Reactivity of [Pt(P'Bu$_3$)$_2$] with Zinc(I/II) Compounds: Bimetallic Adducts, Zn–Zn Bond Cleavage, and Cooperative Reactivity

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**ABSTRACT:** Metal-only Lewis pairs (MOLPs) based on zinc electrophiles are particularly interesting due to their relevance to Negishi cross-coupling reactions. Zinc-based ligands in bimetallic complexes also render unique reactivity to the transition metals at which they are bound. Here we explore the use of sterically hindered [Pt(P'Bu$_3$)$_2$] (1) to access Pt/Zn bimetallic complexes. Compounds [(P'Bu$_3$)$_2$Pt → Zn(C$_6$F$_5$)$_2$] (2) and [Pt(ZnCp*)$_2$] (3) (Cp* = pentamethylylcyclopentadienyl) were isolated by reactions with Zn(C$_6$F$_5$)$_2$ and [Zn$_2$Cp*$_2$], respectively. We also disclose the cooperative reactivity of 1/ZnX$_2$ pairs (X = Cl, Br, I, and OTf) toward water and dihydrogen, which can be understood in terms of bimetallic frustration.

## INTRODUCTION

The unique features of bimetallic complexes are behind the rapid development that has recently taken place in the field. Among these complexes, metal-only Lewis pairs (MOLPs), that is, bimetallic compounds in which the two metal atoms are held together exclusively by a dative M → M bond, constitute a fascinating family. MOLPs constructed around Lewis acidic zinc(II) fragments are particularly appealing due to their relevance to Negishi cross-coupling catalysis. In fact, recently reported [(PCy$_3$)$_2$Pt]$_2$ (1) to access Pt/Zn bimetallic complexes. Compounds [(P'Bu$_3$)$_2$Pt → Zn(C$_6$F$_5$)$_2$] (2) and [Pt(ZnCp*)$_2$] (3) (Cp* = pentamethylylcyclopentadienyl) were isolated by reactions with Zn(C$_6$F$_5$)$_2$ and [Zn$_2$Cp*$_2$], respectively. We also disclose the cooperative reactivity of 1/ZnX$_2$ pairs (X = Cl, Br, I, and OTf) toward water and dihydrogen, which can be understood in terms of bimetallic frustration.

The parent monometallic components remain inactive. On these grounds, we decided to inspect the formation and reactivity of zinc-containing MOLPs based on [Pt(P'Bu$_3$)$_2$] (1). In doing so, we have examined its reactivity with a range of zinc precursors, more precisely ZnX$_2$ (X = Cl, Br, I, and OTf) toward water and dihydrogen, which can be understood in terms of bimetallic frustration.
Scheme 1. Reaction of $[\text{Pt}(\text{P}^3\text{Bu}_3)_2]$ (1) with Zinc (Pseudo)halides and Organozinc Compounds$^a$

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\[
\begin{array}{c|c|c|c}
\text{P}^3\text{Bu}_3 & \text{ZnX}_2 \text{ or ZnR}_2 & \text{Pt} & \text{No reaction} \\
\hline
\text{P}^3\text{Bu}_3 & \text{Zn(C}_6\text{F}_5)_2 & \text{Pt} & \text{10 equiv} \\
\hline
\end{array}
\]
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$^a$Top: X = Cl, Br, I, and OTf; R = Me, Et, and Ph, C$_5$Me$_5$; solvent = C$_6$D$_6$, CD$_2$Cl$_2$, THF, or C$_6$H$_5$F.

MOLP formation in Pt(0) compounds due to the reduced s character of the Pt–P bonds in the bimetallic adduct.$^{5,12}$ Alongside this, a new set of $^{31}$P{1H} resonances at −115.7, −157.4, and −162.0 ppm (cf. Zn(C$_6$F$_5$)$_2$: $\delta = -118.0, -152.5$, and −160.5 ppm) was recorded.

