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Transition Metal Frustrated Lewis Pairs

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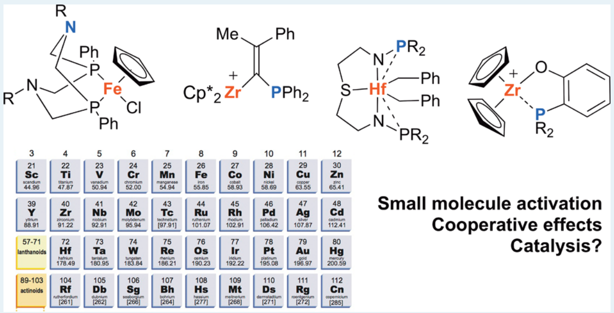
ABSTRACT: Frustrated Lewis pair chemistry, in which solution phase combinations of Lewis acid Lewis base pairs (FLPs) act cooperatively to activate small molecules, is one of the most exciting recent developments in main group chemistry. Far less developed but of growing interest are FLP systems containing transition metals as one of the Lewis acid/base components. This Perspective reviews recent developments in this area and makes connections to existing research into cooperative and ligand assisted catalysis.



KEYWORDS: *frustrated Lewis pairs, cooperative effects, ligand-assisted reactions, small molecule activation*

■ INTRODUCTION

Frustrated Lewis pair chemistry, in which solution phase combinations of Lewis acid Lewis base pairs (FLPs) act cooperatively to activate small molecules, is one of the most exciting recent developments in main group chemistry.[1] Initial studies focused on the heterolytic cleavage of dihydrogen, which offers the promise of metal-free catalytic hydrogenation.[2] This aspect has continued to be developed,[3] and several useful and unprecedented hydrogenation reactions have been described, perhaps most remarkably, the simple hydrogenation of aromatic amines;[4] however, the diversity of reactions reported is large and continues to grow.[5] The pioneering bulky phosphine and fluorinated borane systems (P^tBu_3/$B(C_6F_5)_3$) first reported by Stephan have been modified so that the specific reactivity of FLP systems can be controlled by subtle steric and electronic alterations to either the Lewis acidic or basic components. A significant recent advance has been the realization that steric "frustration" of Lewis adduct formation by incorporation of bulky Lewis base substituents is not necessary, so long as an equilibrium exists between free Lewis acid/base and the Lewis pair.[6−8] Such systems have been the key to recent catalytic reactions in which the enhanced acidity of the Lewis base-hydrogen activation product, with bases such as fluorinated aryl phosphines[7] or simple ethers,[8] leads to turnover. A great deal of work has also focused on extending the range of main group FLPs to other main group Lewis acids, particularly aluminum.[9] Linking the two components of the FLP into a single amphoteric molecule has also led to interesting results.[10]

Far less developed but of growing interest are FLP systems containing transition metals as one of the Lewis acid/base components. The benefits in extending the FLP concept to transition metals include the obvious greater structural diversity, but transition metal complexes have long been exploited as Lewis acid catalysts for a variety of organic synthetic transformations[11] and are used interchangeably with main group Lewis acids, depending on the specific substrate and transformation of interest. On a practical note, the synthetic protocols to modify the fluorinated boranes widely used in FLP chemistry can often be challenging. Contrast this with the endless possibilities for ligand modification to modulate the properties of metal systems—donor atom type, denticity, sterics, electronics—based on simple synthetic protocols. Transition metals also have an established track record of reaction types, such as migratory insertion, oxidative addition, and reductive eliminations that are the cornerstones of homogeneous catalysis. Combining such reactivity with the powerful activation chemistry of FLPs offers new possibilities for the design of catalysts that are difficult to envisage if one is restricted to main group systems alone.

This Perspective reviews recent work in the area. It is not a completely comprehensive review of transition metal FLPs; as will be discussed later, transition metal frustrated Lewis pairs can be viewed in the wider context of "cooperative effects" in catalysis, and inevitably, there are a great many examples of cooperativity or ligand-assisted reactions (often predating the development of main group FLPs) that could be viewed as FLPs but are not included here. Rather, this article presents work in which the original authors make clear their inspiration from main group FLP chemistry while putting this in context of selected examples of wider cooperative effects. This is a nascent area of chemistry but one ripe with possibilities, and we can confidently predict that readers of this Perspective in coming years will find many more examples of transition metal FLPs in the literature.

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EARLY TRANSITION METALS

Group 4 complexes are prominent examples of electrophilic, Lewis acidic transition metal complexes with much development over the past 30 or so years driven by applications in metallocene and postmetallocene olefin polymerization catalysis.[12] The possibility of replacing main group Lewis acids with such complexes was hinted early in the development of FLP chemistry,[13] and an example of the activation of N_2O by a zirconocene phosphine pair was reported in a wider study of the activation of this small molecule by main group pairs.[14] Reaction of $[Cp^*_2Zr(OMe)][B(C_6F_5)_4]$ with $t\text{-}Bu_3P$ and subsequent treatment with N_2O gave the N_2O FLP-activated product $[Cp^*_2Zr(OMe)ON_2P^tBu_3][B(C_6F_5)_4]$.

