



### Cooperative activation of X–H (X = H, C, O, N) bonds by a Pt(0)/Ag(I) metal-only Lewis pair†

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**Metal-only Lewis pairs made of Pt(0)/Ag(I) combinations have been previously reported, but their cooperative reactivity remains unexplored. Here we demonstrate that these systems are capable of synergistically activating a wide variety of X–H (X = H, C, O, N) bonds, including those in dihydrogen, alkynes, water and ammonia.**

Since the seminal works of Werner at the end of the 19th century, the chemistry of transition metal complexes has been mostly defined by the acidic character of the metal centre, to which basic ligands can bind by means of dative bonds. In contrast, the potential of transition metals to behave as electron donors has remained less explored, despite its fundamental role in oxidative addition reactions or in the coordination of  $\pi$ -acidic ligands.<sup>1</sup> More recently, the interest in electron-rich transition metal complexes capable of coordinating  $\sigma$ -acceptor ligands (Z-type ligands) has grown enormously.<sup>2</sup> This unusual reverse flux of electrons provides the metal centre with uncommon stereoelectronic properties and reactivity patterns.<sup>3</sup> In this context, the use of unsaturated transition metal fragments instead of p-block  $\sigma$ -acceptors has become a successful strategy to access heterobimetallic compounds containing M  $\rightarrow$  M dative bonds.<sup>4</sup> A fascinating class among these bimetallic entities are metal-only Lewis pairs (MOLPs),<sup>5</sup> in which two metal fragments are held together exclusively through a M–M interaction. Within this field, the use of group 11 metals acting as Lewis acids for the synthesis of MOLPs is well-documented.<sup>6</sup> In the case of silver, accessing these bimetallic targets acquires particular relevance in connection to the use of silver species as halide abstractors<sup>7</sup> or transmetallation reagents,<sup>8</sup> as well as due to the photoluminescent properties of silver-containing heterometallic compounds.<sup>9</sup>

In addition, TM  $\rightarrow$  Ag dative bonds have served as an experimental gauge to calibrate the basicity of transition metals.<sup>10</sup> Moreover, metal–metal interactions involving silver centres are key in catalysis, where the so-called silver effect has been regularly invoked in a variety of transition-metal catalysed transformations.<sup>11</sup> Likewise, well-defined silver-based heterobimetallic catalysts can outperform their monometallic parent precursors and provide unusual selectivities.<sup>12</sup> On this basis, and following our recent results on bimetallic bond activation using the basic Pt(0) compound [Pt(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>] (**1**) in combination with a sterically crowded electrophilic phosphine gold(I) fragment,<sup>13</sup> we decided to investigate the reactivity of Pt(0)/Ag(I) MOLPs. The latter systems find precedent in the recent literature but their cooperative reactivity remains unexplored.<sup>14</sup> A prior work demonstrating the cooperative activation of water using (**1**) and Cu(I) salts, further encouraged us to pursue these research aims.<sup>15</sup>

The formation of Pt  $\rightarrow$  Ag adducts **2** and **3** proceeds readily in benzene or dichloromethane upon mixing [Pt(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>] (**1**) and the corresponding silver salt in the absence of light (Scheme 1), resulting in the instant coloration of the solution from colourless to bright yellow. A chemical shift towards slightly lower frequencies is recorded by <sup>31</sup>P{<sup>1</sup>H} NMR monitoring, accompanied by a pronounced decrease in the <sup>1</sup>J<sub>Pt</sub> coupling constant (**2**:  $\delta$  = 99.6 ppm, <sup>1</sup>J<sub>Pt</sub> = 3298 Hz; **3**:  $\delta$  = 99.2 ppm, <sup>1</sup>J<sub>Pt</sub> = 3244 Hz) with respect to precursor **1** ( $\delta$  = 100.2 ppm, <sup>1</sup>J<sub>Pt</sub> = 4410 Hz). The diminished <sup>1</sup>J<sub>Pt</sub> values in **2** and **3** are expected considered the reduced s character of P–Pt bonds as a consequence of the new Pt  $\rightarrow$  Ag interaction. These data are similar to the NMR changes

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**Scheme 1** Synthesis of Pt(0)/Ag(I) metal-only adducts (NTF<sub>2</sub><sup>−</sup> = [N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>−</sup>; OTf<sup>−</sup> = [OSO<sub>2</sub>CF<sub>3</sub>]<sup>−</sup>).



