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Cooperative Lewis Pairs Based on Late Transition Metals: Activation of Small Molecules by Platinum(0) and B(C₆F₅)₃**

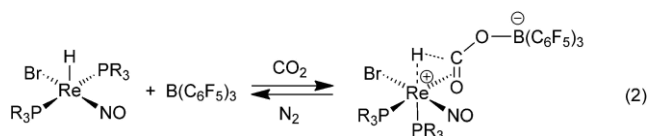
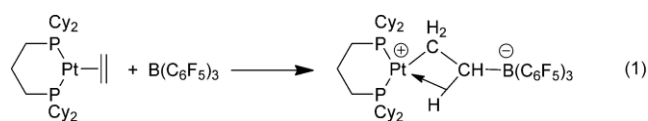
Sebastian J. K. Forrest, Jamie Clifton, Natalie Fey, Paul G. Pringle,* Hazel A. Sparkes, and Duncan F. Wass*

Abstract: A Lewis basic platinum(0)–CO complex supported by a diphosphine ligand and B(C₆F₅)₃ act cooperatively, in a manner reminiscent of a frustrated Lewis pair, to activate small molecules such as hydrogen, CO₂, and ethene. This cooperative Lewis pair facilitates the coupling of CO and ethene in a new way.

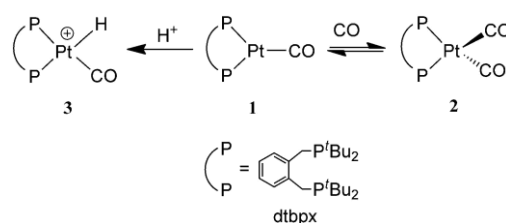
Frustrated Lewis pair (FLP) chemistry, in which Lewis acid–base pairs act cooperatively to activate small molecules such as hydrogen and CO₂, is one of the most exciting recent developments in main group chemistry, not least because of the promise of catalysis with such FLPs.^[1] We^[2] and others^[3,4] have extended this chemistry to transition metal systems, replacing the main group Lewis acid with an electrophilic Group 4 fragment to give highly reactive FLPs. For example, metallocene phosphinoaryloxide FLPs will perform the heterolytic cleavage of H₂, bind and reduce CO and CO₂, promote C–Cl, C–F, and C–O bond cleavage (in cyclic and noncyclic ethers), and catalyze amine–borane dehydrocoupling.^[2] Despite this powerful activation chemistry, the exploitation of these stoichiometric reactions in catalysis remains challenging because of the high oxophilicity of early transition metals—a move to the mid- and late-transition metals beckoned. We have previously pointed out the similarity between frustrated Lewis pair chemistry and the transition metal hydrogenation catalysts reported by DuBois and Bullock^[5] as well as the groups of Morris,^[6] Noyori,^[7] and Shvo.^[8] These are examples of chemical synergy between Lewis acidic metal centers and Lewis basic centers which could broadly be categorized as “cooperative” Lewis pairs.^[9]

Transition metals can also act as a Lewis base: Lewis acids (Z-type ligands) can coordinate to electron-rich metal centers.^[10] Some of these Lewis pairs have been shown to heterolytically cleave H₂ in a manner akin to FLP chemistry: Peters et al. described the addition of H₂ across Fe–B and Ni–B bonds.^[11] Braunschweig et al. reported the reaction shown in Equation (1), in which the Pt⁰–ethene complex reacts with

B(C₆F₅)₃ to give a b-agostic complex, a reaction reminiscent of FLP-chemistry.^[12] Berke et al. reported the reaction shown in Equation (2), in which CO₂ undergoes FLP-type activation by a hydridorhenium/B(C₆F₅)₃ system.^[13]



Bulky electron-rich diphosphine ligands have a long history in organometallic and catalytic chemistry.^[14] We recently reported the ability of such a ligand, dtbpx (see Scheme 1), to impart unusual stability to the low valent Pt⁰ complex 1, which was found to be amphoteric (Scheme 1): the



Scheme 1. Amphoteric properties of 1.

coordination of CO to give 2 (metal as Lewis acid) and protonation to give 3 (metal as base).^[15]

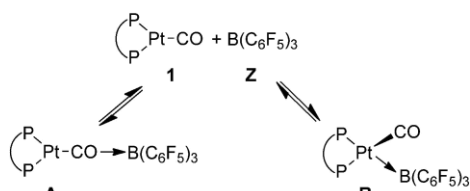
Both of these factors implied that a rich chemistry might result when 1 was combined with other Lewis acids or bases, and indeed we report here that the pairing of 1 with B(C₆F₅)₃ (Z) leads to the cooperative activation of H₂ and CO₂ as well as the coupling of CO and ethene in an unprecedented fashion.

