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Frustrated Lewis Pairs beyond the Main Group: Synthesis, Reactivity, and Small Molecule Activation with Cationic Zirconocene—Phosphinoaryloxide Complexes

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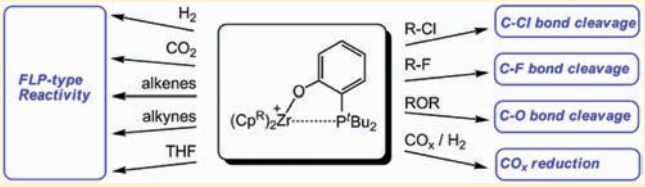
Supporting Information

ABSTRACT: The extension of the frustrated Lewis pair (FLP) concept to the transition series with cationic zirconocene—phosphinoaryloxide complexes is demonstrated. Such complexes mimic the reactivity of main group FLPs in reactions such as heterolytic hydrogen cleavage, CO_2 activation, olefin and alkyne addition, and ring-opening of tetrahydrofuran. The interplay between sterics and electronics is shown to have an important role in determining the reactivity of these compounds with hydrogen in particular. The Zr—H species generated from the heterolytic activation of hydrogen is shown to undergo insertion reactions with both CO_2 and CO. Crucially, these transition metal FLPs are markedly more reactive than main group systems in many cases, and in addition to the usual array of reactions they demonstrate unprecedented reactivity in the activation of small molecules. This includes S_N2 and E2 reactions with alkyl chlorides and fluorides, enolate formation from acetone, and the cleavage of C—O bonds to facilitate S_N2 type reactions with noncyclic dialkyl ethers.



1. INTRODUCTION

Solution phase combinations of sterically hindered ("frustrated") Lewis acid—Lewis base pairs (FLPs) have been the subject of recent interest because of the high latent reactivity of such species in the activation of small molecules. Initial studies focused on the reversible heterolytic cleavage of dihydrogen, which offers the promise of metal-free catalytic hydrogenation.[1−4] However, the diversity of the reactions reported is now 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[2,6] which, in the context of reversible reactions with carbon dioxide and hydrogen, has attracted significant interest.[7] A great deal of work has also focused on extending the range of main group FLPs to other main group Lewis acids (e.g., simple alkyl boranes, allanes,[8,9] and allenes[10]) or bases (e.g., amines[11] carbenes,[12] and sulfides[13]). Linking the two components of the FLP into a single amphoteric molecule has also led to interesting results.[3,14]

While main group FLPs offer a novel and possibly useful way to activate unreactive substrates,[7,14−17] such systems suffer from a common limitation in that, apart from some stoichiometric insertion chemistry,[17,5] the products are often inert toward further reaction. Subsequently, and to the best of our knowledge, only two catalytic transformations with such systems have been demonstrated (imine or enamine hydrogention[18] and deoxygenative hydrogenation of CO_2).[19]

We have been exploring the chemistry of cationic zirconocene—phosphinoaryloxide complexes as analogues of linked main group frustrated Lewis pairs where the Lewis acidic borane component is replaced with an electrophilic transition metal center. Our initial results have demonstrated chemistry which mimics main group frustrated pairs in many regards but which also demonstrates additional reactivity, for example, the catalytic dehydrogenation of amine-boranes,[20] a reaction only demonstrated in a stoichiometric sense with main group FLP systems (Figure 1).[21,22]

Even though the novelty of metal-free catalysis cannot be claimed for a zirconium—phosphine pair, the FLP paradigm is valuable in understanding the reactivity of this system. It is our view that combining the ability of transition metal complexes in catalysis with the capability of FLPs to activate substrate molecules via ditopic activation offers exciting possibilities for exploitation in new activation pathways and reactivity patterns.

In this Article, we explore the reactivity of these transition metal frustrated Lewis pairs more widely in some typical reactions of main groups FLPs: hydrogen cleavage, CO_2 activation, alkene and alkyne addition, and tetrahydrofuran (THF) ring-opening. In all cases, the analogy between these systems is robust and valuable. However, we have also demonstrated new, more potent reactivity in small molecule activation: CO reduction, C-halide cleavage in alkyl chlorides and fluorides, and the cleavage of C—O bonds in acyclic ethers. This rare reactivity is still well-explained using the FLP analogy but unprecedented for the main group FLPs.

Received: August 30, 2011
Published: September 29, 2011

dx.doi.org/10.1021/ja207936p | J. Am. Chem. Soc. 2011, 133, 18463–18478

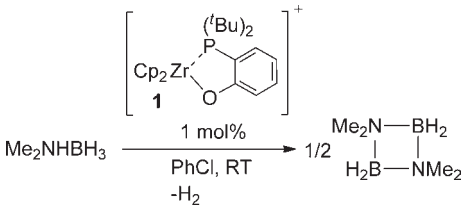
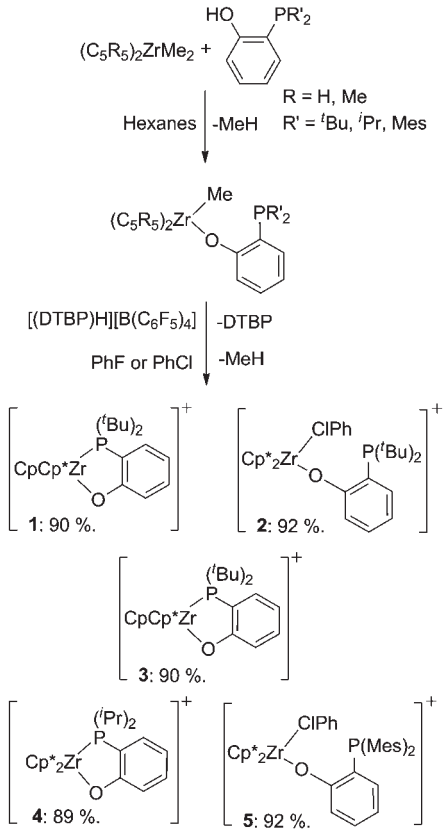


Figure 1. Amine-borane dehydrogenation with **1**. Counterion = $[B(C_6F_5)_4]^-$.