The molecular structure of 2 was authenticated by single-crystal X-ray diffraction studies (Figure 1a) confirming the proposed bimetallic formulation. This represents the first example of a Pt(0)/organozinc MOLP. It exhibits a T-shaped geometry around the platinum center, slightly distorted due to the steric pressure exerted by the tert-butyl groups in close proximity to the perfluorinated aryl rings (P–Pt–P = 165.32(4)$^\circ$). As in other bisphosphine Pt(0)-based MOLPs, the Pt–P bond distances (2.325 Å on average) are modestly elongated with respect to that of precursor 1 (2.25 Å).$^{14}$ The Pt–Zn bond length (2.4663(6) Å) is shorter than in the related [(phen)Ar$_2$Pt$^{II}$ → Zn(C$_6$F$_5$)$_2$] (phen = phenanthroline) adduct, which contains a less basic Pt(II) donor (2.5526(5) Å),$^6$ and just marginally longer than that in [(C$_7$F$_3$)$_2$Pt → ZnBr$_2$] (2.4040(6) Å).$^{10}$ Steric constraints in 2 force the perfluorophenyl rings to bend away from the platinum center, with the C25–Zn–C31 angle of 117.73(18)$^\circ$ being significantly reduced compared to those of Zn(C$_6$F$_5$)$_2$ (172.6)$^5$ and even [(phen)Ar$_2$Pt$^{II}$ → Zn(C$_6$F$_5$)$_2$] (134.8)$^6$.

At variance with its fluorinated analogue, the less acidic ZnPh$_2$ does not react with 1, as monitored by variable temperature NMR and visually inferred by the colorless appearance of the reaction mixture even after prolonged periods of time. Similarly, no Pt → Zn interactions were detected upon addition of 10 equiv of ZnR$_2$ (R = Me, Et, and Ph, C$_5$Me$_5$) to C$_6$D$_6$ solutions of 1, again pointing out the need for a highly electrophilic Zn center to overcome the distortion of the linear Pt(0) precursor to accommodate the bimetallic dative bond. Next, we examined the reactivity of 1 with the Zn(I) dimer [Zn$_2$Cp*$_2$]$^+$ in light of its capacity to form zinc-rich polymetallic complexes with transition metal precursors.$^{16}$ For instance, Fischer has investigated the reactivity between [Zn$_2$Cp*$_2$] and low-valent M(0) precursors (M = Ni, Pd, and Pt), recurrently identifying the homolytic cleavage of the Zn–Zn bond by insertion of the transition metal.$^{17}$

$^{31}$P{1H} NMR monitoring of an equimolar mixture of 1 and [Zn$_2$Cp*$_2$] in C$_6$D$_6$ showed the release of free phosphine (δ = 63.0 ppm) without any other detectable intermediate. It soon became evident that a 3-fold excess of the Zn(I) dimer was required to achieve complete consumption of 1. Under these conditions, the highly unstable compound [Pt(ZnCp*$_3$)$_6$] (3) forms as the major species (ca. 80% NMR yield) by insertion of the Pt center into the Zn–Zn bonds of three molecules of [Zn$_2$Cp*$_2$]. (Scheme 2). Compound 3 slowly precipitates as bright orange crystals, which allowed us to ascertain its heptametallic structure by X-ray diffraction analysis (Figure 1b). It can be described as an unusual 16-electron octahedral complex in which each vertex is occupied by a neutral 1-5-coordination (d$_{Zn-C}$ ≈ 2.24–2.37 Å), and a second pair binds to the C$_5$ ligand in an η$^2$-fashion. The third pair exhibits an η$^1$-binding (shortest d$_{Zn-C31}$ = 2.06(3) Å; the rest >2.6 Å). While the former two pairs

Figure 1. ORTEP diagram of compounds 2 and 3. Hydrogen atoms have been excluded, and methyl groups of Cp* ligands are represented in wire-frame format for clarity. Thermal ellipsoids are set at 50% probability.

Scheme 2. Synthesis of Compound 3 by the Reaction between 1 and [Zn$_2$Cp*$_2$]

\[
\begin{align*}
\text{P}^3\text{Bu}_3 \text{Pt} & \xrightarrow{25 \text{C}, 20 \text{ min}} \text{C}_6\text{H}_6 \quad \text{Cp}^*\text{Zn} \quad \text{ZnCp}^* \quad 2 \text{P}^3\text{Bu}_3 \\
\text{P}^3\text{Bu}_3 & \text{Pt} \quad 3 \text{ZnCp}^* \quad \text{Cp}^*\text{Zn}_2 \quad \text{ZnCp}^* + \text{2P}^3\text{Bu}_3 \\
\end{align*}
\]

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present Pt–Zn bond distances (2.419(3) and 2.401(4) Å) comparable to prior examples,\(^{17}\) the \(\eta^1\)-bound ZnCp\(^*\) fragment displays a Pt–Zn bond (2.238(7) Å) shortened by 0.34 Å with respect to the sum of the covalent radii (2.58 Å).\(^{18}\) In THF-\(d_6\) solution, a single \(^1\)H NMR resonance at 1.92 ppm indicates rapid dynamic exchange among the possible conformations of the ZnCp\(^*\) ligands. In fact, low temperature NMR (up to \(-80\) °C) was insufficient to freeze the dynamic process.

