


 Cite this: *Chem. Commun.*, 2022, 58, 9144

 Received 31st May 2022,
 Accepted 19th July 2022

DOI: 10.1039/d2cc03089f

rsc.li/chemcomm

A highly constrained *cis*-dihydride platinum complex trapped by cooperative gold/platinum dihydrogen activation†

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A series of Au(I)/Pt(0) combinations that behave as bimetallic frustrated Lewis pairs activates dihydrogen in a cooperative manner. The steric bulk of the terphenyl phosphines that stabilize both fragments allows for the isolation of a rather unique and highly distorted *cis*-type dihydride platinum(II) structure.

In the last fifteen years, frustrated Lewis pair (FLP) systems have become a major research topic in main group chemistry and catalysis, mainly due to their ability to activate small molecules and perform a broad range of catalytic transformations.¹ Although first developed by combining main group Lewis acids and Lewis bases with high steric profiles to prevent quenching by donor–acceptor interactions, the FLP concept has been progressively extended to transition metals due to the enormous structural and electronic diversity of their complexes. Inspired by pioneering work of Wass² and Erker³ on zirconium/phosphine FLPs, we have pursued the design of frustrated systems in which the two components are based on transition metals.⁴

Among these studies, we have investigated in detail Au(I)/Pt(0) pairs⁵ comprised of [(PR₂Ar')Au(NTf₂)] and Pt(P^tBu₃)₂ fragments, where Ar' stands for bulky terphenyl groups (C₂H₃-2,6-Ar₂) and NTf₂ for the weakly coordinating triflimide anion (see Fig. 1a). Since the activation of dihydrogen has become a benchmark reaction to gauge FLP reactivity,⁶ we exposed the aforesaid Au(I)/Pt(0) pairs to H₂ gas, which led us

to postulate the first genuine bimetallic FLP mechanism for dihydrogen cleavage.^{5c} Besides, our studies indicated a strong influence of the gold fragment steric properties on the rate of bond activation and also on the resulting product distribution.

Encouraged by our recent access to the highly congested Pt(0) compound Pt(PMe₂Ar^{Dtbp2})₂ (Dtbp = 3,5-di-*tert*-butylphenyl) (Fig. 1a),⁷ and by the still lively debate on the precise mechanism of dihydrogen activation by FLPs,⁸ we report herein our studies on the contrasting reactivity offered by three Au(I)/Pt(PMe₂Ar^{Dtbp2})₂ pairs towards H₂ (Fig. 1b). The combination of two metallic fragments stabilized by terphenyl phosphine ligands have allowed us to isolate unique models of *cis*–*trans*-isomerization in platinum(II) dihydrides, mostly associated to unhindered and highly reactive complexes.⁹

Before investigating the reactivity of the 1:2 pairs with dihydrogen, we first examined the potential formation of bimetallic adducts **3** characterized by a dative Pt → Au bond (Scheme 1). The existence of acid–base interactions in FLP

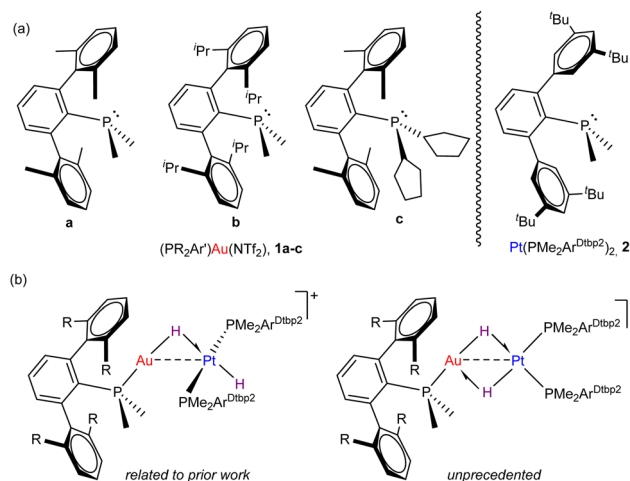


Fig. 1 (a) Terphenyl phosphine ligands used in this work to stabilize Au(I) and Pt(0) compounds (NTf₂⁻ (triflimide) = [N(SO₂CF₃)₂]⁻); (b) key bimetallic Au(I)/Pt(II) dihydride isomeric structures isolated and characterized herein.