observed in the formation of a trimetallic compound of formula  $[(PCy_3)_2Pt \rightarrow Ag^+ \leftarrow Pt(PCy_3)_2]$  previously described by the group of Braunschweig.<sup>14c</sup> However, in our case the use of slightly coordinating anions such as triflimide ( $NTf_2^-$ ,  $[N(SO_2CF_3)_2]^-$ ) or triflate ( $OTf^-$ ,  $[OSO_2CF_3]^-$ ) seems to prevent the formation of the trimetallic compound in favour of the bimetallic MOLPs **2** and **3**. This was demonstrated by the reaction of **1** with 0.5 equivalents of silver salts  $AgNTf_2$  or  $AgOTf$ , which results in the formation of equimolar mixtures of unreacted **1** and compounds **2** and **3**, respectively. Interestingly, the use of silver reagents containing less coordinating counteranions (*i.e.*  $BF_4^-$  and  $PF_6^-$ ) also led to Pt/Ag MOLPs, as inferred from  $^{31}P\{^1H\}$  NMR studies, but those displayed limited stability. More precisely, they evolved towards the cyclometalation of one of the *tert*-butyl fragments of a  $P^tBu_3$  ligand to yield compounds  $[Pt^{II}(\kappa^2P,C-P^tBu_2CMe_2CH_2)(P^tBu_3)]^+$  ( $\delta(^{31}P\{^1H\}) = 55.9, 23.2$  ppm (d,  $^2J_{PP} = 319$  Hz)) and  $[Pt^{II}(P^tBu_3)_2H]^+$  ( $\delta(^{31}P\{^1H\}) = 86.3$  ppm,  $^1J_{PPt} = 2723$  Hz;  $\delta(^1H) = -33.0$  ppm ( $^1J_{HPt} = 2224$  Hz)).<sup>15</sup> The same reactivity was noticed upon dissolving compounds **1** or **2** in tetrahydrofuran. An identical transformation was latterly reported using a ferrocenium salt as the one-electron oxidant,<sup>16</sup> a role presumably played by the silver salt in the compounds reported herein.

The molecular structures of compounds **2** and **3** were authenticated by single-crystal X-ray diffraction studies, confirming the proposed bimetallic formulation of the metal-metal core. While compound **2** crystallized as a monomer in the solid state (Fig. 1), the structure of **3** reveals a dimeric configuration with two triflate anions as bridging fragments (Fig. S1, ESI<sup>†</sup>). Nevertheless, diffusion NMR experiments ruled out a dimeric formulation as the main species in solution. The structures are otherwise comparable to previous Pt(0) Lewis adducts,<sup>13,14c,17</sup> exhibiting slightly distorted T-shaped configurations around the metal centre ( $P-Pt-P = 167.07(5)$  (**2**) and  $174.69(4)^\circ$  (**3**)). The Pt-P bond distances ( $2.30$ – $2.32$  Å) are elongated in comparison to precursor **1** ( $2.25$  Å).<sup>18</sup> This may be attributed to the release of electrons from the platinum centre towards the silver atom, in analogy to the Pt-P bond lengthening observed upon one-electron oxidation of precursor **1**, whose origin is still a matter of debate.<sup>19</sup>

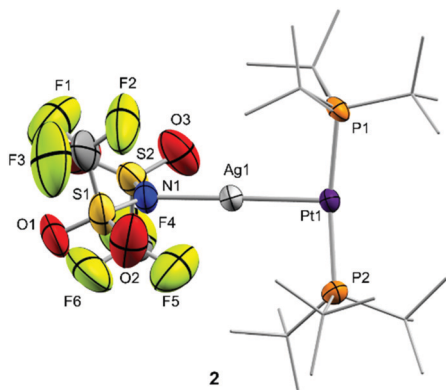


Fig. 1 ORTEP diagram of compound **2**; for the sake of clarity hydrogen atoms are excluded and some substituents have been represented in wireframe format, while thermal ellipsoids are set at 50% probability.



Scheme 2 Cooperative activation of  $H_2$  and alkynes mediated by **2**.