Compound 3 strongly resembles the closed-shell 18-electron \([\text{Pt}(\text{ZnCp})_4(\text{ZnR})_4]\) species (R = Me and Et) described by Fischer and co-workers.\(^{17e}\) The latter compounds exhibit rather long Zn···Zn distances (ranging from 2.812 to 3.115 Å), which have been regarded as noninteracting or only weakly interacting.\(^{17e}\) Similar Zn···Zn distances were found in 3 (>3.0 Å). To confirm the negligible interaction between the zinc centers in 3, we computationally explored the topology of the model system Pt(ZnH)\(_8\) analogous to the model Pt(ZnH)\(_8\) used by Fischer and Frenking to understand the bonding situation in \([\text{Pt}(\text{ZnCp})_4(\text{ZnR})_4]\).\(^{17b,e}\) using the QTAIM (Quantum Theory of Atoms in Molecules) method (see computational details in the Supporting Information). Figure 2 shows the Laplacian distribution of Pt(ZnH)\(_6\) computed in the Zn–Pt–Zn plane. The solid lines connecting the atomic nuclei are the bond paths, while the small green spheres indicate the corresponding bond critical points.

| compound | \(\text{Pt}(\text{ZnH})_6\) | \(\text{Pt}(\text{ZnH})_8\) | \(\text{Pt}(\text{ZnH})_8^{\text{a}}\) |
|----------|--------------------------|--------------------------|--------------------------|
| \(\Delta E_{\text{elstat}}\) | -234.1 | -288.9 | -279.0 |
| \(\Delta E_{\text{elstat}}\) | 434.7 | 468.8 | 486.0 |
| \(\Delta E_{\text{disp}}\) | -518.4 (77.5%) | -575.6 (76.0%) | -583.4 (76.3%) |
| \(\Delta E_{\text{orb}}\) | -145.5 (21.8%) | -175.2 (23.1%) | -181.6 (23.7%) |
| \(\Delta E_{\text{int}}\) | -4.8 (0.7%) | -6.9 (0.9%) | - |
| \(q(Pt)\) | -0.21 | -0.21 | - |

\(^{a}\)Energy values (kcal/mol) taken from ref 17b. \(^{b}\)Percentage values in parentheses give the contributions to the total attractive energy \(\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}\). \(^{c}\)Computed Hirshfeld charges at the platinum center.

def2-TZVPP level including the original data reported previously for Pt(ZnH)\(_8\) (\(D_{4d}\)) computed at the rather similar ZORA-BP86/TZ2P//RI-BP86/def2-TZVPP level. From the data in Table 1, the resemblance between both Pt(0) compounds becomes evident. Although the computed interaction energy, \(\Delta E_{\text{int}}\), is higher in Pt(ZnH)\(_8\) (which is not surprising as the Pt center interacts with two additional one-electron ZnH ligands), in both cases, the platinum atom bears a small negative charge, which is consistent with the chosen neutral fragments. Despite that, the main contribution to the bonding comes from the electrostatic interactions, representing ca. 76–77% of the total attractions. The contribution resulting from orbital interactions (mainly involving the d atomic orbitals of platinum) is significantly much lower and those coming from dispersion interactions can be considered as negligible. This therefore indicates that the bonding in newly prepared compound 3 (and the analogous \([\text{Pt}(\text{ZnCp})_4(\text{ZnR})_4]\)) can be viewed mainly as a result of the electrostatic interactions between the platinum center and the surrounding ZnCp\(^*\) ligands.

We next interrogated the ability of these Pt/Zn bimetallic pairs to activate both polar and nonpolar bonds using water and dihydrogen as model substrates. We mainly directed our efforts toward pairs containing inorganic zinc salts, as organozinc compounds (\(1/\text{ZnR}_2, 2\) and 3) were rapidly hydrolyzed in the presence of water. Besides, those species remained inactive toward \(\text{H}_2\) under all attempted conditions. In contrast, equimolar benzene suspensions of 1 and \(\text{ZnX}_2\) (\(X = \text{Cl}, \text{Br}, \text{I}, \text{and OTf}\)) readily react with \(\text{H}_2\text{O}\) (5 equiv) by means of O–H bond activation (Scheme 3).\(^{11,12}\) It is

\begin{center}
\textbf{Scheme 3. Activation of Polar O–H Bond by Pt(0)/Zn(II) FLPs}
\end{center}

![Scheme 3. Activation of Polar O–H Bond by Pt(0)/Zn(II) FLPs](image-url)
important to remark that 1 does not react with water on its own even under more forcing conditions (80 °C, 24 h).