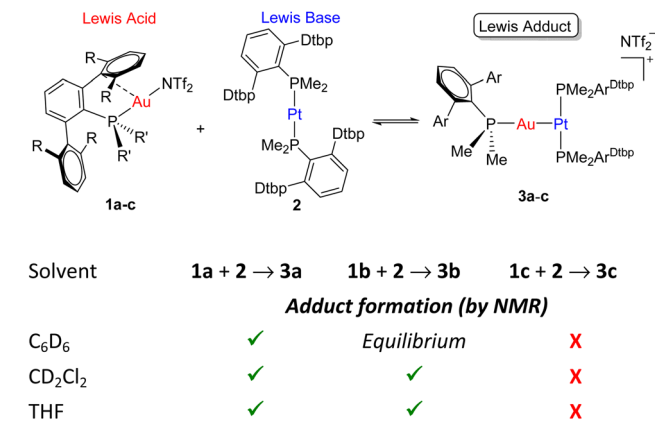
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† Electronic supplementary information (ESI) available: Synthesis and characterization data of new compounds, NMR spectra, variable temperature and kinetic experiments and crystal data. CCDC 2175895 and 2175896. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2cc03089f>

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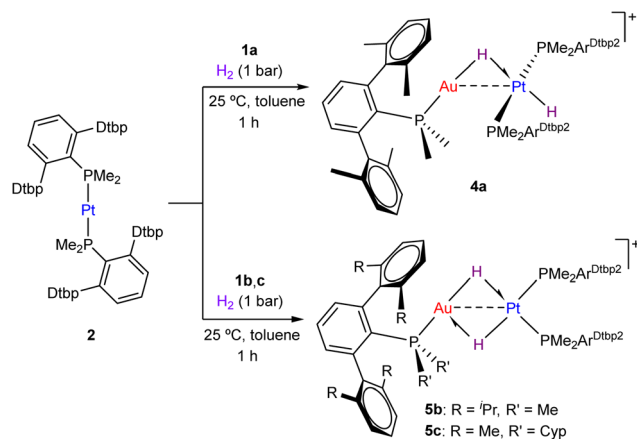
Scheme 1 Bimetallic Lewis adduct formation in 1:2 systems.

systems has a profound impact on their cooperative reactivity. As such, the presence of Pt → Au bonds greatly diminishes the reactivity of Au(I)/Pt(0) pairs, though it does not quench their frustrated reactivity as they may behave as thermally induced FLPs.^{5c} Thus, we examined the combination of Pt(0) compound 2 and Au(I) triflimide complexes **1a–c** (Scheme 1) bearing phosphines PMe₂Ar^{Xyl2} (**1a**), PMe₂Ar^{Dipp2} (**1b**) and PCyp₂Ar^{Xyl2} (**1c**) (Cyp = cyclopentyl) and using solvents of different polarity.

As anticipated, the steric hindrance of the phosphines coordinated to gold (PCyp₂Ar^{Xyl2} > PMe₂Ar^{Dipp2} > PMe₂Ar^{Xyl2})¹⁰ is crucial to modulate the equilibrium between Lewis adduct formation and complete bimetallic frustration. The more congested **1c** is unable to coordinate to compound 2, contrasting with related examples based on [Pt(0)(PR₃)₂] species that recurrently led to the formation of metal-only Lewis pairs.¹¹ Conversely, when compound 2 is combined with one equivalent of **1a**, the corresponding bimetallic Lewis adduct **3a** is formed. It exhibits ³¹P{¹H} NMR signals at −23.2 and 13.5 ppm due to PMe₂Ar^{Xyl2} and PMe₂Ar^{Dipp2}, respectively. The former reveals a pronounced decrease of the ¹J_{Pt} coupling constant to 3077 Hz (cf. 3794 Hz in 2), while the latter signal is flanked by ¹⁹⁵Pt satellites (²J_{Pt} = 2060 Hz), both features indicative of formation of adduct **3a**.

An interesting situation is found in the case of compound **1b** bearing the intermediate size phosphine PMe₂Ar^{Dipp2}, which upon equimolar combination with 2 in C₆D₆ seems to be in equilibrium between adduct formation and monometallic fragments. We infer this from the corresponding ³¹P{¹H} NMR spectrum, which shows broadened signals for the two monometallic species which sharpen upon cooling the NMR probe, a behaviour comparable to our prior studies with Au(I)/Pt(0).^{5c} Solvent effects have an important influence in traditional FLP systems,¹² and the same applies herein. Thus, in more polar solvents as CD₂Cl₂ or THF compound **3b** cleanly forms (³¹P{¹H} NMR, δ 11.5 (¹J_{Pt} = 3054 Hz), −25.4). It is likely that the higher propensity to solvate the departing triflimide anion upon adduct formation favours the formation of the latter.