We became interested in developing a transition metal system that mimics and extends main group FLP chemistry, and our cationic group 4 metallocene phosphinoaryloxide complexes are the most widely studied transition metal FLP to date.[15] Synthetic protocols for cationic group 4 metallocene chemistry are well-established, and related methods have been reported for these cationic group 4 metallocene phosphinoaryloxides. The structures and reactivity of such complexes are highly dependent on both the steric bulk of the phosphine fragment and the metallocene, with the expected trend that increasing the steric bulk of either one increases to degree of "frustration" between the Lewis acid and Lewis basic components of the complex. For example, the cyclopentadienyl derivative **2** (Figure 1) is isolated as a complex with a long (2.8826(5) Å) but persistent Zr−P bond, whereas the pentamethylcyclopentadienyl complex **1** has no Zr−P interaction in the solid state or solution; instead, being isolated as a labile chlorobenzene or fluorobenzene solvate. Similar effects are seen when varying the steric bulk of the phosphine fragment so that a combination of $P(t\text{-}Bu)_2$ or $P(\text{mesityl})_2$ with pentamethylcyclopentadienyl ligands gives no Zr−P interaction, but the less encumbered $P(i\text{-}Pr)_2$ gives a Zr−P bond (2.8215(8) Å).

Changes to the metal can also influence the nature of the metal-phosphine interaction, with the M−P bond in isostructural compounds decreasing in the order Hf > Zr ≫ Ti, as expected. Titanium complexes give useful insight into how changes in oxidation state can also influence the degree of frustration, with the related Ti(III) derivative having a longer Ti−P bond compared with the Ti(IV) analogue.[16] In general, these transition metal FLPs result in reactivity patterns that are predicted by the FLP concept, even in cases when specific reactions are not known for main group systems (Figure 1).

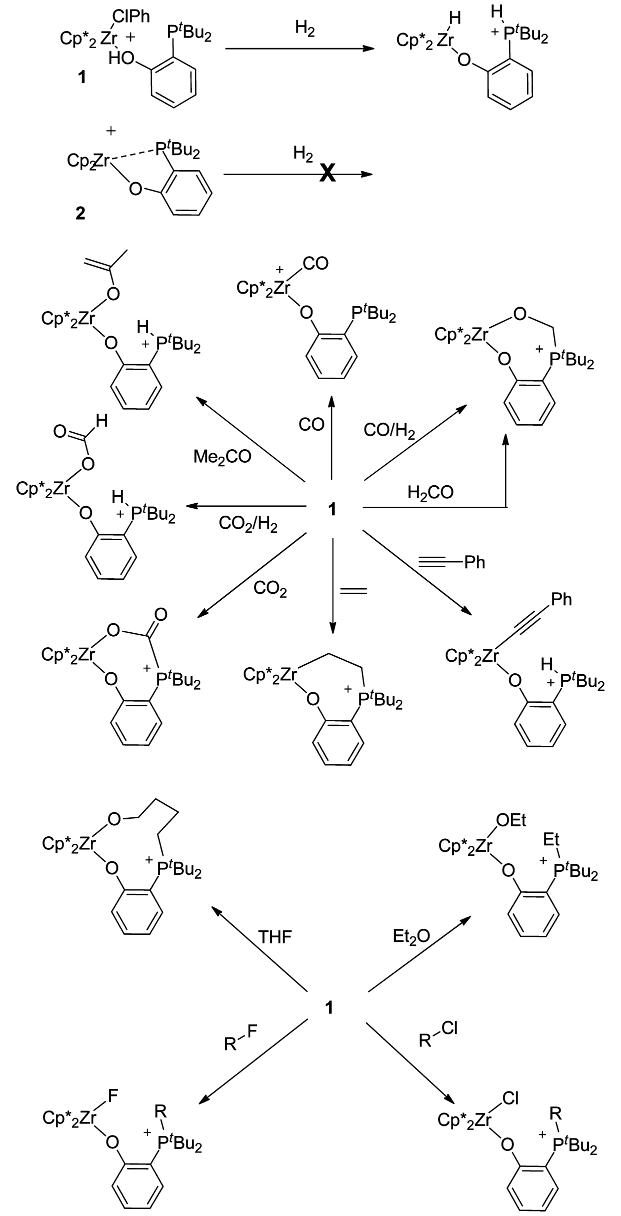

Figure 1. Reactivity of zirconocene phosphinoaryloxide FLPs.

Compound **1** rapidly cleaves dihydrogen in a heterolytic fashion across the Zr and P centers to irreversibly give a Zr−H phosphonium complex in high yield, even under very mild conditions. Heterolytic hydrogen cleavage proves to be very sensitive to the nature of the ancillary ligands so that the Cp derivative **2** does not cleave hydrogen under these conditions, but the intermediately bulky Cp/Cp* derivative rapidly and reversibly activates hydrogen. Although it is tempting to correlate activation with the presence and length of a Zr−P bond, the fact that a $P(i\text{-}Pr)_2$ derivative that has an even shorter Zr−P bond than **2** also reversibly activates hydrogen suggests that more subtle arguments are needed.