Scheme 1. Synthesis of Compounds 1−5[a]



[a] DTBP = 2,6-di-*tert*-butylpyridine. Counterion = $[B(C_6F_5)_4]^-$.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Zirconocene−Phosphinoaryloxide Complexes. We recently reported[20] the synthesis of the zirconocene−phosphinoaryloxide complexes **1** and **2** (see Scheme 1). The zirconium center in **1** was found to be stabilized by a long Zr−P interaction. We reasoned that increasing the bulk of the zirconocene fragment with the permethylcyclopentadienyl analogue **2** would hinder this interaction, albeit at the supposed cost of decreased electrophilicity of the zirconium center.[23] We report here the X-ray crystal structure of **2** (Figure 2) which confirms the absence of a Zr−P interaction in the solid state, revealing the presence of a coordinated chlorobenzene, disordered over two positions with an occupancy ratio of 0.77:0.23. In order to explore the limit of the Zr−P interaction in our system, we chose to synthesize **3** which was expected to possess intermediate

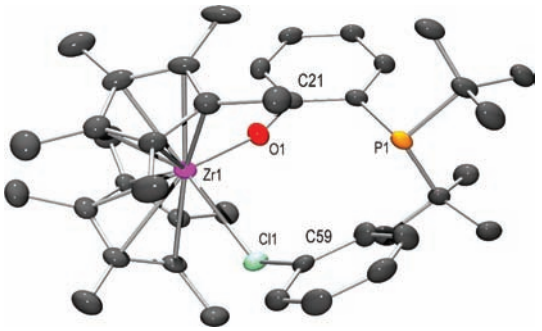


Figure 2. POV-ray representation of the molecular structure of **2**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoid is drawn at the 50% probability level. The minor component of the disordered chlorobenzene solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1 Cl1 2.740(1), Zr1 O1 1.980(3), Zr1 P1 4.613(1), O1 C21 1.359(5). O1 Zr1 Cl1 95.4(1), C59 Cl1 Zr1 129.0(2), C21 O1 Zr1 161.7(3).

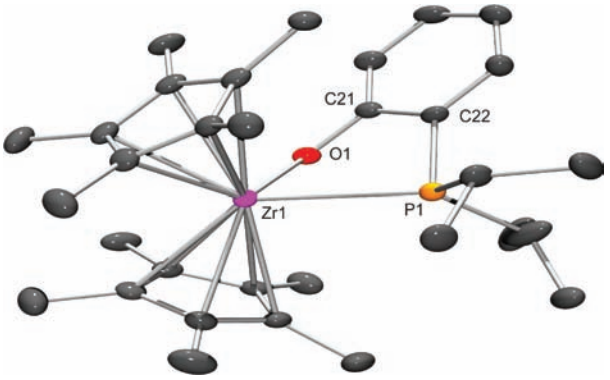


Figure 3. POV-ray representation of the molecular structure of **4**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoid is drawn at the 50% probability level. Selected bonds length (Å) and angles (deg): Zr1 P1 2.8215(8), Zr1 O1 2.025(2), C21 O1 1.368(4), P1 C22 1.818(3). P1 Zr1 O1 70.77(6), O1 C21 C22 119.2(3), C21 C22 P1 114.7(2), C22 P1 Zr1 89.9(1).

sterics and electronics to **1** and **2**. The synthesis was achieved using the previously reported protocol starting from $CpCp^*ZrMe_2$ (Scheme 1). The presence of a Zr−P bond is corroborated by the near identical ^{31}P NMR spectra of **1** and **3** (54.4 vs 53.3 ppm), although efforts to grow crystals suitable for X-ray crystallography to allow direct bond length comparison with **1** were unsuccessful. However, the calculated distances at two levels of theory, 3.068 Å (B3LYP) and 2.918 Å (M06-2X) support the expectation of an elongated Zr−P bond relative to **1** (found to be 2.883 Å from the X-ray, and calculated to be 2.935 Å from B3LYP and 2.870 Å from M06-2X level simulations).

We have also modified the phosphine component of these systems; substitution of the *tert*-butyl groups in **2** for *iso*-propyl groups leads to the isolation of **4** via a similar method. As expected for this less bulky phosphine, solution ^{31}P NMR data (23.9 ppm) and X-ray crystallography (Figure 3) confirm the presence of a Zr−P bond. The Zr−P bond is shown to be shorter than that in **1** by ca. 2% (2.821 vs 2.883 Å). Finally, the synthesis of **5** was accomplished in an analogous way. The lack of a Zr−P implicated by the similarity of the ^{31}P NMR shifts of

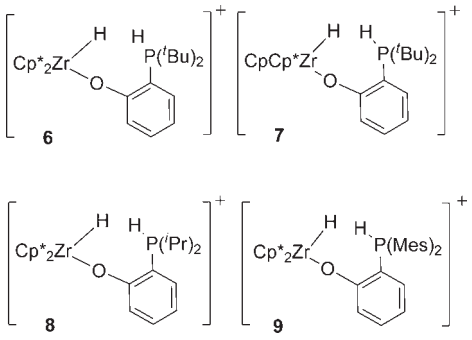


Figure 4. Structures of compounds **6**–**9**. Counterion = $[B(C_6F_5)_4]^-$.

