviour in [**2-Ag**] as demonstrated in the plots of Figure 2 strongly suggest this is a homogeneous process.

The conversion of **2-Ag** to *d_{10}*-**4-Ag** involves two competitive C-H activation processes, one that eliminates water from the Pt hydroxo and a competitive process that exchanges the proteo phenyl group for a deuterated phenyl group (Scheme 4). Since neither of these processes occurs with a significant rate at room temperature in the silver free complex **2**, the role the silver ion plays in enhancing the rate of these processes is phenomenologically evident, but mechanistically unclear. In the case of the degenerate phenyl group exchange steps, it is well known that cationic Pt(II) phenyl derivatives mediate C-H activations via OA[34-37] or σ bond metathesis[38] pathways. It may be that the silver ion provides access to such an intermediate Pt(II) phenyl cation,[22, 39, 40] which is ligated by the excess water present. In the case of the irreversible elimination of HOD and production of the *bis*-phenyl complex **4-Ag**, perhaps the presence of the silver ion renders the Pt center more electrophilic, enhancing the rate of 1,2-addition to the Pt-OH bond. However, in the absence of further mechanistic investigations, the key point is that the presence of the silver ion in these compounds clearly lowers the barrier to C-H(D) activation in these neutral Pt(II) complexes, such that the heterogeneous pathways available at higher temperatures[17] are avoided.



Scheme 4. Activation of C_6D_6 by **2-Ag**

Summary

Complexation of Ag(I) ions to square planar Pt(II) diimine compounds is a well studied phenomenon that usually involves direct interactions between the silver and platinum metal centres. In the case of the platinum hydroxo compounds **1-3**, treatment with $AgNTf_2$ yields adducts in which the silver ion interacts with the hydroxo ligands, as evidenced by both ^{195}Pt NMR data and an X-ray structural analysis of **1-Ag**. Interestingly, these silver complexes activate the C-D bonds of the NMR solvents employed under much milder conditions than what was observed for the silver-free systems. While the origin of this "silver effect" is not clear, the increased electrophilicity of the Pt(II) centre as a result of silver complexation to the –OH moiety is likely a factor in the enhanced proclivity towards C-D bond cleavage reactions in these systems.

Experimental section

General Considerations

For a detailed description of general procedures, see the ESI.

Synthesis of [(ArN=C(An)-C(An)=NAr)Pt(OH)$_2$] [AgNTF$_2$], Ar = 3,5-bis-(2,6-di*iso*propyl)benzene, 1-Ag: 1 (0.035g, 0.029 mmol, 1 eq) and $AgNTf_2$ (0.003g, 0.031 mmol, 1.07 eq) were added to a round bottom flask. Dry THF (25 mL) was introduced by vacuum transfer and the solution was allowed to stir at room temperature for 10 minutes before removing the solvent *in vacuo*. Dry hexanes (2 x 10mL) was introduced by vacuum transfer, the solution was sonicated for 20 minutes, and the solvent removed *in vacuo* to leave an orange powder. X-ray quality crystals were grown by vapour diffusion of hexanes into a benzene solution at room temperature. Yield: 0.035g 78%. ^{1}H NMR (600 MHz, THF-*d_8*, 298K): δ = 0.79 (broad s, 2H, Pt-OH-Ag), 1.09 (m, 12H, CH(C*H*$_3$)$_2$), 1.13 (m, 12H, CH(C*H*$_3$)$_2$), 1.21 (m, 24H, CH(C*H*$_3$)$_2$), 2.87 (m, 4H, C*H*(CH$_3$)$_2$), 2.94 (m, 4H, C*H*(CH$_3$)$_2$), 7.23 (m, 8H, Ar-CH), 7.32 (m, 6H, Ar-CH), 7.47 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar$_{Naphth}$-C*H*), 7.51 (d, $^4J_{H-H}$ = 1 Hz, 4H, Ar-C*H*), 7.67 (d or d, $^3J_{H-H}$ = 8 Hz, 2H, Ar$_{Naphth}$-C*H*), 8.53 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar$_{Naphth}$-C*H*). ^{13}C NMR (125 Mz, THF-*d_8*, 298K): δ□= 24.65 (broad s, (CH(*C*H$_3$)$_2$), 31.84 (*C*H(CH$_3$)$_2$), 32.0 (*C*H(CH$_3$)$_2$), 117.9, 120.0, 122.2, 123.1 (Ar-CH), 123.5 (Ar-CH), 123.7 (Ar-CH$_{Naphth}$), 129.5 (Ar-CH), 130.5 (Ar-CH$_{Naphth}$), 132.1 (Ar-CH$_{Naphth}$), 133.7 (Ar-CH), 133.9, 138.6, 144.2, 146.4 (N=*C*-Ar). ^{195}Pt NMR (107 MHz, THF-*d_8*, 298K): δ = -1276 ppm. ^{19}F NMR (376 MHz, THF-*d_8*, 298K): δ = - 81.8 ppm. IR (NaCl plates, THF film): 3609 cm^{-1} (m, OH). The corresponding Ag-Pt-OD was made from (NN)Pt(OD)$_2$ made using D_2O instead of H_2O. IR (NaCl plates, THF film): 2678 cm^{-1} (m, OD). HR-ESIMS of **1-Ag**, Calcd for $C_{74}H_{85}AgN_3O_2Pt$ (M – N(SO$_2$CF$_3$)$_2$ + CH$_3$CN): 1350.5342. Found: 1350.5327. Anal. Calcd. for $C_{74}H_{82}AgF_6N_2O_6PtS_2$ (**1-Ag**): C. 55.85; H, 5.20; N, 2.64 and $C_{78}H_{90}AgF_6N_3O_7PtS_2$ (**1-Ag** + THF): C, 56.35; H, 5.46; N, 2.53. Found: C, 56.23; H, 5.56; N, 2.50.