There is a large body of work concerning the hydrogenation of d^0 metal complexes, and the rate of hydrogenolysis is noted to be strongly dependent on the nature of the ancillary ligands, and more specifically, is substantially faster for Cp* compounds compared with the analogous Cp compounds. One argument is that the relatively electron-rich Cp* ligand provides extra electron density for backbonding to η^2-dihydrogen intermediates.[17] This serves to explain the observed trends seen here and is supported by preliminary calculations. Titanium gives different results, characterized by a propensity to be reduced by hydrogen to a Ti(III) species. Neutral Ti(III) FLPs of the type $[Cp_2Ti(2\text{-}OC_6H_4P(t\text{-}Bu)_2)]$ can also be obtained via the reversible chemical reduction of Ti(IV) species or reaction of phosphino alcohol synthons with Ti(III) precursors.[16] The reactivity of these d^1 species holds exciting possibilities but remains to be explored.

The reactivity of these Zr−P pairs has been explored with olefins, alkynes, acetone, THF, and CO_2, reacting in ways previously observed for main group systems in every case.[15] The potential of main group FLPs to sequester and activate CO_2 is an exciting advance, since it implicates the utility of this substrate in catalytic reactions. In this regard, the reaction of the hydrogen activation product of zirconocene phosphinoaryloxide FLPs with CO_2 to give the formate complex as an intermediate for stepwise CO_2 reduction is a promising result. Synthesis gas and CO chemistry in general is a foundation of much of the current petrochemical industry, and this area is starting to be explored for main group FLPs with interesting results. Complex **1** when treated with CO forms a surprisingly stable nonclassical CO complex (υ_{co} = 2163 vs 2144 cm^{-1} for free CO). Reaction of the hydrogen activation product of **1** with CO or direct reaction with 1:1 CO/H_2 results in a single stepwise reduction of the CO to a bound formaldehyde complex. Reacting **1** with gaseous formaldehyde also obtains the same complex.

When exploring the solubility characteristics of these complexes, an unexpected result was that they react rapidly and cleanly with CH_2Cl_2 to yield the C−Cl cleaved products. In fact, this is a general reaction, and zirconocene phosphinoaryloxide FLPs react with a range of alkyl chlorides in the same way. The same reactivity patterns are observed, even with alkyl fluorides. Clearly, the strength of the Zr−F bond provides a strong driving force for this reaction, but complexes capable of the cleavage of unactivated C−F bonds are rare and suggest possible applications in defluoronation reactions. A related reaction is C−O cleavage for ethers. This is well-known for THF in main group systems, and virtually identical reactivity patterns were observed many years previously when Lewis bases were combined with electrophilic transition metals, although this was not recognized as an example of a frustrated Lewis pair at the time. However, this reaction is more general for zirconocene phosphinoaryloxide FLPs, which react with noncyclic ethers such as diethyl ether to give C−O cleavage products. This is a rare S_N2 type reaction of diethyl ether in which the nuclephilic nature of the ethoxide appears to be drastically increased by the presence of the electrophillic zirconium center. This FLP-type reactivity of THF adducts has also allowed investigation of the isolobal group 3 (lanthanum) metallocene phosphinoaryloxide complex, the synthesis of which is frustrated by the dearth of reliable methods for obtaining coordinating solvent-free complexes. However, THF adducts of such complexes are easily synthesized and prove to be surprisingly stable in solution with respect to ring-opening of the coordinated THF. Only after 3 days at 110 °C is the ring-opened product observed, confirming the analogy to the Zr system and, indeed, main group FLPs.

Group 3 systems inspired by FLP chemistry have been more extensively studied by Piers et al., developing chemistry based on a decamethylscandocinium cation and $HB(C_6R_5)_3$ anion (Figure 2).[18]

Although unreactive toward propene and D_2, exposure of a solution of **3** to 1 atm of CO resulted in the formation of **4** and **5** in 12 h with structures based on **5** favored by the introduction of a *para*-hydrogen to the fluorinated borane. Further work focused on the catalytic deoxygenative hydrosilation of carbon dioxide.[19] Exposure of a solution of **3-F** to 1 atm CO_2 instantaneously led to the formation of $[Cp^*_2Sc][HCO_2B(C_6F_5)_3]$ **6-F** by acceptance of hydride from the anion (Figure 3). DFT studies revealed a plausible mechanism in which the unusual binding mode of the carbon dioxide leads to high electrophilicity on the central carbon atom, which along with the spatial proximity of the hydride on boron yields rapid conversion to HCO_2^-.

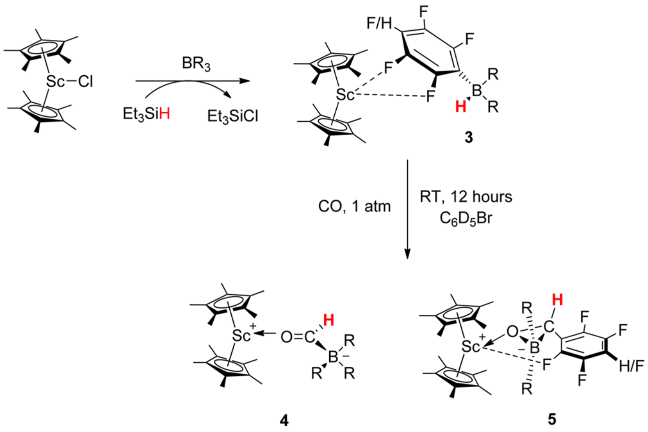

Figure 2. Generation of scandium-based FLP **3** and subsequent reaction with CO.