5 relative to its neutral precursor (−26.8 vs −32.9 ppm). The mesityl substituents of compound **5** are expected to give a substantially less basic phosphine,[24] while retaining the necessary steric bulk to "frustrate" coordination[25] to the zirconium center.

2.2. Reactivity with Hydrogen. With this range of complexes in hand, we sought initially to explore the heterolytic cleavage of dihydrogen when the steric bulk of both the zirconocene and phosphine components is varied. We have previously reported the heterolytic activation of dihydrogen with **2**, yielding the surprisingly stable complex **6** (Figure 4). Interestingly, we found that **1** was unreactive toward dihydrogen (2 bar, ambient temperature), suggesting that the presence of a Zr−P interaction was a key feature in such a system, as might be expected by analogy to main group FLPs. Exposure of the intermediately bulky complex **3** to low pressures of dihydrogen (1−2 bar) at ambient temperature resulted in an immediate color change from orange to yellow, and the ^{31}P NMR spectrum revealed >99% conversion to a new species at 20.1 ppm ($^1J_{PH}$ = 467 Hz). Only in situ characterization was possible, since attempts to isolate the material lead only to recovery of **3**, but based on NMR data the compound is formulated as **7**. The reconversion of **7** to **3** upon isolation indicated the reaction was reversible, and indeed simply degassing the solution via three freeze−pump−thaw cycles gave 50% conversion to **3**, while complete removal of the solvent under reduced pressure gave >99% conversion to **3**. The system was cycled three times in this way, demonstrating that the reaction is fully reversible at room temperature and requires only mild vacuum to induce hydrogen release. Given the contrasting reactivity of the Cp system **1** (no reaction under these conditions) and the Cp* system **2** (facile but irreversible H_2 cleavage to give **6**), the reversible nature of hydrogen addition in the Cp/Cp* mixed system **3** shows how subtle ligand alterations can have a big influence on reactivity. Compound **4**, with a less bulky phosphine moiety, reacts incompletely at 2 bar of hydrogen, giving ca. 10% conversion to a new species (15 ppm, $^1J_{PH}$ = 459.6 Hz) assigned as **8** and concomitant broadening of the original resonance assigned to **4**. These observations are consistent with a dynamic binding of H_2 in solution. Such reactivity is initially surprising when it is considered that **1**, which also has a Zr−P bond, was found to be unreactive under the same conditions. It is possible that the bulkier *tert*-Bu-substituted phosphine in **1**, despite resulting in a thermodynamically weaker longer Zr−P bond compared to **3**, affords kinetic protection of this bond which is not present in the less encumbered *iso*-Pr derivative. Preliminary calculations (vide infra) also suggest an electronic component. Compound **5**, with a bulky but less basic mesityl-substituted phosphine, reacts extremely rapidly with

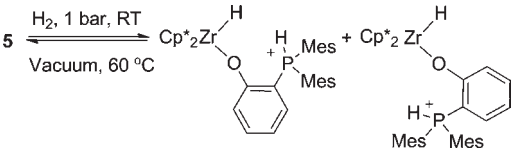


Figure 5. Tentative rotomers of **9** in solution. Counterion = $[B(C_6F_5)_4]^-$.

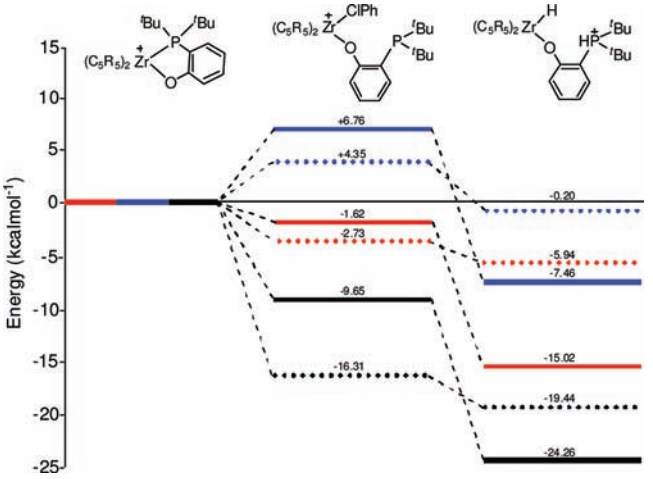


Figure 6. Calculated energies for $[(C_5R_5)_2Zr(PhCl)(O(C_6H_4)P^tBu_2)]$ (**1**, **2**, or **3**) and $[(C_5R_5)_2Zr(H)(O(C_6H_4)PH^tBu_2)]$ (**6**, **7**, or product derived from **1**) relative to $[(C_5R_5)_2Zr(O(C_6H_4)P^tBu_2)]$ compounds. Blue lines, $C_5R_5 = C_5H_5$; red lines, $C_5R_5 = C_5H_5/C_5Me_5$; black lines, $C_5R_5 = C_5Me_5$. Solid lines indicate B3LYP calculations; dashed lines indicate M06-2X level calculations.

dihydrogen, giving 100% conversion to two (in ca. 1:9 ratio) spectroscopically distinct P−H species with near identical $^1J_{PH}$ coupling constants (493.8 and 494.4 Hz). By analogy to related literature systems, we tentatively assign this to two rotomers of **9** (Figure 5).[26] Degassing the solution and warming to 60 °C in an open system resulted in complete regeneration of **5** within ca. 3 h.