Synthesis of [(ArN=C(An)-C(An)=NAr)Pt(OH)(C$_6$H$_5$)][AgNTF$_2$], Ar = 3,5-bis-(2,6-di*iso*propyl) benzene, 2-Ag:

2 (0.058g, 0.046 mmol, 1 eq) and $AgNTf_2$ (0.005g, 0.046 mmol, 1 eq) were added to a round bottom flask. Dry THF (25 mL) was introduced by vacuum transfer, and the solution was allowed to stir at room temperature for 10 minutes before removing the solvent *in vacuo*. Dry hexanes (2 x 10mL) was introduced by vacuum transfer, the solution was sonicated for 20 minutes, and removed *in vacuo* to leave a purple powder.

Yield: 0.047g 62%. ^{1}H NMR (400 MHz, C_6D_5Br, 298K): δ = 0.39 (s, 1H, Pt-OH), 0.88 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (m, 24H, CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 2.39 (septet, 2H, C*H*(CH$_3$)$_2$), 2.75 (septet, 2H, C*H*(CH$_3$)$_2$), 2.91 (m, 4H, C*H*(CH$_3$)$_2$), 6.89 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 6.90 (d, $^4J_{H-H}$ = 1 Hz, 2H, Ar-H), 6.97 (t, $^4J_{H-H}$ = 1 Hz, 1H, Ar-H), 7.04 (t, $^3J_{H-H}$ = 7 Hz, 1H, Pt-C_6H_5 *para*), 7.12-7.18 (m, 8H, Ar-H), 7.21 (d of d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.26 (m, 2H, Ar-H), 7.28-7.34 (m, 6H, Ar-H), 7.48 (d, $^4J_{H-H}$ = 1 Hz, 2H, Ar-H), 7.52 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.86 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.99 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*). ^{13}C NMR (125 MHz, C_6D_5Br, 298K): δ = 23.9 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 30.0 (*C*H(CH$_3$)$_2$), 30.6 (*C*H(CH$_3$)$_2$), 30.9 (*C*H(CH$_3$)$_2$), 118.8, 120.7 (Ar-CH), 121.0, 121.3 (Ar-CH), 122.0, 122.8 (Ar-CH$_{Naphth}$), 123.0 (Ar-CH), 123.3 (Ar-CH$_{Naphth}$), 124.8 (Pt-C_6H_5 *para*), 128.3 (Ar-CH), 128.7 (Ar-CH), 128.8 (Ar-CH), 128.9 (Ar-CH), 130.2 (Ar-CH$_{Naphth}$), 130.5, 131.2 (Ar-CH$_{Naphth}$), 131.1, 131.9 (Ar-CH), 132.0 (Ar-CH), 132.3 (Ar-CH), 136.9, 137.0, 142.7, 143.3, 144.1, 145.5, 146.4, 148.0, 171.7 (N=*C*-Ar), 173.7 (N=*C*-Ar). ^{195}Pt NMR (107 MHz, C_6D_5Br, 298K): δ = -2242 ppm. ^{19}F NMR (376 MHz, THF-d_8, 298K): δ = - 79.9 ppm. IR (NaCl plates, THF film): 3590 cm^{-1} (w, OH). The corresponding Pt-OD was made from (NN)Pt(C_6H_5)(OD) made using D_2O instead of H_2O. IR (NaCl plates, THF film): 2647 cm^{-1} (w, OD). Anal. Calcd. for $C_{80}H_{86}AgF_6N_3O_5PtS_2$: C, 58.21; H, 5.25; N, 2.55. Found: C, 58.79; H, 5.41; N, 2.05.