When complex 1 and Z are mixed in toluene, the ³¹P, ¹H, ¹¹B, and ¹⁹F NMR spectra at ambient temperature appear unchanged from that of the starting materials and at 90 °C the signals are only slightly broadened. However when the 1/Z mixture is dissolved in PhCl, the ³¹P NMR signals are significantly broadened (w_{1/2} = 40 Hz) but remain close to the

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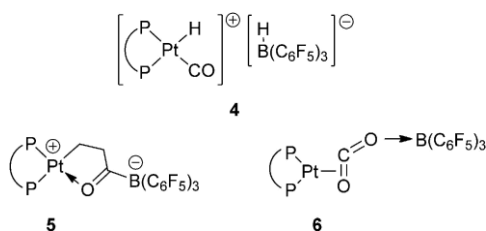
original chemical shifts. The signals broaden further at temperatures down to 60 °C but no extra signals were resolved. These observations are consistent with a Lewis acid/ base interaction between the components.^[16] To shed light on this interaction, solvated DFT-D calculations were performed on the two adducts A and B that can be envisaged to form between 1 and Z (Scheme 2).^[17] Formation of both adducts



Scheme 2. Potential adducts of 1 with Z.

was found to be favorable in terms of solvated potential energies, but slightly disfavored when free energy corrections were included (see the Supporting Information (SI) for a more detailed discussion).

Samples of the 1/Z pair reacted with H₂, C₂H₄, and CO₂ to give complexes 4, 5 and 6 respectively.



The 1/Z pair in C₆D₅Cl solution was converted quantitatively (according to ³¹P NMR spectroscopy) to 4 over 10 h under 1 atm of hydrogen. The cationic^[18] and anionic^[19] components of 4 have been previously characterized (with other counterions) and thus the solution structure assignment of 4 is unambiguous. Crystals of compound 4 were grown from a H₂-saturated chlorobenzene/hexane solution and the X-ray crystal structure is shown in Figure 1. The position of the H

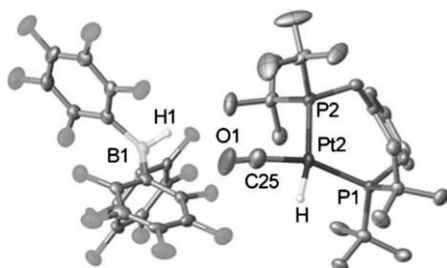
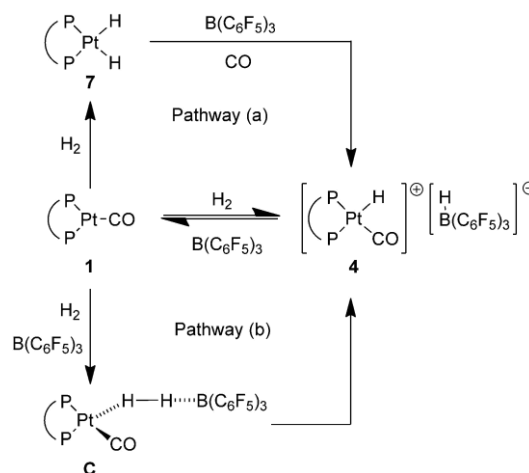


Figure 1. Crystal structure of 4. For clarity all hydrogen atoms (apart from H1 and H) are omitted. Selected bond lengths [Å] and angles [°]: Pt2–P1 2.3196(11), Pt2–P2 2.3884(12), Pt–C25 1.893(6), Pt–H 1.616; P1–Pt2–P2 103.67(4), P1–Pt–C25 156.74(19), P2–Pt2–C25 99.58(19). Further details of the structure are given in the SI.

atom attached to Pt was inferred and added fixed at the expected location.

We were interested in the mechanism of this reaction, because heterolytic hydrogen cleavage is often considered the archetypal reaction in main group FLP chemistry. Two plausible pathways for the reaction of H₂ with 1/Z are shown in Scheme 3. In pathway (a) H₂ adds to 1 with loss of



Scheme 3. Reaction of 1/Z with H₂.