Given the superior stability of compound **2** over **3**, we chose the former to investigate its reactivity and compare the outcomes with its independent components, that is, compounds **1** and  $AgNTf_2$ . We examined the reactivity of **2** towards the activation of hydrogen, alkynes and polar X-H bonds ( $X = O, N$ ), including those in water and ammonia. Compound **2** cleanly evolves in the presence of  $H_2$  under mild conditions (1 atm,  $-20^\circ C$ ) to yield the heterobimetallic Pt(II)/Ag(I) dihydride **4** that contains a terminal and a bridging hydride (Scheme 2). Related Pt/Ag heterobimetallic hydrides have been previously prepared by mixing platinum(II) dihydrides with silver salts.<sup>20</sup> Nevertheless, it is important to remark that neither precursor **1** nor  $AgNTf_2$  exhibit any reactivity towards dihydrogen even under harsher conditions (4 atm,  $60^\circ C$ ). This demonstrates that both metals are required for the cleavage of the H-H bond to take place. The course of the reaction can be monitored by  $^{31}P\{^1H\}$  NMR spectroscopy, following the appearance of a new resonance at 94.6 ppm ( $^1J_{PPt} = 2660$  Hz) due to the heterobimetallic dihydride **4**. This compound exhibits fluxional behavior in solution, as evinced by a single and distinctive low-frequency  $^1H$  NMR resonance ( $-4.89$  ppm) at  $25^\circ C$  due to the two hydride ligands. This signal appears as an apparent double quartet due to coupling to  $^{107,109}Ag$  ( $^1J_{AgH} = 120$  Hz) and  $^{31}P$  ( $^2J_{HP} = 10$  Hz), and it is flanked by  $^{197}Pt$  satellites ( $^1J_{HPt} = 778$  Hz). The dynamic process is quenched at temperatures below  $-50^\circ C$ , at which the initial signal is split into two resonances at  $-3.98$  ( $^1J_{AgH} = 182$ ,  $^1J_{HPt} = 570$  Hz) and  $-5.21$  ( $^1J_{AgH} = 44$ ,  $^1J_{HPt} = 984$  Hz) ppm due to the bridging and terminal hydrides, respectively (Fig. S4, ESI<sup>†</sup>). The barrier for the exchange was determined by standard line-shape analysis ( $\Delta G_{298}^\ddagger = 13.2$  kcal mol $^{-1}$ ). It could result from either fast tilting of the square-planar  $Pt(H)_2(P^tBu_3)_2$  fragment or rapid dissociation/coordination of the silver salt. In fact, the lability of the  $Pt \rightarrow Ag$  bond is attested by the reaction of **1** with 0.5 equivalents of  $AgNT_2$  under  $H_2$  atmosphere, which forms an equimolar mixture of compound **4** and unreacted **1** after 5 hours and eventually evolves to a *ca.* 1:1 mixture of the former and  $Pt(H)_2(P^tBu_3)_2$ , along with variable amounts of  $[Pt^{II}(P^tBu_3)_2H]^+$  as a recurrent side-product. Having in mind that precursor **1** does not react with  $H_2$  under our experimental conditions, the



formation of  $\text{Pt}(\text{H})_2(\text{P}^t\text{Bu}_3)_2$  may imply transfer of silver from hydride **4** to unreacted **1** forming compound **2**, which could subsequently be hydrogenated by the synergistic action of silver.

We next investigated the reactivity of **2** towards acetylene and phenylacetylene (Scheme 2). Compound **1** acts as a catalyst for the polymerization of  $\text{C}_2\text{H}_2$ , provoking the rapid precipitation of a dark purple solid upon exposure to the gas. The formation of the polymer is, however, visibly inhibited in the presence of the silver salt, in which case the trinuclear  $[(\text{P}^t\text{Bu}_3)_2(\text{H})\text{Pt}(\mu\text{-CCH})\text{Ag}(\mu\text{-CCH})\text{Pt}(\text{H})(\text{P}^t\text{Bu}_3)_2]$  (**5**) is obtained in almost quantitative spectroscopic yield. Analogous reactivity is derived from the addition of phenylacetylene, resulting in the formation of the heterobimetallic dibridged bisacetylide **6**. Similarly to our studies with  $\text{H}_2$ , neither precursor **1** nor the silver salt exhibit any reactivity towards phenylacetylene as monometallic species. Compounds **5** and **6** are related to other Pt/Ag bridging acetylides that have been prepared by the addition of silver salts to pre-formed platinum(II) acetylides,<sup>21</sup> an approach that contrasts to the bimetallic cooperative alkyne activation described herein. The new heterobimetallic compounds are characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances at 83.4 (**5**) and 82.8 (**6**) ppm flanked by  $^{195}\text{Pt}$  satellites ( $^1J_{\text{PPT}} = 2782$  and 2759 Hz, respectively), shifted to lower frequencies by *ca.* 16 ppm with respect to their precursor **2**. These compounds are thermally unstable in solution, particularly complex **5**. However, we managed to grow single-crystals of the latter species. X-ray diffraction studies revealed the trimetallic formulation of the dibridged  $\sigma,\pi$  bisacetylide (Fig. 2). The Pt...Ag distance is markedly elongated (3.634(9) Å) compared to the metallic Lewis pair **2** (2.658(1) Å), indicating that the dative Pt→Ag bond is no longer present. The  $\sigma,\pi$ -bridged acetylide fragments are characterized by short bond distances with the silver nuclei ( $d_{\text{Ag-centroid}}$  2.216(6) Å), along with relatively lengthened Pt–C bond distances ( $d_{\text{Pt-C}}$  2.107(12) Å) compared to other compounds of formula  $[\text{Pt}(\text{H})(\text{CCR})(\text{PR}_3)_2]$  (*ca.* 1.9–2.0 Å).<sup>22</sup> The formulation of compounds **5** and **6** as trimetallic bisacetylides was corroborated in solution by the reactions of equimolar