As expected, by analogy with main group FLPs, increasing steric bulk lengthens the interaction between the basic phosphine and electrophilic Zr center until it becomes "frustrated" (albeit, as is always observed with such zirconocenes, a "vacant" coordination site is not observed and a labile solvent[27] or anion interaction persists).[28] However, this does not always correlate to increased reactivity when kinetic stabilization of the Zr−P is considered. Insight into the subtle differences observed in the hydrogenation of these compounds can be drawn from the large body of work concerning the hydrogenation of d^0 metal complexes. Of particular relevance to this work are the studies concerning the rate of hydrogenolysis of neutral and cationic metallocene alkyls. In these studies, 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 to 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.[29] This not only serves to explain the observed trends in hydrogenation but may help to explain why a CO complex is accessible with **2** but not with **1** and why **2** reacts immediately with ethene while **1** is inert (vide infra). Preliminary calculations comparing the relative

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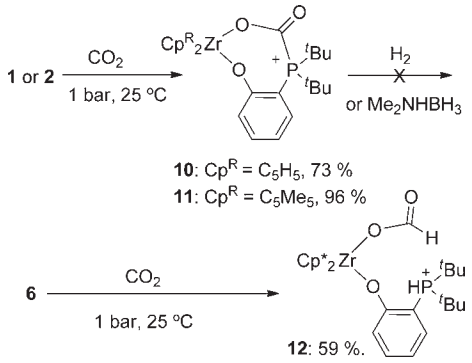


Figure 7. Summary of reactivity of **1**, **2**, and **6** with CO_2. Counterion = $[B(C_6F_5)_4]^-$.

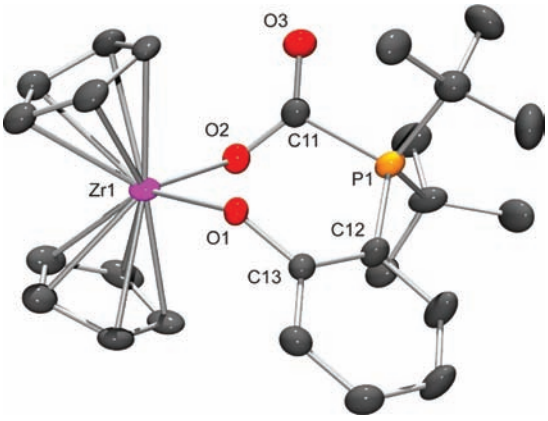


Figure 8. POV-ray representation of the molecular structure of **10**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1 O1 2.019(2), Zr1 O2 2.086(2), O2 C11 1.298(4), C11 O3 1.208(5), C11 P1 1.892(4), P1 C12 1.822(4), O1 C13 1.355(4). O1 Zr1 O2 86.9(1), O2 C11 O3 127.9(3), O3 C11 P1 117.4(3), P1 C11 O2 114.5(3), P1 C12 C13 124.7(3), C13 O1 Zr1 134.2(2).

energies of **1**, **2**, and **3** (B3LYP and M06-2X) support our experimental observations and imply that **6** and **7** possess fundamentally different ground state energies (Figure 6).

2.3. Reactivity with Carbon Dioxide. One of the most exciting examples of FLP induced reactivity is the reversible binding of carbon dioxide, first reported by Stephan and Erker et al.[30] The potential of these systems to sequester and activate CO_2 implicates the utility of this substrate in catalytic reactions. Advances have been made in this regard, although current systems are unrealistic in terms of technological application because of the reactive coreagents necessary. Exposure of chlorobenzene solutions of **1** or **2** to 1 bar CO_2 at room temperature resulted, in both cases, in an immediate reaction. Interestingly, and crucially in supporting the analogy with FLP systems, the related Lewis base−free zirconium complexes, $[Cp_2ZrOR]$-$[MeB(C_6F_5)_3]$ (R = Me and ^{t}Bu), are found to be completely unreactive toward CO_2, highlighting the pivotal role of the phosphine in these systems.[31] The products were fully characterized and unambiguously assigned to **10** and **11** (Figure 7), with both compounds being structurally characterized (**10** in Figure 8, **11** in the Supporting Information). The IR spectra exhibited a