Next, we investigated the cooperative reactivity of these Au(I)/Pt(0) pairs towards hydrogen. It is important to note that neither gold precursor **1** nor complex 2 could react with dihydrogen (1 bar) even under harsher reaction conditions

Scheme 2 Reaction of Au(I)/Pt(0) bimetallic pairs with H₂ in toluene solution.

(80 °C, up to 1 week) to those attempted with the bimetallic pairs. In contrast, pairs **1:2** rapidly reacted with dihydrogen, though the selectivity of the transformation was highly dependent on the terphenyl phosphine anchored to gold. First, addition of H₂ under mild conditions (1 bar, 25 °C) to an equimolar mixture of **1a:2** in C₆D₆ produced the new hetero-bimetallic Au–Pt complex **4a** (Scheme 2). The formulation of **4a** was rapidly inferred from two distinctive low-frequency signals in its ¹H NMR spectrum at −1.15 (²J_{HPt} = 100, ¹J_{HPt} = 585 Hz) and −6.93 (¹J_{HPt} = 1223 Hz) ppm, corresponding to a bridging and a terminal hydride, in analogy to the previously reported compound [(PMe₂Ar^{Dipp2})Au(μ-H)Pt(P^tBu₃)₂(H)].^{5a} In contrast, the bulkier Au(I) precursors **1b** and **1c** led to a different spectroscopic pattern upon combination with 2 and exposure to dihydrogen (1 bar, 25 °C). In those cases, a single hydridic signal for two protons was recorded at −4.03 (²J_{HP} = 57, ¹J_{HPt} = 581 Hz) and −4.28 ppm (²J_{HP} = 51, ¹J_{HPt} = 564 Hz) for the pairs **1b:2** and **1c:2**, respectively.

We initially postulated a rapid equilibration between a terminal and bridging hydride as in **4a** to account for the sole low-frequency signal recorded. In fact, we could investigate such a solution dynamic process for compound **4a** through exchange spectroscopy (EXSY) experiments at variable temperature (from 30 to 55 °C, in tol-*d*₈). An Eyring analysis led to the activation parameters ΔG₂₉₈[‡] = 17.6 kcal mol^{−1}, ΔH[‡] = 8.7 kcal mol^{−1} and ΔS[‡] = −29.7 cal mol^{−1} (see Scheme S1 and Fig. S22 in the ESI[†]). We tentatively attribute the high negative value calculated for the entropic parameter to coordination of the triflimide anion to the electrophilic gold centre in the key transition state of the exchange process.

Nonetheless, we were unable to split the single hydride signal at ca. −4 ppm after hydrogenation of pairs **1b:2** and **1c:2** even at low temperature (−80 °C). This fact, along with their corresponding ³¹P{¹H} spectra, which clearly differs from that of **4a** (see ESI[†]), and also the appearance of distinctive infrared signals due to hydride ligands at 2144 (**1b:2** + H₂) and 2141 (**1c:2** + H₂) cm^{−1}, dissimilar to that of **4a** (2064 cm^{−1}), led us to consider the formation of a rare *cis*-type dihydride



structure with a Au(μ -H)₂Pt core. Trogler and co-workers investigated in the 1980s the *cis-trans* isomerization of square-planar Pt(II) dihydride complexes of formula Pt(PR₃)₂(H)₂,^{9,13} demonstrating that only in the case of particularly small phosphines the *cis*-isomer can be detected (e.g. 20% and 3% of *cis*-isomer in toluene solution for PMe₃ and PEt₃, respectively, while completely undetected for bulkier ligands).⁹ Though electronic arguments (*trans* influence) seems to support the preference for the *cis*-isomer, *trans*-dihydrides are thermodynamically favoured,¹⁴ in part due to the dominance of steric effects. In fact, the only available information on these elusive isomers derive from the use of chelating phosphine ligands that geometrically constrain the *cis*-conformation.¹⁵ However, no other unconstrained *cis*-dihydrides complexes have been reported since the early work of Trogler,¹⁶ despite widespread examples of square planar Pt(II) *trans*-dihydrides.¹⁷

Our assumption of a bis-(μ -H) core is consistent with our ¹H NMR data compared to the aforesaid limited examples of Pt(II) *cis*-dihydrides and also fits with our simulation using *gnmr* software (Fig. S15, ESI[†]). However, it seems rather surprising, even more considering an additional interaction with the bulky [(PCyp₂Ar^{Xy12})Au]⁺ fragment, that a *cis*-type dihydride isomer may exist for such an extremely crowded environment.