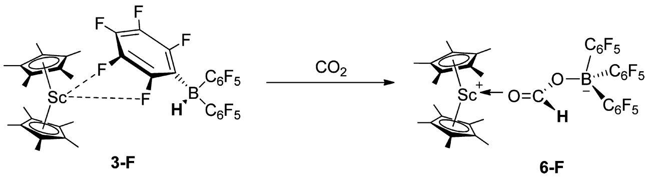

Figure 3. Reaction of scandium-based FLP **3-F** with CO_2.

Attempts to complete an analogous reaction in which a C−C bond would be formed, that is, via reaction of CO_2 with $[Cp^*_2Sc][MeB(C_6F_5)_3]$, led to formation of the scandium ion pair, but no reaction was observed with CO_2.

Returning to metallocene phosphinoaryloxide FLPs, although the powerful stoichiometric reactivity is interesting and augers well for future development, to date, the only reaction reported for such FLPs that achieves catalytic turnover is the dehydrocoupling (or dehydrogenation) of amine-boranes.[15a] This reaction has attracted significant attention because of the potential for the parent amine-borane NH_3BH_3 as a hydrogen storage material and, in general, as a controlled route to new inorganic polymers.[20] A wide variety of substituted amine-boranes have been investigated, and the products of dehydrocoupling are both a function of the amine substituents and the catalyst used.[21] In many cases, Me_2NHBH_3 is a common model substrate that dehydrocouples to give the cyclic dimer $[Me_2NBH_2]_2$ with most catalysts. Treatment of Me_2NHBH_3 with 1 mol % of **2** results in rapid evolution of hydrogen and the expected cyclic dimer $[Me_2NBH_2]_2$ in >98% yield after only 10 min at room temperature (Figure 4).

The activity of this catalyst (in this case, a TOF of ~500 h^{-1}) is exceptional compared with all known group 4 systems.[21] Other metallocene phosphinoaryloxide FLPs in which the metal and substitution pattern are varied are also successful to various degrees. Despite the superficial similarity of these systems to previous group 4 metallocene catalysts for amine-

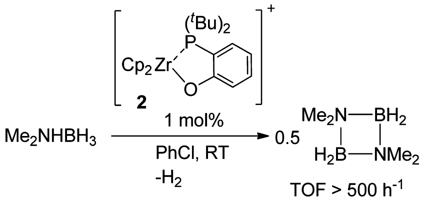

Figure 4. Catalytic amine-borane dehydrocoupling with transition metal FLP **2**.

borane dehydrogenation (for example those based on Ti(II) species formed in situ either from $[Cp_2TiCl_2]/^{n}BuLi$ or as well-defined $[Cp_2Ti(PMe_3)_2]$ complexes), the mechanisms by which the two catalyst familes operate are fundamentally different. The $[Cp_2TiCl_2]/^{n}BuLi$ catalyst relies on an oxidative/reduction Ti(II)/Ti(IV) manifold; it is notable that the heavier homologues are reported to be either much slower (Zr) or inactive (Hf), presumably because of the greater difficulty in shuttling between these oxidation states, as compared with titanium.[22] By contrast, only high-valent zirconium is present in the FLP system, and preliminary mechanistic studies point to a mechanism related to that proposed for stoichiometric dehydrogenation with the metal-free Lewis pair $P^{t}Bu_3/B(C_6F_5)_3$,[23] only with the crucial difference that dihydrogen elimination is facile for the transition metal FLPs, regenerating the active catalyst and leading to catalytic turnover. Several catalytic intermediates have been isolated, included an example of a Shimoi-type σ-complex. Crucially, the essential nature of the phosphine fragment is again highlighted, since the known complex $[Cp_2ZrO^{t}Bu][B(C_6F_5)_4]$ is inactive for this reaction.[24]

A different zirconocene-phosphine FLP has been developed by Erker and co-workers on the basis of a synthetic strategy of insertion of a diphenylphosphino-substituted alkyne into a Zr–CH_3 bond to give the FLP **7** (Figure 5). Even with the strong Zr–P interaction (2.6670(7) Å) for this system, reactivity toward typical FLP substrates was demonstrated.[25] Initial studies involving addition of alkyl isonitriles and pivalonitrile led to simple coordination to the Zr center with little change to the Zr–P bond length (2.667(1) Å in **7** vs 2.711(1) Å in **8**).