CO in a classical organometallic oxidative addition reaction to give 7, followed by hydride abstraction with recoordination of CO. We previously reported that 1 reacts with H₂ in the absence of Z to give the dihydride complex 7, but this reaction is slow (50 % complete in 5 days) and yields a multitude of side products,^[15] in contrast to the rapid and clean formation of 4 in the presence of Z. Pathway (b) involves H₂ addition across the Pt···B in A or B to give C, a heterolytic-type mechanism reminiscent of FLP chemistry. Preliminary DFT-D calculations indicate species C was almost isoenergetic with A and B when considering potential energies (a more detailed discussion can be found in the SI).

Treatment of 1/Z in C₆D₅Cl with C₂H₄ gave a single product 5. Crystals of 5 were grown from ethene-saturated PhCl/hexane and its structure (Figure 2) shows that the CO of 1 and the ethene have combined to form a five-membered metallacycle with the borane bound to the carbon adjacent to the oxygen. The ³¹P and ¹H NMR data for 5 are consistent, with the structure in solution being the same as in the solid state.

The mechanism of this coupling of ethene and CO is intriguing. We previously showed^[15] that C₂H₄ displaces CO from 1 to give 8. Treatment of 8 with Z gave the b-agostic structure 9 (Scheme 4), an analogue of the product of the reaction shown in Equation (1).^[15] Crystals of 9 were grown from PhCl/hexane and its X-ray crystal structure is shown in Figure 3. Addition of CO to a PhCl solution of 9 resulted in the quantitative formation of 5 according to ¹H, ¹¹B, ¹⁹F, and ³¹P NMR spectroscopy. These observations support the viability of pathway (i) in Scheme 4 involving 8 and 9 as intermediates as well as the metallocyclobutanone adduct 10. It is also possible that 10 is accessed more directly from

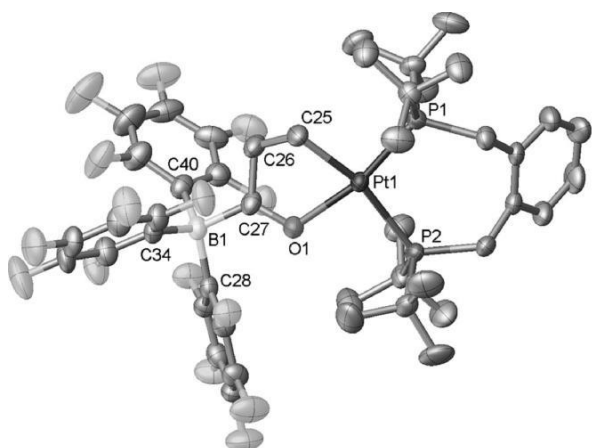


Figure 2. Crystal structure of 5. For clarity all hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.2576(14), Pt1–P2 2.4099(15), Pt–C25 2.2119(5), Pt1–O1 2.162(3), C25–C26 1.528(7), C26–C27 1.510(8), C27–O1 1.272(6), C27–B1 1.658(8); P1–Pt1–P2 102.74(5), P1–Pt1–C25 91.60(15), C25–Pt1–O1 76.62(17), O1–Pt1–P2 89.59(10), O1–C27–B1 124.9(5), O1–C27–C26 114.7(5), C26–C27–B1 120.1(4), C27–B1–C28 109.1(4), C27–B1–C34 101.6(4), C27–B1–C40 101.8(4). Further details of the structure are given in the SI.