Synthesis of [(ArN=C(An)-C(An)=NAr)Pt(OH)(Me)][AgNTF$_2$], Ar = 3,5-bis-(2,6-di*iso*propyl) benzene, 3-Ag:

3 (0.042g, 0.035 mmol, 1 eq) and AgNTf$_2$ (0.004g, 0.036 mmol, 1.03 eq) were added to a round bottom flask. Dry THF (25 mL) was introduced by vacuum transfer and the solution was allowed to stir at room temperature for 10 minutes before removing the solvent *in vacuo*. Dry hexanes (2 x 10mL) was introduced by vacuum transfer, the solution was sonicated for 20 minutes, and the solvent removed *in vacuo* to leave an purple powder. Yield: 0.047g, 62%. ^{1}H NMR (400 MHz, C_6D_5Br, 298K): δ = 0.50 (broad s, 1H, Pt-OH-Ag), 1.01 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (m, 24H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{H-H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{H-H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.49 (s, 3H, Pt-CH$_3$), 2.96 (m, 8H, C*H*(CH$_3$)$_2$), 7.03 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.07 (s, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 7.16-7.23 (m, 8H, Ar-H), 7.33 (m, 4H, Ar-H), 7.52 (s, 2H, Ar-H), 7.61 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.83 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*), 7.95 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar$_{Naphth}$-C*H*). ^{13}C NMR (125 MHz, C_6D_5Br, 298K): δ = -10.8 (Pt-CH$_3$), 24.0 (CH(*C*H$_3$)$_2$), 2 x 24.1 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 30.5 (*C*H(CH$_3$)$_2$), 2 x 30.8 (*C*H(CH$_3$)$_2$), 118.6, 120.73, 121.0 (Ar-CH), 121.3 (Ar-CH), 122.7 (Ar-CH$_{Naphth}$), 122.9 (Ar-CH), 123.0 (Ar-CH), 126.6, 128.7 (Ar-CH), 128.9 (Ar-CH), 130.0 (Ar-CH$_{Naphth}$), 130.6 (Ar-CH$_{Naphth}$), 131.3 (Ar-CH), 131.8 (Ar-CH), 132.0, 137.3, 142.8, 142.9, 144.2, 145.0, 145.3, 146.6, 146.7, 170.0 (N=*C*-Ar), 173.7 (N=*C*-Ar). ^{195}Pt NMR (107 MHz, C_6D_5Br, 298K): δ = -2167 ppm. ^{19}F NMR (376 MHz, THF-d_8, 298K): δ = - 81.4 ppm. IR (NaCl plates, THF film): 3571 cm^{-1} (w, OH). The corresponding Pt-OD was made from (NN)Pt(CH$_3$)(OD) made using D_2O instead of H_2O. IR (NaCl plates, THF film): 2647 cm^{-1} (w, OD). Anal. Calcd. for $C_{73}H_{78}AgF_6N_3O_5PtS_2$: C, 56.71; H, 5.33; N, 2.65. Found: C, 56.13; H, 5.49; N, 2.22.

Synthesis of [(ArN=C(An)-C(An)=NAr)Pt(C_6H_5)$_2$][AgNTF$_2$], Ar = 3,5-bis-(2,6-di*iso*propyl)benzene, 4-Ag:

4 (0.045g, 0.033 mmol, 1 eq) and AgNTf$_2$ (0.003g, 0.038 mmol, 1.2 eq) were added to a round-bottomed flask. Dry benzene (10 mL) was introduced by vacuum transfer and the solution was allowed to stir at room temperature for 10 minutes before removing the solvent *in vacuo*. Dry hexanes (2 x 10 mL) was introduced by vacuum transfer, the solution was sonicated for 2 minutes, and the volatiles removed *in vacuo* to leave an air stable purple powder. Yield: 0.045 g 77%. ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 0.95 (d, $^3J_{H-H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{H-H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{H-H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.39 (d, $^3J_{H-H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 2.63 (septet, $^3J_{H-H}$ = 7 Hz, 4H, C*H*(CH$_3$)$_2$), 2.89 (septet, $^3J_{H-H}$ = 7 Hz, 4H, C*H*(CH$_3$)$_2$), 6.84 (t, $^3J_{H-H}$ = 7 Hz, 2H, Pt-C_6H_5 *para*), 6.93 (d, $^4J_{H-H}$ = 1 Hz, 4H, Ar-CH), 6.93 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar$_{Naphth}$-C*H*), 7.11 (m, 6H x Ar-CH, 4H x Pt-C_6H_5 *meta*), 7.22 (d, 4H, Ar-CH), 7.28 (t, 4H, Ar-CH), 7.58 (m, 2H x Ar$_{Naphth}$-C*H*, 4H x Pt-C_6H_5 *ortho*). ^{13}C NMR (125 Mz, C_6D_6, 298K): δ = 24.0 ((CH(*C*H$_3$)$_2$), 24.3 ((CH(*C*H$_3$)$_2$), 24.4 ((CH(*C*H$_3$)$_2$), 25.1 ((CH(*C*H$_3$)$_2$), 30.1 (*C*H(CH$_3$)$_2$), 30.6 (*C*H(CH$_3$)$_2$), 120.7 (Ar-CH), 122.3 (Ar-CH), 123.1 (Ar-CH), 124.1 (Ar-CH$_{Naphth}$), 124.5 (Pt-C_6H_5 *para*), 127.7, 128.3 (Ar-CH$_{Naphth}$), 128.5 (Ar-CH), 130.3 (Ar-CH$_{Naphth}$), 131.1 (Ar-CH), 131.7, 135.7 (Pt-C_6H_5 *ortho*), 137.6, 142.5, 145.5, 145.7, 146.7, 147.3, 173.5 (N=*C*-Ar). ^{195}Pt NMR (107 MHz, C_6D_6, 298K): δ = -2942 ppm. ^{19}F NMR (376 MHz, C_6D_6, 298K): δ = - 77.9 ppm. Anal. Calcd. for $C_{86}H_{90}AgF_6N_3O_4PtS_2$: C, 60.38; H, 5.30; N, 2.46. Found: C, 60.13; H, 5.62; N, 2.23.

Preparation of C_6D_6/H_2O Stock solutions:

Two stock solutions were made in 5 mL volumetric flasks containing hexamethylbenzene standard (0.007g, 8.63 mM/L). In a glove-box designated for water usage, 27 uL (30 mM/L) of degassed H_2O was added via micropipette to one flask. Dry C_6D_6 was measured into both flasks and they were stored in their respective glove-boxes under argon in sealed glass vessels.

Representative procedure for monitoring conversion of 2-Ag to 4-Ag: A 5.05 mMol/L solution of **2-Ag** (0.025g) in wet C_6D_6 stock solution (30 mMol/L H_2O, 3.0 mL) was prepared in the glovebox. Aliquots of 0.4 mL were syringed into 4 separate j-young NMR tubes, and each sealed with a Teflon screw tap. The tubes were immediately frozen at -35°C in the glovebox freezer until used for a kinetic run. The tube was kept frozen and only thawed directly before insertion into the preheated NMR probe (600 MHz) to begin the cycling program. A total of 8 scans were taken each time increment with a delay time between each scan of 20 seconds to ensure proper integration.

Crystal structure analysis

X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius

KappaCCD diffractometer; full details can be found in the independently deposited crystallographic information files.

Acknowledgements

This research was supported by the Natural Sciences and Engineering Council of Canada in the form of a Discovery Grant to W.E.P. and a Post Graduate Scholarship to T.L.L. W.E.P. also thanks the Canada Research Chair secretariat for a Tier I CRC (2013-2020) and T.L.L. thanks Alberta Innovates Technology Futures for scholarship support.

Notes and references

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† Electronic Supplementary Information (ESI) available: X-Ray data for **2-Ag** (CCDC 1010710). General experimental procedures and NMR spectral data for **2-Ag** and **3-Ag**, speciation plot of **3-Ag** to **4-Ag**, concentration versus time plots for the conversion of **2-Ag** to **4-Ag** at 295K with and without added H_2O, concentration versus time plot for **2** in C_6D_6 at 308 K and IR spectra for OD and OH complexes of **1-Ag**, **2-Ag**, and **3-Ag**. See DOI: 10.1039/b000000x/

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Graphical Abstract

Addition of stoichiometric Ag(I) salt to monomeric Pt(II) hydroxo complexes supported by a bulky diimine ligand results in significantly enhanced rates of C-H activation relative to the silver free systems.