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. We and others 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, metalocene 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. 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 oxophilicity of early transition metals—

Frustrated Lewis Pairs

Scheme 1. Amphoteric properties of 1.

1. Amphoteric properties of 1.

Bulkly electron-rich diphosphine ligands have a long history in organometallic and catalytic chemistry. 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 coordination of CO to give 2 (metal as Lewis acid) and protonation to give 3 (metal as base).

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 ^{31}P, ^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 PPh₃Cl, the ^{31}P NMR signals are significantly broadened ($\Delta$), but remain close to the
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. 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). Formation of both adducts 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 cationic18 and anionic19 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 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 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, 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).

Subsequent 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 showed15 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). 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 metalloyclobutane 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–C1 2.162(3), C25–C26 1.528(7), C25–C27 1.510(8), 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), C25-Pt1-O1 109.1(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–C25 105.3(5), P1–Pt1–C44A 113.7(6), C43A–P1–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.

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), Pt1–C25 2.084(8), P1–C25 1.949(3), C25–B1 1.262(3), C25–O1 1.904(2) &). 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).

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 base is purely C-bound, and compounds 12 in which a side-on bound C–O is observed (compound 12: C–O bond lengths 1.266(3) and 1.355(3), Ni–C 1.868(2), Ni–O 1.904(2) &). 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).

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 $J_{PC} = 45$ Hz. The $^{13}$C NMR spectrum of $^{6}$ at 40 $^\circ$C showed a doublet at 186.5 ppm, $J_{PC} = 45$ Hz.

It is remarkable that the formation of 6 from 1 amounts to the of a simple ligand substitution.

The product of the reaction of 1/Z with $^{13}$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 [C$_2$O$_5$] 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 $^{13}$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 CO$_2$ and CO rather than a simple ligand substitution.

In conclusion, the 1/Z pair reacts cooperatively with all of the small molecules H$_2$, CO$_2$, and ethene in a manner reminiscent of FLP chemistry, the Pt$^0$ 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


![Scheme 5. Proposed pathway for the formation of 6.](image-url)