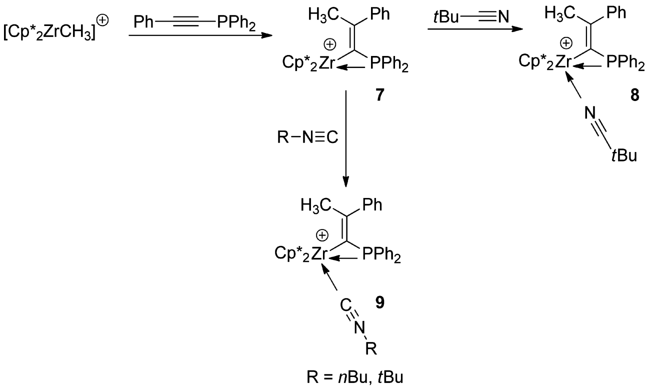

Figure 5. Synthesis of zirconium/phosphorus-based FLP **7** and reaction with alkyl isonitriles and pivalonitrile.

However, reaction with a variety of other unsaturated reagents led to small molecule activation in an FLP-like manner (Figure 6). Upon addition of *t*-butyl isocyanate or CO_2, the respective Zr–P inserted products **10** and **11** were generated. The reaction with *t*-butyl isocyanate had resulted in addition of the carbonyl group across the Zr–P bond, generating a 5-membered metallaheterocyle, with the phosphorus adding to the sp center of the isocyanate. Similarly, the CO_2 product resembles that of previous systems, with a Zr–O bond length of 2.097(2) Å.

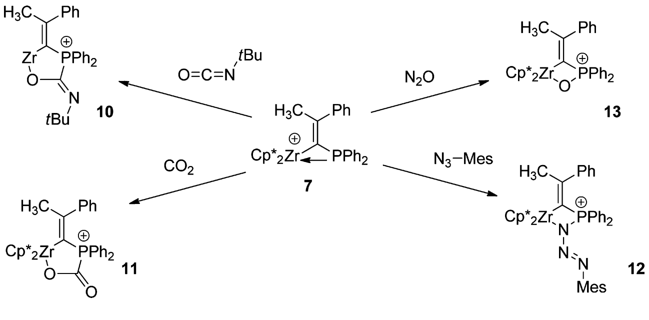

Figure 6. Small molecule activation of FLP **7**.

Addition of mesityl azide led to the rapid insertion of the terminal mesityl azide nitrogen into the Zr–P bond **12**, resulting in a 4-membered ring with the N_3-mesityl unit lying trans at the N(2)–N(3) double bond. Reaction with N_2O led to the unprecedented oxidation at the phosphine and generation of N_2 and **13.**

Exposure of a solution of **7** in CH_2Cl_2 to 1.5 bar of H_2 led to the generation of **14** and **15** in a 1:1 mixture (Figure 7). This is thought to be generated via the dihydrogen intermediate **7-H$_a$**, which rapidly converts to **7-H$_b$** by protonolytic cleavage of the Zr–C(sp^2) σ-bond.[26] This highly reactive species can then react with a CH_2Cl_2 solvent molecule, cleaving a C–Cl bond to generate the postulated intermediate **16**, which is known to react with an additional CH_2Cl_2 molecule, liberating CH_3Cl and **15**. Further evidence for this postulated dihydrogen intermediate was proven by reaction of **7** with H_2 in benzene-d_6 in the presence of minimal THF. This led to generation of the zirconium salt **17** with a THF molecule stabilizing the Zr^+ and the alkenylphosphane **18**.

This rapid hydrogen cleavage and further reaction is clearly potentially useful in catalytic reactions involving hydrogen transfer, and indeed, exposure to a number of alkenes generally gave good conversions (for example, styrene was hydrogenated to ethylbenzene in 93% conversion in 30 min at 1 mol % loading). With conjugated enones, the enone undergoes 1,4-addition with phosphorus acting as the nucleophile to generate the 7-membered metallocycle. The carbonyl oxygen is bonded to zirconium, forming an endocyclic zirconium enolate fixed in the *Z* confirmation. Compound **7** also undergoes analogous 1,4-addition with ynones, giving a 7-membered metallocyle that also shows interaction between the centrally bonded =C= and zirconium (2.382(3) Å).

Early transition metal FLP chemistry is not limited to metallocene systems. Stephan and co-workers have developed hafnium complexes **19** with tridentate mixed-donor sulfur-phosphinoamide ligands (Figure 8).[27] There is also a degree of interaction between the hafnium metal center and phosphorus, for example, with **19-Ph** exhibiting P–Hf bonds of 2.6897(8) and 3.0743(8) Å.

Exposure of these complexes to a CO_2 atmosphere led to the synthesis of different complexes, depending on the basicity of the phosphine Lewis base. Species **22** reveals double CO_2 capture with iPr P-substituents. A more complex reactivity pattern is observed with Ph P-substituents, including a bimetallic species **20**, a corresponding monomer **21**, and a double CO_2 product that in this case is unstable upon removal of the CO_2 atmosphere, reverting to **20**.