However, in the presence of zinc halides formation of trans-[PtHX(PBU3)2] (X = Cl, Br, and I; 4, Scheme 3) is evidenced by a distinctive low-frequency 1H NMR resonance due to the metal hydride (δ = −19.2 (4a, Cl), −18.4 (4b, Br), and −16.4 (4c, I) ppm), exhibiting scalar coupling to both 31P (JHP ≈ 12 Hz) and 195Pt (JHP ≈ 1100 Hz) nuclei. In the case of Zn(OTf)2, the reduced coordinating capacity of the triflate moiety compared to halide anions led to the cationic hydrido-aquo complex trans-[PtH(OH)2(PBU3)2]+(5) as the only observable product. Formation of compounds 4 and 5 is accompanied by the appearance of a fine precipitate of zinc hydroxide salts.

As mentioned briefly above, water activation by combining 1 with transition metal Lewis acids [Cu(CH3CN)4]PF6 and AgNTf2,12 has recently been reported. Formation of an intermediate characterized by a Pt → M dative interaction is proposed as the initial step in both cases, after which the cooperative cleavage of the O–H bond takes place. Our experiments indicate that bimetallic adduct formation is not favored for zinc salts; thus, an FLP-type mechanism seems more likely. In fact, we have already demonstrated that compound 1 acts as a Lewis basic site in bimetallic FLPs by partnering it with sterically crowded Au(I) compounds.19 Our prior mechanistic investigations allowed us to conclude that the Pt(0)/Au(I) pairs mediate the cleavage of the H–H bond in dihydrogen by a genuine FLP mechanism.190 We wondered if the same would apply for the Pt/Zn pairs investigated herein. Once again, it is worth mentioning that neither 1 nor zinc (pseudo)halides react with H2 on their own (Scheme 4a). Similarly, the combination of 1 and zinc halides in benzene or THF did not provide any reactivity upon exposure to H2 (2 bar, 70 °C). However, in the presence of the more acidic Zn(OTf)2, dihydrogen activation proceeds smoothly to generate Pt(II) dihydride 620 even under mild conditions (H2 1 bar, 25 °C, 5 h; Scheme 4b). Compound 6 is produced in ca. 85% spectroscopic yield, exhibiting a characteristic 1H NMR resonance at −2.91 ppm (JHP = 16.4 Hz, JHPt = 780.6 Hz). Formation of 6 suggests a catalytic role of Zn(OTf)2 during the hydrogenation of 1, which has previously been observed for the hydrogenation of imines catalyzed by the same zinc species.23 In fact, decreasing the amount of Zn(OTf)2 to only 5 mol % with respect to 1 under otherwise identical conditions led to the formation of 6 in comparable yields. In fact, the amount of zinc and the nature of the solvent did not have any apparent influence on the extent of dihydride produced, which was obtained in yields between 80 and 90% in all cases. Attempts to reach full hydrogenation of 1 were unsuccessful despite longer reaction times, higher temperatures and increasing loadings of zinc. These observations imply that hydrogenation of 1 is a reversible process. We confirmed this idea by adding Zn(OTf)2 (10 mol %) to a THF-d6/C6D6 (2:1) solution of dihydride 6 in a sealed NMR tube (Scheme 4c).

Reaction monitoring evidenced evolution to a mixture of both 1 and 6 in a ca. 2:3 ratio after 5 h, as well a minute amount of free H2 identified by an 1H NMR peak at 4.42 ppm. Replacing the atmosphere by H2 (1 bar) led to 6 in around 85% yield.