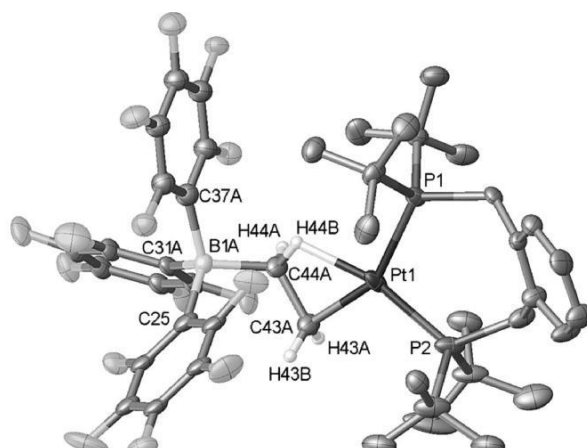
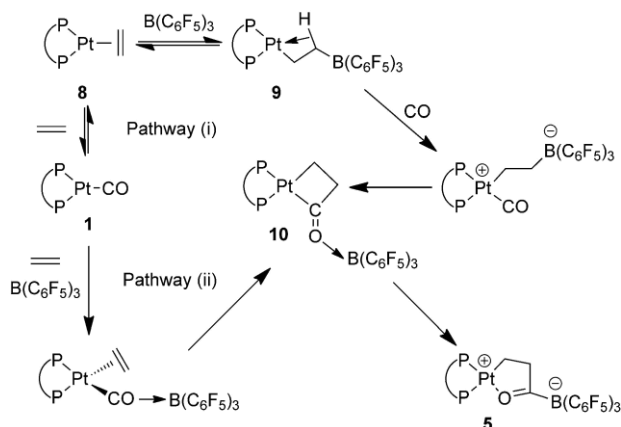


Figure 3. Crystal structure of 9. Complex 9 cocrystallized with 5 due to not fully excluding CO gas from the reaction mixture; the atoms corresponding to 5 are omitted for clarity. For clarity all hydrogen atoms (apart from H43A, H43B, H44A, and H44B) are omitted. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.3583(17), Pt1–P2 2.243(2), Pt1–C43A 2.057(16), Pt1–C44A 2.457(14), C43A–C44A 1.50(2), B1A–C44A 1.711(7); P1–Pt1–P2 103.50(7), P2–Pt1–C43A 105.3(5), P1–Pt1–C44A 113.7(4), C43A–Pt1–C44A 37.4(5), C44A–B1A–C25 108.1(9), C44A–B1A–C31A 106.2(8), C44A–B1A–C37A 108.6(8). Further details of the structure are given in the SI.



Scheme 4. Proposed pathways for the formation of 5.

1/Z through a novel borane-promoted insertion (pathway (ii) in Scheme 4). The ultimate step in both of the proposed pathways to 5 in Scheme 4 is also novel: a rearrangement of 10 involving a borane migration from O to C. Investigations are underway to probe this mechanism in more depth both experimentally and computationally.

The 1/Z mixture in C_6D_5Cl reacted over 3 days with CO_2 to give a major species (70 %) whose ^{31}P NMR parameters at 90 °C (δ 68.4, $J_{PP} = 3562$ Hz; 35.5, $J_{PP} = 3082$ Hz) are consistent with 6. Structure 6 was shown in a single-crystal X-ray structure (Figure 4) to have CO_2 bound between the platinum and boron and to feature an $h^2-C=O$ interaction.

As expected, the C–O bond lengths in 6 (1.262(3) and 1.273(3) Å) are longer than they are in free CO_2 , (1.155(1) Å).^[20] It is interesting to compare this to the phosphine–borane FLP system 11 (C–O bond lengths 1.2081(15) and 1.2988(15) Å) in which the phosphine Lewis

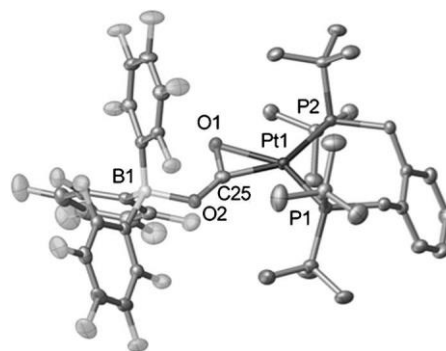
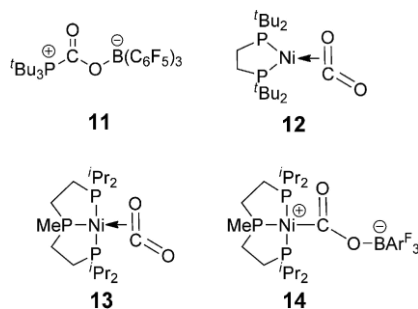


Figure 4. Crystal structure of 6. For clarity all hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.2249(7), Pt1–P2 2.3464(7), Pt–O1 2.2084(18), Pt1–C25 1.949(3), C25–O1 1.262(3), C25–O2 1.273(3), B1–O2 1.562(3); P1–Pt1–P2 104.55(2), P1–Pt1–C25 110.76(8), P2–Pt1–O1 110.15(5), C25–Pt1–O1 34.63(9), O1–C25–O2 127.5(3), O1–C25–Pt1 83.98(16), O2–C25–Pt1 148.6(2), C25–O2–B1 121.9(2), O2–B1–C26 112.0(2), O2–B1–C32 101.7(2), O2–B1–C38 103.5(2). Further details of the structure are given in the SI.