■ MID AND LATE TRANSITION METALS

Explicit examples of FLPs based on late transition metals are yet to be reported, although FLP-inspired systems are now emerging. There is also a much more substantial body of work concerned with heterolytic hydrogen cleavage with combinations of mid/late transition metals and bases.[28] This predates the development of main group FLP chemistry by some years but clearly has a close relationship with it. The recent work of

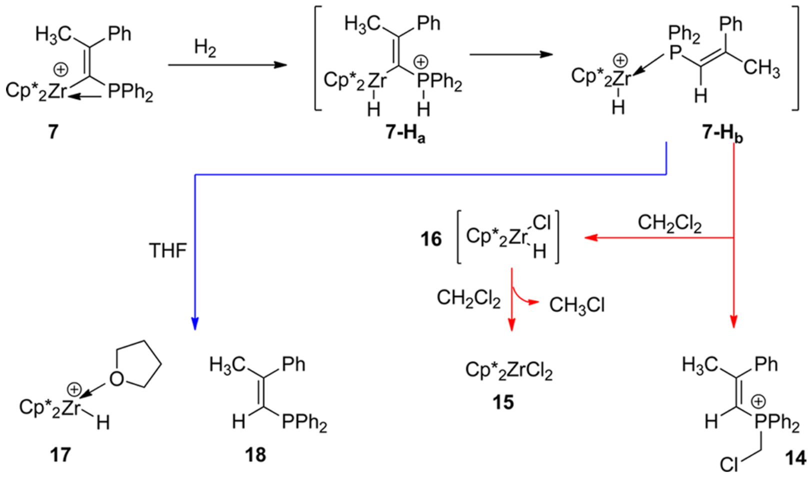

Figure 7. Heterolytic cleavage of dihydrogen by FLP 7.

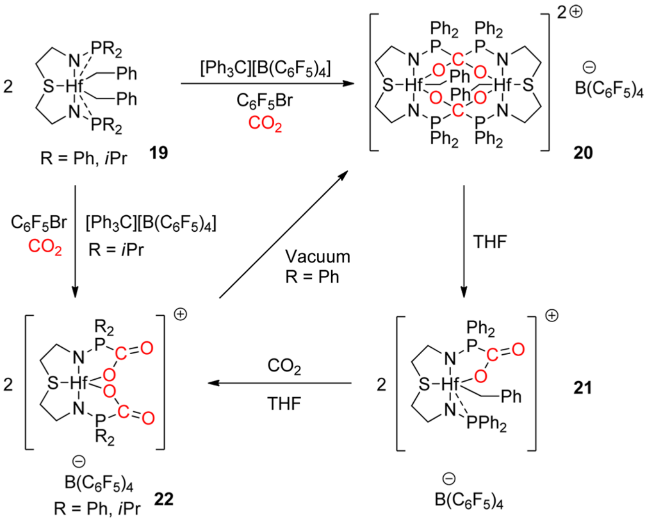

Figure 8. Activation of CO_2 by hafnium/phosphorus complex **19**.

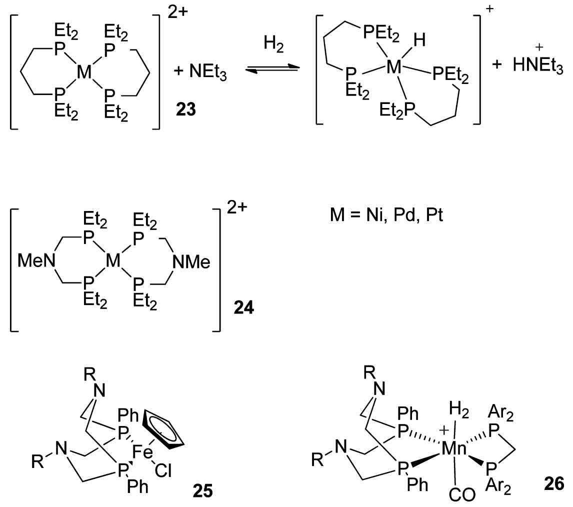

Figure 9. Heterolytic cleavage of dihydrogen by combination of mid/late transition metals and bases.

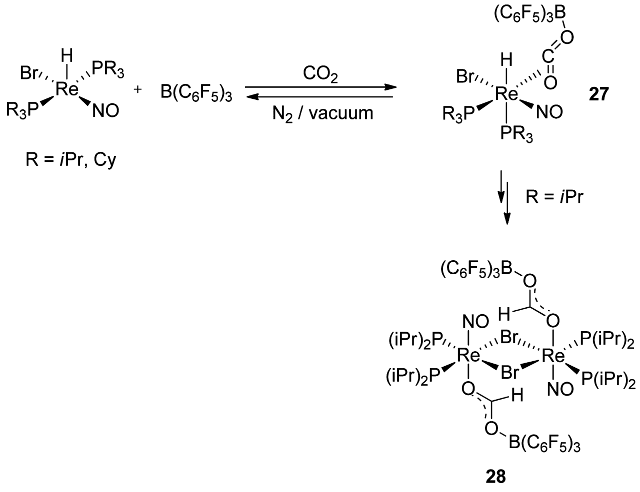

Figure 10. CO_2 capture by rhenium-hydride/boron-based pair.

DuBois and Bullock with various complexes containing either internal or external bases is particularly noteworthy;[29] a number of systems capable of heterolytic hydrogen cleavage are illustrated in Figure 9.