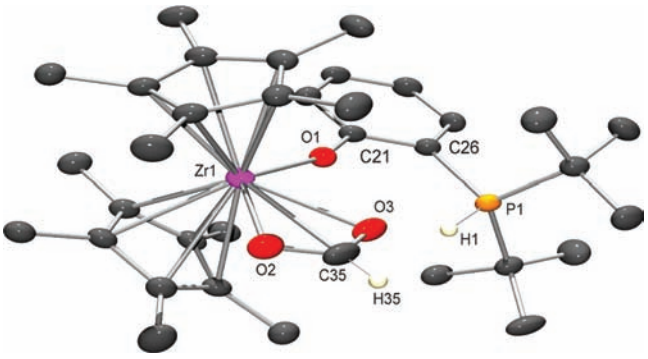


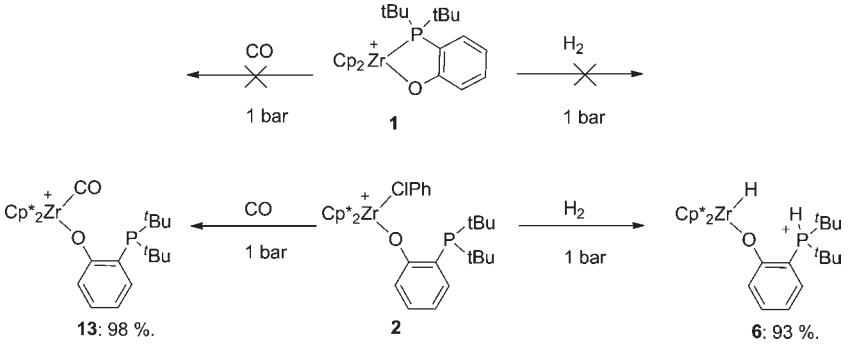
Figure 9. POV-ray representation of part of the molecular structure of **12**. All hydrogen atoms and borate anion have been omitted for clarity. The crystal structure of **12** contains disorder in the formate group, where it is bound through either one or both oxygen atoms in a ratio of 0.53:0.47. An illustration of the other component is shown in the Supporting Information. Thermal ellipsoid is drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1 C35 2.360(2), C35 O2 1.124(2), Zr1 O1 1.952(1), O1 C21 1.360(2), P1 C26 1.837(2). O2 C35 Zr1 179.1(2), O1 Zr1 C35 90.10(6), C35 Zr1 O1 90.10(6), Zr1 O1 C21 168.7(1), O1 C21 C26 121.9(1).

sharp stretch at 1694 and 1697 cm^{-1} for **10** and **11**, respectively, which is similar to main group FLP systems.[32] However, unlike the two main group systems, these transition metal analogues do not liberate CO_2 upon thermolysis and are thermally stable up to 80 °C;[33] instead they slowly decompose to as yet unidentified products upon prolonged thermolysis. Although thermodynamically robust, the CO_2 is kinetically labile and was readily displaced by THF or dichloromethane (DCM) to yield products in which these solvents have reacted (see sections 2.5 and 2.6). Treatment of **10** or **11** with hydrogen showed no reaction (2 bar, ambient temperature). However, the dihydrogen activation product **6** reacted immediately with CO_2, to give the unusual monomeric formate complex **12** in quantitative yield (Figure 9). This intermediate for stepwise CO_2 reduction suggests promise for these systems in this important area, and the identification of an η^2 binding mode of the formate ligand in **12** illustrates a subtle difference compared with main group analogues where only an η^1 bonding mode is noted.[17,34] Recent work by Stephan and Menard has demonstrated that stoichiometric reduction of CO_2 to methanol using an FLP triad is possible using ammonia borane as the reducing agent.[35] Unfortunately, analogous attempts to reduce the coordinated CO_2 in **11** and **12** with amine boranes were unsuccessful and resulted only in the previously observed dehydrocoupling reactions.[20]

2.4. Reactivity with Carbon Monoxide. There is only one example of CO activation with traditional main group FLPs.[36] This may be in part due to the lack of a stable $(C_6F_5)_3B-CO$ adduct.[37,38] While in this instance **1** proved inert to CO, **2** reacted immediately, giving a bright red solution and a small but noticeable change in the $^{31}P\{^1H\}$ NMR shift (from 7.4 ppm in **2** to 5.6 ppm) (Scheme 2). Isolation of this species confirmed its identity as **13**, and it constitutes a rare example of a Zr(IV) carbonyl compound (Figure 10). Complex **13** is surprisingly stable; although exceedingly air and moisture sensitive, it is stable at room temperature and may be isolated as a solid by drying in vacuo.

The carbonyl ligand in **13** (Figure 10) is nonclassical in nature[39−41] with a ν_{co} higher than that of free CO (ν_{co} = 2163

Scheme 2. Comparison of the Reactivity of 1 and 2 toward H_2 and CO[a]



[a] Counterion = $[B(C_6F_5)_4]^-$.

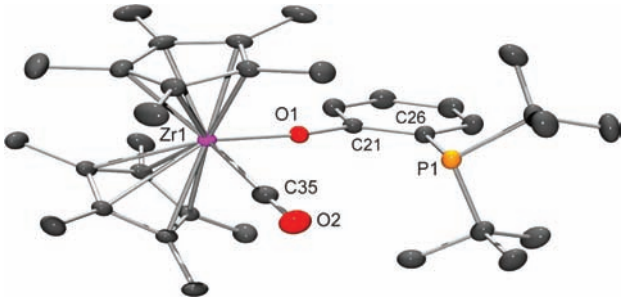
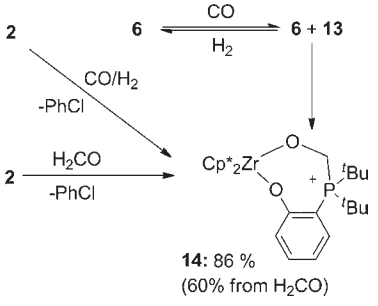


Figure 10. POV-ray representation of the molecular structure of **13**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1 C35 2.360(2), C35 O2 1.124(2), Zr1 O1 1.952(1), O1 C21 1.360(2), P1 C26 1.837(2). O2 C35 Zr1 179.1(2), O1 Zr1 C35 90.10(6), C35 Zr1 O1 90.10(6), Zr1 O1 C21 168.7(1), O1 C21.