The presence of zinc is also essential for dehydrogenation, since in its absence the release of H2 could not be detected even by heating 6 under dynamic vacuum (70 °C, 50-mbar, Scheme 4d). This process resembles both the dehydrogenation of [PtH(PCy3)2] promoted by C60,22 as well as the role played by Zn(CF3)2 in facilitating biaryl reductive elimination from Zn(II) complexes.6

The mechanism of reversible heterolytic dihydrogen splitting holds great interest due to its connection to hydrogen production and the action of hydrogenase enzymes. It has also been largely studied as a benchmark transformation to gauge FLP behavior and, despite its apparent simplicity, remains a topic of intense research.24 In this line, the absence of adduct formation from the pair 1/Zn(OTf)2 along with its cooperative bond activation could be understood in terms of FLP principles.25 We performed several experiments to gain some preliminary mechanistic information. First, we determined the kinetic isotopic effect (KIE) for H2 versus D2 splitting, which has a strong inverse value of 0.59 ± 0.1 (see the Supporting Information for details). This is an uncommon finding that compares well with our previously reported Pt(0)/Au(I) bimetallic FLP (KIE = 0.46 ± 0.04), where a genuine frustrated mechanism was ascertained.196 We postulated that the origin for such a strong inverse KIE derived from an FLP productlike transition state whose bimetallic structure offered an assortment of H-containing bending modes that contribute to the zero-point energy (ZPE). We anticipate that a similar transition state in the present system (B in Scheme 5) would analogously derive in a strong inverse KIE, as observed experimentally. Direct oxidative addition of dihydrogen over 1 to form cis-[PtH2(PBU3)2] followed by Zn-assisted isomerization4 could be considered an alternative mechanism (C in Scheme 5). However, solutions of 1/Zn(OTf)2 catalyze rapid (t1/2 < 15 min) exchange between H2 and D2 to produce HD (δ = 4.36 ppm, JHD = 42.6 Hz) in a statistical amount, which seems to disfavor a classical oxidative addition route. In fact, the individual monometallic species mediate the exchange at a considerably slower pace (t1/2 > 2 days). Interestingly, compound [PtH(PBU3)2]+, which would be an intermediate during FLP-type H2 activation, promotes H/D scrambling at a rate comparable to the bimetallic pair. This agrees with its existence as a transient intermediate during the hydrogenation of 1, thus supporting the idea of a bimetallic FLP mechanism (through B in Scheme 5).

### Scheme 4. Reactivity of Bimetallic Pair 1/Zn(OTf)2 with H2

|  | Reaction | Conditions | Result |
|---|----------|------------|--------|
| (a) | 1 + H2 (1 bar) | 70 °C, C6H6 | No reaction |
| (b) | Pt/C6H6 or THF | C6H6 (1 bar) | PBU3 + PBU3 → Pt − H2 |
| (c) | Zn(OTf)2 | THF-−d6/C6D6 (2:1) | 25 °C, 5 h | 6 + 1 |
| (d) | Vacuum | 70 °C, C6H6 | 5 × 10−2 bar | No reaction |
experiments cannot yet rule out a more traditional bimetallic H₂ activation route implying a transient dative Pt → Zn bond (A in Scheme 5) or the active participation of triflate substituents.²⁶

ConclusionsIn summary, we report the formation of two new Pt/Zn polymetallic complexes. While the metal-only Lewis adduct [(P̃Bu₃)₂Pt → Zn(C₆F₅)₂] (2) represents the first Pt(0)/organozinc MOLP, the reaction between [Pt-(P̃Bu₃)₂] (1) and [Zn₂Cp⁶] yields the hexametallic, homoleptic compound [Pt(ZnCp⁶)] (3). At variance with previous Zn-rich polymetallic compounds, the latter does not fulfill the 18 valence electron rule, since it is considered an octahedral 16-electron species. While these complexes remain inactive toward dihydrogen, pairing I with Zn(OTf)₂ results in cooperative dihydrogen cleavage. Preliminary kinetic and isotopic exchange experiments support a bimetallic FLP-type mechanism. Similarly, the activation of O–H bonds in water proceeds readily in the presence of Pt/Zn pairs, while the individual components reveal no activity.

■ EXPERIMENTAL SECTION

General Considerations. All preparations and manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 3 Å molecular sieves, and degassed prior to use. Toluene (C₇H₈) and diethyl ether were distilled under nitrogen over sodium. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over sodium/benzophenone, benzophenone. (D₆)Benzene was dried over molecular sieves (3 Å), respectively. All solvents were dried, stored over 3 Å molecular sieves, and degassed prior to use. Toluene (C₇H₈) and the solution was stirred for 30 min, then kept at room temperature.