Berke and co-workers exploited the Lewis basic properties of metal hydrides in combination with an external Lewis acid to activate CO_2 (Figure 10).[30] Exposure of $16e^-$ complexes of the type $[ReHBr(NO)(PR_3)_2]$ (R = *iso*-propyl or cymene) to a CO_2 atmosphere did not result in any reactivity. However, upon addition of the Lewis acid $B(C_6F_5)_3$, reversible CO_2 capture was seen to generate complexes **27**. Over time, reorganization led to the generation of the η^1-formato complex **28** (for R = *iso*-propyl).

Addition of a 2 M excess of silane led to the stoichiometric formation of a number of silicon containing products, including the reduced CO_2 in the form of $(Et_3SiO)_2CH_2$. The catalytic hydrogenation of CO_2 in the presence of a number of sterically hindered bases (e.g., triethylamine, $P(tBu)_3$, and TMP) was also studied. This led to the formation of the formate-base ion pair, $[HCOO^-][Base^+]$, with TON varying from 7 (Et_3N) to 174 (di-*iso*-propylamine) leading to the conclusion that the efficacy of CO_2 hydrogenation increases with a more basic, sterically crowded base. A similar approach has been described with intramolecular Lewis acid functions, in which the stepwise reduction of CO is observed.[31]

Stephan and co-workers developed a system based on ruthenium supported by a tripodal $N((CH_2)_2NHPiPr_2)_3$ ligand,

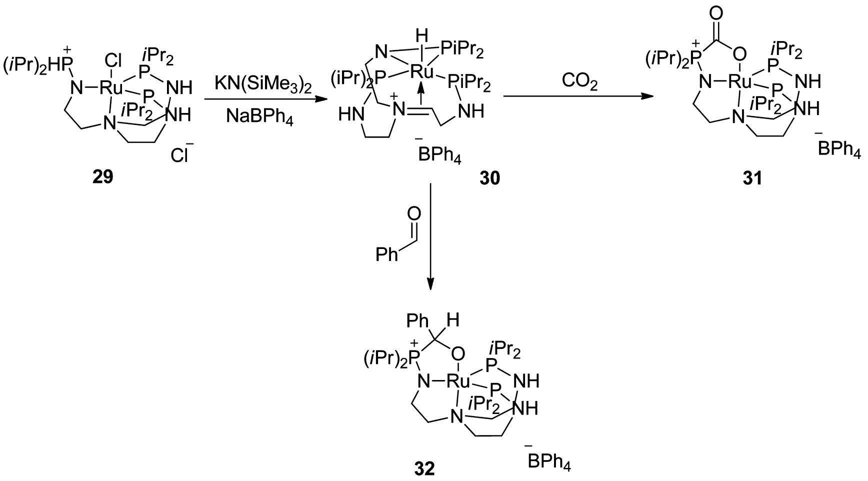

Figure 11. Synthesis of ruthenium complex **30** and subsequent reactivity with CO_2 and benzaldehyde.

29 (Figure 11).[32] Halide and subsequent proton abstraction with $KN(SiMe_3)_2$ followed by anion metathesis led to the generation of an FLP-like species **30**.

The ring strain associated with the 3-membered Ru−P−N ring could be relieved by addition of CO_2 to generate **31**. The bound CO_2 is thermally stable up to 80 °C but can be released by additional of a 5 M excess of HBpin, yielding MeOBpin and $O(Bpin)_2$. To probe the mechanism, complex **32**, similar to the hydroboration intermediate, was prepared by reaction of the FLP **30** with benzaldehyde. Reaction of **32** with HBpin resulted in formation of $PhCH_2OBpin$, suggesting the mechanism occurs via a captured aldehyde-like intermediate.

■ COOPERATIVE CATALYSIS, LIGAND ASSISTED REACTIONS, INTERNAL BASES

Cooperative effects in catalysis, in which reactions are facilitated by direct involvement of the supporting ligand framework, usually by means of an internal base, are well established. Such systems have been widely reviewed.[33] There is a striking similarity between the heterolytic cleavage of hydrogen that is an essential feature of these cooperative transition metal catalysts and main group FLPs, a connection that has been made previously.[33a,34] Examples of complexes in which cooperative effects between internal Lewis bases and the metal center are important include most spectacularly the asymmetric catalytic hydrogenation results obtained with Noyori−Morris type catalysts (**33** and **35**, Figure 12).[35]

The involvement of the basic nitrogen donor atoms in hydrogen cleavage, which therefore shuttle between amine and amide ligand types during catalysis, has been well established. Related systems have been developed by Shvo[36] **36** and Casey **34**[37] (also Figure 12) in which substituted cyclopentadienone ligands act as the internal base and facilitate cleavage of hydrogen. The structures of such complexes, in which the pendant oxygen cannot coordinate the metal center because of the rigid architecture enforced by coordination of the η^4-cyclopentadienone or η^5-hydroxycyclopentadienyl, could be considered a type of Lewis pair 'frustration' and is again crucial for their successful application as catalysts.