Scheme 3. Postulated Route to the Formation of 14 from 2, CO, and H_2[a]



[a] Counterion = $[B(C_6F_5)_4]^-$.

for **13** vs 2144 cm^{-1} for free CO).[43,42] It is also slightly higher than data for the related d^0 complexes $[Cp_3M(CO)][MeB(C_6F_5)_3]$ (M = Zr, Hf).[43,44] Although stable to vacuum, the CO ligand in **13** is kinetically very labile and is rapidly and irreversibly replaced by THF or even DCM to yield the corresponding reaction products (see sections 2.5 and 2.6). Exposure of solutions of **13** to hydrogen results in rapid displacement of CO and formation of **6**, while exposure of solutions

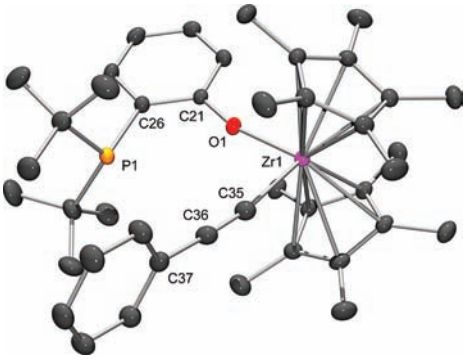


Figure 11. POV-ray representation of the molecular structure of **15**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bonds length (Å) and angles (deg): Zr1 O1 2.026(1), O1 C21 1.332(2), Zr1 C35 2.231(2), C35 C36 1.215(3), C36 C37 1.442(3). C35 Zr1 O1 91.92(6), Zr1 O1 C21 164.5(1), O1 C21 C26 122.1(1), C21 C26 P1 120.8(1), C35 C36 C37 175.9(2).

of **6** to CO results in elimination of H_2 and formation of mixtures of **6** and **13** (Scheme 2). Upon standing, **13** and **6** slowly react to form the coordinated formaldehyde complex **14** (Scheme 3). This transformation may be achieved more directly by leaving solutions of **2** under 10 bar of 1:1 CO/H_2 for ca. 14 days. Although no other intermediates are observed during the course of the reaction, we suggest that **14** forms via coordination of CO to **6**, followed by CO insertion and rearrangement. An independent synthesis of **14** was carried out by reacting **2** with gaseous formaldehyde. Analogous reactions of aldehydes with a linked main group FLP has been demonstrated.[45] This reactivity represents a single stepwise reduction of CO with hydrogen, and similar "double" reductions (to methoxide) have been observed in Zr[46] and recently in U[47] sandwich complexes.

2.5. Reactivity with Alkenes and Alkynes. The reaction of FLPs with alkenes[48,49] and alkynes[50,51] is a well documented and general[9] reaction. Depending on the specific reagents, deprotonation (terminal alkynes only), 1,2-addition, or (in one case)[51] 1,1-carboration may occur. The selectivity has been correlated to the basicity of the Lewis basic component, with less basic aryl-phosphines favoring a 1,2-addition.[50] The intramolecular phosphine−allane system developed by Uhl et al.[9] gives mixtures of deprotonation and 1,2-addition products at room temperature and upon warming to 70 °C fully

dx.doi.org/10.1021/ja207936p |J. Am. Chem. Soc. 2011, 133, 18463–18478

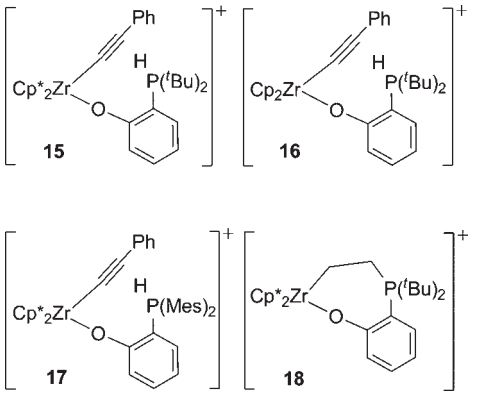


Figure 12. Compounds **15**−**18**. Counterion = $[B(C_6F_5)_4]^-$.

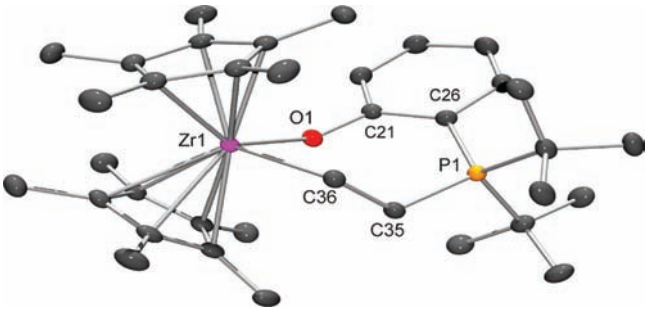


Figure 13. POV-ray drawing of the molecular structure of **18**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bonds length (Å) and angles (deg): Zr1 O1 2.0364(9), O1 C21 1.330(2), P1 C26 1.798(1), C35 P1 1.809(1), C35 C36 1.552(2), C36 Zr1 2.327(1). C36 Zr1 O1 83.26(4), O1 C21 C26 123.1(1), C21 C26 P1 124.2(1), P1 C35 C36 119.6(1), C35 C36 Zr1 111.68(9).

converts to the 1,2-addition product, suggesting that 1,2-addition is the thermodynamic product.

Treatment of **2** with excess phenylacetylene immediately decolorized the solution and gave rise to a characteristic P−H resonance at 26.7 ppm ($^1J_{PH}$ = 472.7 Hz). Isolation and structural characterization of **15** confirmed that a deprotonation rather than 1,2-addition type reaction to the alkyne had occurred (Figures 11 and 12). Exactly the same result was observed with the less bulky analogue **1** to give **16** (Figure 12). Given the importance of Lewis basicity for this reaction in main group systems, we also investigated compound **5**. This reacts in exactly the same way to give **17** (Figure 12), evidenced by a characteristic P−H resonances at −20.6 ppm ($^1J_{PH}$ = 468.9 Hz). All three compounds **15**−**17** were found to be thermally stable to 100 °C, showing no sign of rearrangement.