The Supporting Information is available free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) (a) Campos, J. Bimetallic Cooperation Across the Periodic Table. Nat. Rev. Chem. 2020, 4, 696–702. (b) Farley, C. M.; Uyeda, C. Organic Reactions Enabled by Catalytically Active Metal–Metal Bonds. Trends Chem. 2019, 1, 497–509. (c) Berry, J. F.; Thomas, C. M. Multimetallic Complexes: Synthesis and Applications. Dalton Trans. 2017, 46, 5472–5473. (d) Berry, J. F.; Lu, C. C. Metal–Metal Bonds: From Fundamentals to Applications. Inorg. Chem. 2017, 56, 7577–7581. (e) Pye, D. R.; Mankad, N. P. Bimetallic Catalysis for C−C and C−X Coupling Reactions. Chem. Sci. 2017, 8, 1705–1718. (f) Bauer, J.; Braunshweig, H.; Dewhurst, R. D. Metal-Only Lewis Pairs with Transition Metal Lewis Bases. Chem. Rev. 2012, 112, 4329–4346.

(2) (a) Alvarez, R.; De Lera, A. R.; Aurrerecochea, J. M.; Durana, A. Bimetallic Intermediates in the Formation of Nucleophilic Allenylzincs from Allenylhalopalladums: A DFT Study. Organometallics 2007, 26, 2799–2802. (b) Fuentes, B.; García-Melchor, M.; Lledós, A.; Morante, F.; Casares, J. A.; Upmanyu, G.; Espinet, P. Palladium Round Trip in the Negishi Coupling of trans-PdMeCl(PMe3)2 with ZnMeCl: An Experimental and DFT Study of the Transmetalation Step. Chem. - Eur. J. 2010, 16, 8596–8599. (c) Oeschger, R. J.; Chen, P. A Heterobimetallic Pd–Zn Complex: Study of a d3−d0 Bond in Solid State, in Solution, and in Silico. Organometallics 2017, 36, 1465–1468. (d) Paenur, E.; Gershoni-Poranne, R.; Chen, P. Trends in Metallophilic Bonding in Pd–Zn and Pd–Cu Complexes. Organometallics 2017, 36, 4854–4863.

(3) (a) Casares, J. A.; Espinet, P.; Fuentes, B.; Salas, G. Insights into the Mechanism of the Negishi Reaction: ZnRX versus ZnR2 Reagents. J. Am. Chem. Soc. 2007, 129, 3508–3509. (b) delPozo, J.; Gómez, J.; Casares, J. A.; Alvarez, R.; Espinet, P. Organometallic Nucleophiles and Pd: What Makes ZnMe2 Different? Is Au Like Zn? Organometallics 2015, 34, 3120–3128.

(4) (a) Liu, Q.; Lan, Y.; Liu, J.; Li, G.; Wu, Y.-D.; Lei, A. Revealing a Second Transmetalation Step in the Negishi Coupling and Its Competition with Reductive Elimination: Improvement in the Interpretation of the Mechanism of Bialy Syntheses. J. Am. Chem. Soc. 2009, 131, 10201–10210. (b) van Asselt, R. V.; Elsevier, C. J. Rigid bidentate nitrogen ligands in organometallic chemistry and homogeneous catalysis. 8. On the Mechanism of Formation of Homocoupled Products in the Carbon–Carbon Cross-Coupling Reaction Catalyzed by Palladium Complexes Containing Rigid Bidentate Nitrogen Ligands: Evidence for the Exchange of Organic Groups between Palladium and the Transmetalating Reagent. Organometallics 1994, 13, 1972–1980.

(5) Liberman-Martin, A. L.; Levine, D. S.; Ziegler, M. S.; Bergman, R. G.; Tilley, T. D. Lewis Acid–Base Interactions Between Platinum(II) Diaryl Complexes and Bis(perfluorophenyl)zinc: Strongly Accelerated Reductive Elimination Induced by a Z-type Ligand. Chem. Commun. 2016, 52, 7039–7042.

(6) (a) Bajo, S.; Alférez, M. G.; Alcaide, M. M.; López-Serrano, J.; Campos, J. Metal-only Lewis Pairs of Rhodium with p and d-Block Metals. Chem. - Eur. J. 2020, 26, 16833–16845. (b) Lohrey, T. D.; Maron, L.; Bergman, R. G.; Arnold, J. Heterotetrametallic Re-Zn-Zn-Re Complex Generated by an Anionic Rhienium(I) β-Diketiminato. J. Am. Chem. Soc. 2019, 141, 800–804. (c) Gour, J. J.; Qiu, Y.; Khade, R. L.; Chan, N. H.; Filatov, A. S.; Zhang, Y.; Lewis, J. C. Synthesis, Characterization, and Theoretical Investigation of a Transition State Analogue for Proton Transfer during C-H Activation by a Rhodium-Pincer Complex. Organometallics 2019, 38, 1407–1412. (d) Jayathine, U.; Mazzacano, T. J.; Bagherzadeh, S.; Mankad, N. P. Heterobimetallic Complexes with Polar, Unsupported Cu–Fe and Zn–Fe Bonds Stabilized by N-Heterocyclic Carbenes. Organometallics 2013, 32, 3986–3992.