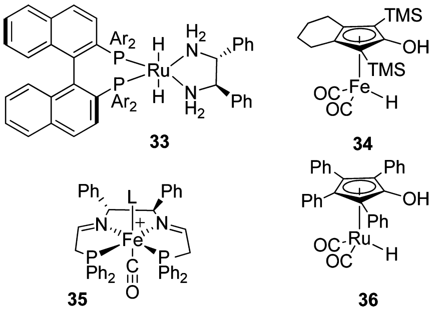

Figure 12. Selected examples of cooperative or ligand assisted hydrogenation catalysts.

One point of difference between transition metals and main group systems is the possibility for coordination of the hydrogen molecule in a $M-\eta^2-H_2$ fashion prior to reaction with base. This coordination activates the hydrogen molecule, in particular, by causing a significant increase in acidity, with a pK_a as low as −6 in some cases.[38] At this pK_a, similar to that of sulfuric acid, deprotonation by even mild bases is not unexpected. There have been several studies that provide elegant experimental methods for determining this change in pK_a upon coordination,[10] and there is the expected strong correlation between lower the pK_a in the coordinated hydrogen complex favoring hydrogen activation. Although a stepwise coordination followed by deprotonation mechanism therefore seems to differentiate these transition metal systems from the concerted mechanisms often invoked for hydrogen activation with main group FLPs, in fact, the picture is more complicated. Although $M-\eta^2-H_2$ complexes have been isolated as intermediates in many cases, there are also examples in which such species are not observed directly, and yet, hydrogen cleavage still occurs. In fact, hydrogen cleavage and ligand-assisted hydrogenation reaction by transition metals in general are not easily categorized, and in reality, there are likely to be many intermediate cases; this subject has been review in detail by Morris.[39]It should also be noted that for main group FLPs, precoordination of substrates (specifically alkenes) as Van der Waals complexes is emerging as an important consideration.[40]

There are many other related examples of complexes designed with internal bases for cooperative reactivity that could be used to make the analogy with main group FLPs.[41] Cleavage of hydrogen across a transition metal and a main group Lewis acid (typically a borane, such as a boratrane complex) is also an area of recent interest. This approach, related but orthogonal to having an internal Lewis base, has been recently reviewed.[42] There are many possibilities for extending this chemistry.

It is also worth highlighting examples in the vast literature on cocatalysts for metallocene and postmetallocene olefin polymerization catalysts, in which ion-pairing effects, such as weak interactions between fluorinated aryl borate and aluminate counterions and cationic alkyl metallocene fragments, have proved to be crucial.[43] Although it seems to stretch the analogy to suggest this interaction is a type of FLP, the specific counterion used can have a profound effect on issues such as polypropylene or polyacrylate tacticity, implying both parts of the pair are important in determining reactivity. In certain cases for acrylate polymerization, the concerted reactivity of cation and anion has been exploited in what Chen terms “amphicatalytic polymerization”.[44]

There is also a large, established chemistry in which small organic molecules that are already bound to a transition metal center undergo reaction with Lewis acids or bases, in this context usually thought of as electrophiles or nucleophiles. Indeed, the ability of transition metal complexes to activate coordinated molecules toward reactivity patterns that would not be observed in the free molecules is a central feature in the utility of all organometallic chemistry. Nucleophilic attack on coordinated olefins is an excellent example, an extremely well studied reaction that has an important role in catalysis; for example, in the Wacker process.[45] To suggest that this reaction is an example of FLP chemistry seems to be overextending the analogy, and yet, even here, the boundaries between the chemistries are not clear-cut; in early transition metal d^0 systems, the lack of metal-to-olefin retro-donation results in only a handful of examples of isolable metal olefin complexes,[46] and a situation closer to FLP systems for nucleophilic attack in such cases could be proposed.

SUMMARY AND OUTLOOK

It is clear that FLP chemistry is not limited to the main group but can be extended to the entire periodic table. The transition series provides fertile ground for development, and any complex that has Lewis basic or Lewis acidic properties could potentially form a component of an FLP. This is an area at an early stage of development, but initial results are extremely promising, and given the myriad possibilities for complex design, it seems to be at the cusp of considerable growth.

It is also reasonable to say that frustrated Lewis pairs in general are a subset of wider cooperative effects in small molecule activation and catalysis. As it is becoming increasing apparent that complete steric frustration between the Lewis acidic and basic components is not always necessary,[8] this relationship becomes even clearer: indeed, “cooperative” Lewis pairs rather than “frustrated” Lewis pairs would be a more apt moniker for many systems. Transition metals have a long track record in cooperative catalysis and ligand assisted reactions, and one may speculate whether terming some of these systems as frustrated Lewis pairs is useful. We are of the opinion that viewing some transition metal complexes as such brings fresh insights.

What does the future hold for transition metal FLPs? Clearly there are unlimited combinations of transition metal and main group Lewis acids and bases still to explore. A worthwhile focus for these studies would be to develop a more systematic fundamental understanding of the structure and reactivity of such complexes. But the great, untapped potential of such systems is in catalysis. This is virtually unexplored; even the wider area of “cooperative” catalysis is largely limited to hydrogenation reactions. The diverse small molecule activation chemistry associated with FLPs, when combined with the powerful catalytic chemistry of transition metal complexes, should allow the development of new catalytic processes that are beyond the capabilities of current homogeneous catalysts.

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Notes

The authors declare no competing financial interest.

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