X-Ray diffraction studies allowed us to confirm the contrasting reactivity between the pairs **1a:2** and **1c:2**. While the former leads to the heterobimetallic *trans*-dihydride **4a** (Fig. 2), the latter indeed activates H₂ to yield the unique *cis*-type dihydride **5c** (Fig. 2; and thereby **1b:2** towards *cis*-dihydride **5b**). Compounds **4a** and **5c** were crystallized from their concentrated toluene solutions at 25 °C. Compound **4a** is characterized by a Pt–Au bond distance of 2.7628(7) Å, comparable to other Pt(μ -H)Au species,¹⁸ and further confirming the presence of a bridging hydride. The *trans*-disposition of the Pt(II) fragment is illustrated by an almost ideal P–Pt–P angle of 175.76(10)°. In stark contrast, the analogous angle in compound **5c** is drastically decreased to 107.53(3)°, similar to Pt(II) *cis*-dihydride structures geometrically constrained by chelating phosphines.¹⁵ This structural disposition entails a high proximity between the two PMe₂Ar^{D^{tbp2}} phosphines, which is partly compensated by a slightly elongated Pt–P bond in **5c** (P1–Pt: 2.3178(7) Å) compared to **4a** (2.292(2) and 2.296(2) Å). The Pt centre thus adopts an almost ideal trigonal arrangement with respect to the phosphines and gold fragment (P1–Pt–Au, 125.654(19)°; P2–Pt–Au, 126.32(2)°). This could be rationalized as the coordination of the electrophilic [LAu]⁺ fragment to an electron rich Pt(II) *cis*-dihydride, as previously proposed by Venanzi for other related heterobimetallic species.^{18a}

We decided to investigate the effect of using THF as a polar solvent, which has been shown in the past to drastically affect selectivity in *cis-trans* isomerization.^{9,13} While the outcome of hydrogenation for the pair **1c:2** was not affected by solvent, dissimilar results were found in the case of **1a:2** and **1b:2**. In contrast, using 1,2-difluorobenzene did not offer any difference compared to toluene. For the pair **1a:2**, carrying out the reaction in THF resulted in the appearance of an additional minor Au/Pt species (**4a'**, ca. 25%) with multinuclear NMR resonances very similar to those of **4a**. Two new hydride signals were recorded at

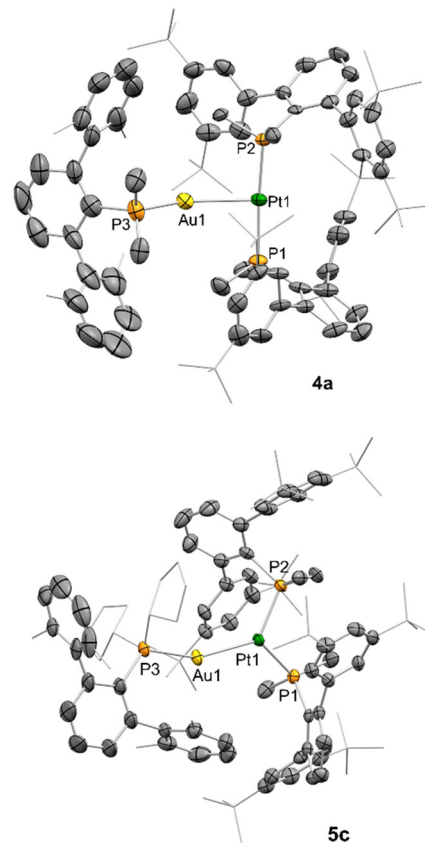
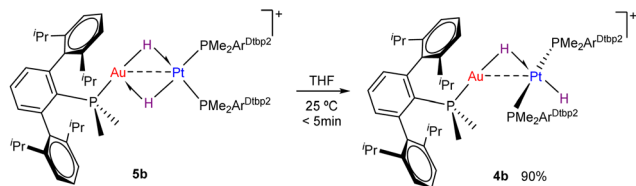


Fig. 2 ORTEP diagrams for compounds **4a** and **5c**. Thermal ellipsoids are drawn at the 50% probability. Metal hydrides could not be located in the difference Fourier electron density map. Counterion and hydrogen atoms omitted and *tert*-butyl, cyclopentyl and methyl groups from aryl rings in wireframe format for clarity.