(7) (a) Bajo, S.; Alférez, M. G.; Alcaide, M. M.; López-Serrano, J.; Campos, J. Metal-only Lewis Pairs of Rhodium with p and d-Block Metals. Chem. - Eur. J. 2020, 26, 16833–16845. (b) Lohrey, T. D.; Maron, L.; Bergman, R. G.; Arnold, J. Heterotetrametallic Re-Zn-Zn-Re Complex Generated by an Anionic Rhienium(I) β-Diketiminato. J. Am. Chem. Soc. 2019, 141, 800–804. (c) Gour, J. J.; Qiu, Y.; Khade, R. L.; Chan, N. H.; Filatov, A. S.; Zhang, Y.; Lewis, J. C. Synthesis, Characterization, and Theoretical Investigation of a Transition State Analogue for Proton Transfer during C-H Activation by a Rhodium-Pincer Complex. Organometallics 2019, 38, 1407–1412. (d) Jayathine, U.; Mazzacano, T. J.; Bagherzadeh, S.; Mankad, N. P. Heterobimetallic Complexes with Polar, Unsupported Cu–Fe and Zn–Fe Bonds Stabilized by N-Heterocyclic Carbenes. Organometallics 2013, 32, 3986–3992.

(8) (a) Bajo, S.; Alférez, M. G.; Alcaide, M. M.; López-Serrano, J.; Campos, J. Metal-only Lewis Pairs of Rhodium with p and d-Block Metals. Chem. - Eur. J. 2020, 26, 16833–16845. (b) Lohrey, T. D.; Maron, L.; Bergman, R. G.; Arnold, J. Heterotetrametallic Re-Zn-Zn-Re Complex Generated by an Anionic Rhienium(I) β-Diketiminato. J. Am. Chem. Soc. 2019, 141, 800–804. (c) Gour, J. J.; Qiu, Y.; Khade, R. L.; Chan, N. H.; Filatov, A. S.; Zhang, Y.; Lewis, J. C. Synthesis, Characterization, and Theoretical Investigation of a Transition State Analogue for Proton Transfer during C-H Activation by a Rhodium-Pincer Complex. Organometallics 2019, 38, 1407–1412. (d) Jayathine, U.; Mazzacano, T. J.; Bagherzadeh, S.; Mankad, N. P. Heterobimetallic Complexes with Polar, Unsupported Cu–Fe and Zn–Fe Bonds Stabilized by N-Heterocyclic Carbenes. Organometallics 2013, 32, 3986–3992.
organometallics: Selective functionalization of [M-(ZnCp*)2(ZnCH3)]+ (M = Ni, Pd, Pt) with terminal alkynes to yield [M(ZnCp*)3(ZnCCSPr2)]+. J. Organomet. Chem. 2018, 860, 78–84. (d) Bolleman, T.; Freitag, K.; Gemel, C.; Seidel, R. W.; Fischer, R. A. Reactivity of [Zn(Cp*)2] toward Transition-Metal Complexes: Synthesis and Characterization of [Cp*M(ZnCp*)2] (M = Ni, Pd, Pt). Organometallics 2011, 30, 4123–4127. (e) Freitag, K.; Molon, M.; Jereb, P.; Dillicht, K.; Rösel, C.; Seidel, R. W.; Gemel, C.; Freking, G.; Fischer, R. A. Zn–Zn Interactions at Nickel and Palladium Centers. Chem. Sci. 2016, 7, 6413–6421. (18) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cresmadas, E.; Barragán, F.; Alvarez, S. Covalent radii revisited. Dalton Trans. 