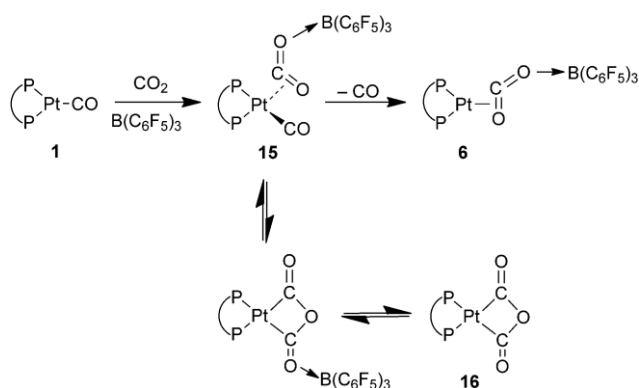
base is purely C-bound,^[21] and compounds 12 in which a side-on bound C–O is observed (compound 12: C–O bond lengths 1.266(3) and 1.200(3), Ni–C 1.868(2), Ni–O 1.904(2) Å).^[22] Compound 13 is somewhat similar to 12 in this regard, although it is noteworthy that 14, with an additional borane and therefore perhaps the closest analogue of 6, reverts to a simple C-bound Lewis base (the nickel species in this case).^[23]

Further support for the assignment of the solution structure of 6 comes from the spectra obtained from treatment of the 1/Z system with labeled $^{13}CO_2$. In the ^{31}P NMR spectrum of the labeled product 6* the signal for P1 which is



cis to the ^{13}C label, is a broad singlet (i.e., J_{PC} is less than the line width of ca. 22 Hz) and the signal for P2, which is trans to the ^{13}C label, is a doublet, with $J_{\text{PC}} = 45$ Hz. The ^{13}C NMR spectrum of **6*** at 40 $^{\circ}\text{C}$ showed a doublet at 186.5 ppm, $J_{\text{PC}} = 45$ Hz.

It is remarkable that the formation of **6** from **1** amounts to the substitution of CO by CO₂ on Pt. The presence of the Lewis acid is crucial, because no reaction was observed between **1** and CO₂ in the absence of B(C₆F₅)₃. It is therefore proposed that the initial reaction of CO₂ and **1**/Z occurs in a cooperative manner to form **15** followed by loss of CO (Scheme 5).



Scheme 5. Proposed pathway for the formation of **6**.

The product of the reaction of **1**/Z with $^{13}\text{CO}_2$ (95 % isotopically pure) was shown by ^{31}P NMR spectroscopy to be a mixture of the expected labeled **6*** and a significant amount (20 %) of unlabeled **6**. The source of unlabeled **6** must be the ^{12}CO ligand in **1**, which suggests that the symmetrical [C₂O₃]² complex **16** forms as a transient (see Scheme 5). Similar scrambling via four-membered metallacycles has been reported to occur upon treatment of [CpM(CO)₂] (M = Fe or Ru) with $^{13}\text{CO}_2$.^[24] This pathway suggests that the reaction of **1**/Z with CO₂ can be thought of as a metal-mediated oxygen transfer between CO₂ and CO rather than a simple ligand substitution.

In conclusion, the **1**/Z pair reacts cooperatively with all of the small molecules H₂, CO₂, and ethene in a manner reminiscent of FLP chemistry, the Pt⁰ complex acting as a transition metal Lewis base. The **1**/Z pair also mediates the coupling of ethene and CO in a new way to yield a rare example of an acyl borate complex. The use of transition

metals as the Lewis acid and now Lewis base components of “frustrated” or “cooperative” Lewis pairs is becoming increasingly established, and augurs well for applications in catalysis. These results may shed new light on classic studies using Lewis acids to promote transition metal CO and CN insertion chemistry.^[25]

Keywords: cooperative effects · frustrated Lewis pairs · small molecule activation

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