Similar trends to other reactions are observed when **1** or **2** are treated with alkenes; **1** exhibited no reaction toward ethene under mild conditions, whereas **2** reacted immediately to give **18** (Figures 12 and 13), which like its main group analogue $^tBu_3P$-$CH_2CH_2B(C_6F_5)_3$ is thermally stable. Attempts to insert CO into the Zr−C bond in either **15**, **16**, **17**, or **18** were unsuccessful under the conditions examined (2 and 10 bar CO, 25 and 100 °C).

2.6. Reactivity with Alkyl Halides. In the course of defining the solubility characteristics of these complexes, we discovered that compounds **1** and **2** react rapidly and cleanly with CH_2Cl_2 to yield the C−Cl cleaved products. This reaction is fast

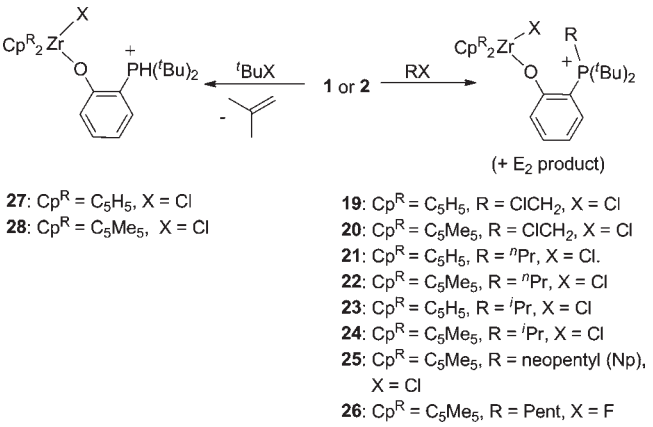


Figure 14. Summary of the reactions of **1** and **2** with fluoro- and chloroalkanes.

(quantitative in less than 1 min for **2**, and ca. 30 min for **1**) and repeatable with stoichiometric amounts of CH_2Cl_2. In this way, **19** and **20** were isolated in quantitative yield (Figure 14, X-ray structure of **20** in the Supporting Information). A similar reaction was observed by Stephan et al. between a titanium complex with $P(o\text{-tol})_3$,[52] and Jordan et al. have also reported similar C−Cl cleavage reactions of zirconium cations in CH_2Cl_2.[27] While these reactions seem commonplace to transition metal Lewis acids, we were surprised to find that no C−Cl cleavage reactions have been reported for the main group systems. The previous parallel reactivity between our systems and the main group promoted a brief investigation using $^tBu_3P/B(C_6F_5)_3$. Mixing a toluene solution of $^tBu_3P$, $B(C_6F_5)_3$, and an excess of 1-chloropropane led to no observed spectroscopic changes after ca. 1 h at room temperature. However, after standing overnight, in addition to unchanged $^tBu_3P$, several other unidentified species were apparent by ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy. Importantly, no $[ClB(C_6F_5)_3]^-$[53] was detected, which may have been expected to form if an analogous reaction had taken place. Building on the previous result, we explored the reactivity of compounds **1** and **2** toward a range of alkyl chlorides. Both **1** and **2** were found to react rapidly with 1-chloropropane or 2-chloropropane to give products reminiscent of S_N2-type reactions **21**−**24** (Figures 14 and 15). The S_N2-type reactions were accompanied by a competing E2-type reaction giving **27** and **28** in varying quantities (see Experimental Section), and consequently, isolation and purification of these compounds was not possible.

In the case of reaction with tertiary alkyl chlorides, only elimination products are observed. The reaction of **1** and **2** with ^{t}BuCl yields **27** and **28**, respectively, in 94% and 92% yield, with the expected isobutylene side-product detected by ^1H NMR spectroscopy. Reaction of **2** with neopentyl chloride gives a ca. 1:2 mixture of S_N2 and E2 products (**25** and **28**). While the S_N2 products must arise from nucleophilic attack, we suggest that the E2 product arises from a Wagner−Meerwein sigmatropic shift (Scheme 4).[54,55]

It is noteworthy that these reactions are performed in chlorobenzene solvent in which the complexes are completely inert; reactivity is orthogonal to the well-known palladium species for coupling reactions with aryl halides.[56]

The same reactivity patterns are observed even with alkyl fluorides. Treatment of **2** with 1-fluoropentane cleanly gives **26** in 69% yield. Although S_N2 reactions of alkyl fluorides are