–2.63 and –8.87 ppm, which appear as broad, as well as those of **4a**. Cooling down the NMR probe sharpened the two pairs of signals, while coalescence was reached at 30 °C (see Fig. S18, ESI[†]). Evaporation of volatiles and addition of toluene reverses the mixture towards clean formation of **4a**. Kinetic parameters for this dynamic process were obtained from lineshape analysis in the temperature interval from –20 to 60 °C, leading to $\Delta H^\ddagger = 16.1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 31.6 \text{ cal mol}^{-1} \text{ K}^{-1}$, which correspond to a ΔG_{298}^\ddagger of $6.7 \text{ kcal mol}^{-1}$ (see ESI[†]). Once more the strong entropic contribution is associated to weak coordination of triflimide to access **4a'**, which in this case would entail desolvation of THF. More interesting is the solvent effect on the pair **1b:2**, where the selectivity was inverted and a mixture of **4b** and **5b** in an approximate 9:1 ratio was recorded by ¹H NMR monitoring (Fig. S17, ESI[†]). In fact, drying under vacuum a toluene solution of pure *cis*-dihydride **5b** and redissolving the residue in THF leads to the same 9:1 ratio of **4b** and **5b** (Scheme 3). This result is opposed to prior studies by Trogler, where shifting to more polar solvents tend to favour *cis*-dihydride species.⁹

To complete these studies and offer a first hint of the bimetallic H₂ cleavage mechanism, we carried out some preliminary studies to determine the kinetic isotope effect (KIE). Those were run in duplicates for the pairs **1a:2** and **1b:2** in both toluene-*d*₈ and THF-





Scheme 3 Isomerization of **5b** into **4b** promoted by THF as solvent.

d_8 at 0 °C to facilitate kinetic analysis (see Fig. S23–S26, ESI†). Interestingly, we calculated inverse KIEs for the reactions carried out in toluene, which account for 0.74 ± 0.04 for the formation of **4a** and an even stronger inverse KIE of 0.49 ± 0.09 associated to the appearance of **5b**. These values correlate well with our prior studies on hydrogen splitting by **1a–b**: $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ pairs (**1a**, 0.46 ± 0.04 ; **1b**, 0.50 ± 0.02), where a genuine bimetallic FLP mechanism could be stated based on a thorough experimental/computational approach.^{5c} On the contrary, kinetic studies performed herein in THF led to normal KIEs of 1.33 ± 0.05 and 2.11 ± 0.55 due to **1a**:**2** and **1b**:**2**, respectively. We are yet unsure on the precise nature of the contrasting KIEs as a function of solvent, but we have already gathered some relevant information that set the basis of our future mechanistic studies. First, similar and distinctive KIEs depend on solvent and not on product distribution, which speaks in favour of a common mechanism for H₂ cleavage. Also, the medium size phosphine seems to provide an ideal scenario to freeze the *cis-trans* isomerization, which cannot be rate-limiting as it occurs very rapidly (or never does occur for the more hindered **5c**). The strong effect of THF on the KIEs likewise suggests an active participation of the triflimide anion, which is expected to be strongly solvated only by the ethereal solvent. It probably has an impact as well on the availability of the electrophilic $[\text{Au}(\text{PR}_2\text{Ar})]^+$ fragment, which agrees with the moderately higher rates of H₂ splitting in THF (see ESI† for details). In addition, the absence of H/D scrambling when exposing compounds **1** to H₂/D₂ atmosphere (1:1) in either toluene or THF rules out the active participation of the ethereal solvent or triflimidate as basic partners for H–H bond cleavage.

In conclusion, we report the bimetallic activation of dihydrogen by three Au(I)/Pt(0) pairs whose monometallic fragments are all stabilized by sterically crowded terphenyl phosphines. Cooperation between the two metals is evinced by complete absence of reactivity for the individual complexes. Besides, having two metallic fragments of great steric bulk allowed us to isolate a unique structure characterized by a Au(μ -H)₂Pt core. It represents virtually the only example of a *cis*-dihydride group 10 d⁸ complex, of relevance for a broad spectrum of catalytic reactions, and in which isomerization is not geometrically quenched by using chelating scaffolds or favoured by particularly small phosphines.

N. H. and F. C. M. synthesised and characterised all new complexes and carried out reactivity studies. M. T. M. synthesised the platinum precursor. M. C. N. and J. C. supervised the overall project. N. H. and F. C. M. wrote the original draft and all authors contributed to review and editing.

This work was supported by the European Research Council (ERC Starting Grant, CoopCat, Project 756575) and Grants PID2019-110856GA-I00 and PID2020-113797R funded by

MCIN/AEI/10.13039/501100011033. We also thank US/JUNTA/FEDER, UE (Grants US-1380849 and US-1262266). F. C. M. acknowledges the Spanish Ministry of Universities for a Margarita Salas fellowship.

Conflicts of interest

There are no conflicts to declare.

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