Fig. 2 ORTEP diagram of compound **5**; for the sake of clarity most hydrogen atoms and the triflimide counteranion have been excluded and some substituents have been represented in wireframe format, while thermal ellipsoids are set at 50% probability.

mixtures of **1** and **2** with the two investigated alkynes, leading to compounds **5** and **6**, respectively, accompanied by complete consumption of the two platinum precursors, that is, using only one equivalent of silver per two platinum nuclei.

We additionally tested the reactivity of **2** towards the activation of polar X–H (X = O, N) bonds. Before discussing these results, it is pertinent to highlight that none of the reagents tested for X–H bond cleavage exhibited any reactivity towards precursor **1**. However, addition of methanol (5 equiv.) to a  $\text{C}_6\text{D}_6$  solution of **2** provides formation of the previously reported<sup>22</sup> cationic T-shaped platinum hydride **7** (*ca.* 80%) after around one hour at 25 °C (Scheme 3). This compound is characterized by a distinctive low-frequency  $^1\text{H}$  NMR resonance at –33.0 ppm ( $^1J_{\text{PPT}} = 2224$  Hz). Its molecular formulation was further confirmed by X-ray diffraction studies (Fig. S2, ESI†). More interestingly, analogous reactivity arises from the addition of water or ammonia, yielding the corresponding cationic Pt-hydride complexes further stabilized by coordination of a water (**8a**) or ammonia (**8b**) ligand, respectively. While the activation of water (50 equiv.) in benzene solution takes up to 12 hours to reach *ca.* 90% completion, likely due to water immiscibility, using wet acetonitrile yields  $[\text{Pt}(\text{H})(\text{CH}_3\text{CN})(\text{P}^t\text{Bu}_3)_2]^+$  (**8c**) instantly. The reaction with ammonia (1 bar) requires heating at 60 °C to form compound **8b** in *ca.* 60% yield after 16 hours.

The activation of X–H bonds in methanol, water and ammonia is accompanied by the appearance of greyish precipitates that we attribute to the corresponding silver alkoxide, hydroxide or amide salts, respectively. The formation of compounds **8a–c** was unequivocally confirmed by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.<sup>23</sup> The solid structure of the aquo/hydride complex **8a** was validated by X-ray diffraction studies (Fig. S3, ESI†).

As stated in the introduction, the cooperative activation of water using a bimetallic Pt(0)/Cu(I) pair has been recently described.<sup>15</sup> However, the cleavage of N–H bonds in ammonia remains a challenge in transition metal chemistry, where formation of Werner-type adducts is typically preferred.<sup>24</sup> Thus, compound **2** adds to the limited list of transition metal systems capable of activating ammonia under mild conditions by virtue of the synergistic cooperation between the two metals.



Scheme 3 Reactivity of compound **2** towards polar X–H (X = O, N) bonds.



In summary, the reactivity of the Pt(0)/Ag(I) MOLP 2 markedly differs from that of its independent metal components. Thus, while [Pt(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>] (1) does not react with H<sub>2</sub>, phenylacetylene, methanol, water or ammonia, the presence of a silver salt readily facilitates the activation of these molecules by X–H (X = H, C, O, N) bond cleavage. These results demonstrate the usefulness of MOLP systems for small molecule activation and, as an immediate consequence, for catalytic applications, a research avenue that we are currently pursuing in our group.

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## Conflicts of interest

There are no conflicts to declare.

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