2008, 2832–2838. (19) (a) Campos, C. Dihydrogen and Acetylene Activation by a Gold(1)/Platinum(0) Transition Metal Only Frustrated Lewis Pair. J. Am. Chem. Soc. 2017, 139, 2944–2947. (b) Hidalgo, N.; Moreno, J. J.; Pérez-Jiménez, M.; Maya, C.; López-Serrano, J.; Campos, J. Evidence for Genuine Bimetallic Frustrated Lewis Pair Activation of Dihydrogen with Gold(I)/Platinum(0) Systems. Chem. - Eur. J. 2020, 26, 5982–5993. (c) Hidalgo, N.; Moreno, J. J.; Pérez-Jiménez, M.; Maya, C.; López-Serrano, J.; Campos, J. Tuning Activity and Selectivity during Alkyne Activation by Gold(I)/Platinum(0) Frustrated Lewis Pairs. Organometallics 2020, 39 (13), 2534–2544. (20) Goel, R. G.; Oginí, W. O.; Srivastava, R. C. Preparation, Characterization and Some Reactions of Bis(tri-tert-butylphosphine)-hydridoplatinum(II) Complexes. Organometallics 1982, 1, 819–824. (21) Werkmeister, S.; Fleischer, S.; Zhou, S.; Junge, K.; Beller, M. Development of New Hydrogenations of Imines and Benign Reductive Hydroaminations: Zinc Triflate as a Catalyst. ChemSusChem 2012, 5, 777–782. (22) Pandolfo, L.; Mazzini, M. Reaction of trans-[Pt(H)2(PCy3)2] with C6H6 reductive elimination of H2 and formation of [Pt(PCy3)3(η2-C6H6)]+. J. Organomet. Chem. 1997, 540, 61–65. (23) (a) Skara, G.; De Vleeschouwer, F.; Geerlings, P.; De Proft, F.; Pinter, B. Heterolytic Splitting of Molecular Hydrogen by Frustrated and Classical Lewis Pairs: A Unified Reactivity Concept. Sci. Rep. 2017, 7, 16024. (b) Daru, J.; Bakó, I.; Stirling, A.; Pápai, I. Mechanism of Heterolytic Hydrogen Splitting by Frustrated Lewis Pairs: Comparison of Static and Dynamic Models. ACS Catal. 2019, 9, 6049–6057. (c) Yepes, D.; Jaque, P.; Fernández, I. Deeper Insight into the Factors Controlling H2 Activation by Geminal Aminoborane-Based Frustrated Lewis Pairs. Chem. - Eur. J. 2016, 22, 18801–18809. (d) Liu, L.; Cao, L. L.; Shao, Y.; Ménard, G.; Stephan, D. W. A Radical Mechanism for Frustrated Lewis Pair Reactivity. Chem. 2017, 3, 259–267. (e) Hamilton, H. B.; Wass, D. F. How Important Are Radical Mechanisms in Frustrated Lewis Pair Chemistry? Chem. 2017, 3, 198–210. (24) (a) Dobrovetsky, R.; Stephan, D. W. tBu3P/ZnR2 (R = Et, i-Pr) Frustrated Lewis Pair Catalysts for Functionalization and Reduction of CO2. Isr. J. Chem. 2015, 55, 206–209. (b) Jochmann, P.; Stephan, D. W. H2 Cleavage, Hydride Formation, and Catalytic Hydrogenation of Imines with Zinc Complexes of C5Me5 and N-Heterocyclic Carbenes. Angew. Chem., Int. Ed. 2013, 52, 9831–9835. (25) Zhang, Y.; Karunananda, M. K.; Yu, H.-C.; Clark, K. J.; Williams, W.; Mankad, N. P.; Ess, D. H. Dynamically Bifurcating Hydride Transfer Mechanism and Origin of Inverse Isotope Effect for Heterodinuclear AgRu-Catalyzed Allyne Semihydrogenation. ACS Catal. 2019, 9, 2657–2663. (26) Nisa, R. U.; Ayub, K. Mechanism of Zn(OTf)2 Catalyzed Hydroamination—Hydrogenation of Alkynes with Amines: Insight from Theory. New J. Chem. 2017, 41, 5082–5090. (27) Frenz, H.-R. C.; Mason, W. R. Electronic Absorption and MCD Spectra for Isoelectronic Linear Two-Coordinate Bis(tri-tert-butylphosphine)metal Complexes of Platinum(0) and Gold(1). Inorg. Chem. 1989, 28, 4370–4373. (28) Fleckenstein, J. E.; Koszinowski, K. Lithium Organozincate Complexes LiZnX2: Common Species in Organozinc Chemistry. Organometallics 2011, 30, 5018–5026.