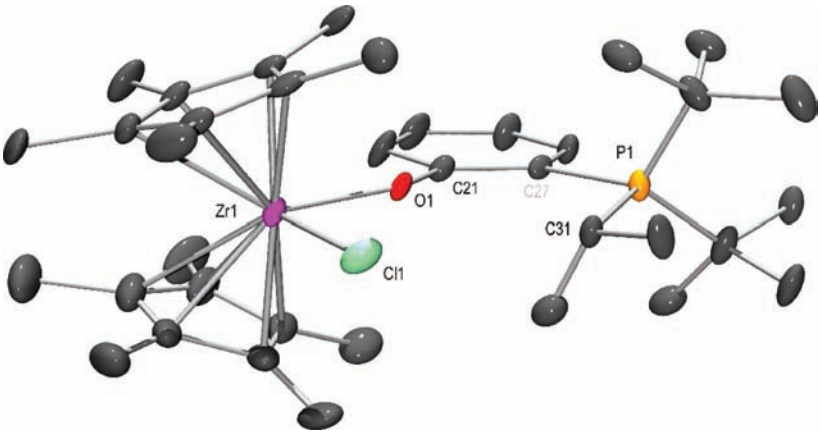
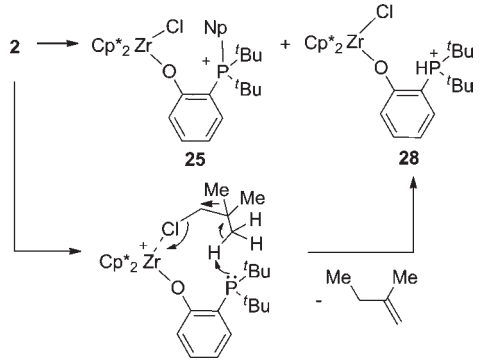
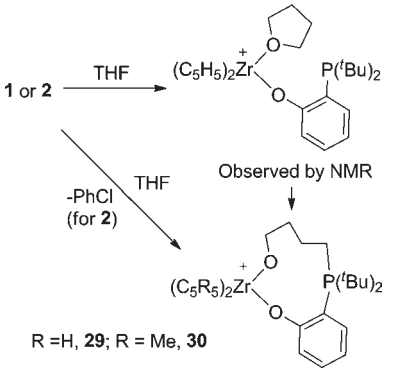


Figure 15. POV-ray representation of the molecular structure of **24**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1 O1 2.051(5), Zr1 Cl1 2.458(2), O1 C21 1.328(9), P1 C31 1.87(1), P1 C26 1.815(7). Cl1 Zr1 O1 94.6(2), Zr1 O1 C21 149.0(5), C27 P1 C31 113.2(4).

Scheme 4. Suggested Wagner−Meerwein Sigmatropic Shift That Occurs during the Formation of 28 via Neopentyl Chloride Activation



Scheme 5. Reaction of 1 and 2 with THF to Give the Ring-Opened Products 29 and 30



known, there are very few examples.[57] Clearly, the strength of the Zr−F bond provides a strong driving force for this reaction in our case, but, nevertheless, complexes capable of the cleavage of unactivated C−F bonds are rare.[58−60]

2.7. Reactivity with Ethers. The activation of ethers and C−O bonds in general has attracted recent interest because of the ubiquity of such groups in biosustainable feedstocks.[61] One of the first reactions observed with main group FLPs was the ring-opening of tetrahydrofuran.[62] We were struck by the fact that virtually identical reactivity patterns were observed many years previously when Lewis bases were combined with electrophilic transition metals. Although not recognized as such at the time, these results could be thought of as an early example of a frustrated Lewis pair, a connection made recently by Stephan and co-workers.[5]

Treatment of **2** with excess THF immediately decolorizes the bright orange solution. After ca. 5 min, the $^{31}P\{^{1}H\}$ NMR spectrum of the colorless solution revealed 100% conversion of **2** to a new singlet resonance at higher chemical shift (42.7 ppm), typical of tetralkylphosphonium center. Layering the reaction mixture with hexane and standing overnight yielded large colorless crystals which were fully characterized and unambiguously identified as **30** (Scheme 5). The structural parameters (Figure 16) are similar to related compounds previously reported.[63,64] Treatment of **1** with THF in the same way leads to the same reactivity but a much slower rate of reaction. Following the reaction by NMR initially revealed signals consistent with opening of the Zr−P bond and formation of a simple THF adduct. Only over the course of ca. 4 days does ring-opening occur, with the concomitant decline of signals for this adduct. Isolation of the sample after this time in the same manner to **30** confirmed that intramolecular ring-opening of THF had occurred to give **29** (X-ray structure in the Supporting Information). We suggest that this substantial difference in rate between **1** and **2** is likely to be related to differences in the geometrical alignment of the coordinated THF in **1** and **2**. For example, in $[Cp_2Zr(Me)(THF)][BPh_4]$, the THF ligand is known to coordinate in an almost perpendicular fashion with respect to the plane formed between the two Cp rings. Although more sterically congested than a parallel binding mode, the orientation maximizes a favorable O−Zr π-bonding interaction. Upon moving to a Cp* ligand set (for example, in $[Cp^*_2Zr(CH_2TMS)(THF)][BPh_4]$), this orientation is too high in energy and the THF adopts a parallel binding mode.[65] If a similar scenario exists in **1** and **2**, then it is conceivable that **2** reacts so much faster than **1** because the phosphine is orientated directly toward the α-carbon of the coordinated THF, whereas in **1** a rotation is required to achieved the same orientation.

The ring-opening of THF by **1** and **2**, while supporting the analogy between frustrated Lewis pairs and our system, is well-known for closely related complexes. More surprising results

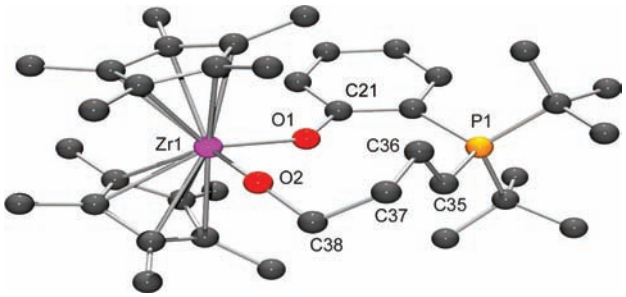


Figure 16. POV-ray representation of the molecular structure of **30**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bonds length (Å) and angles (deg): Zr1 O1 2.0980(9), Zr1 O2 1.9599(9), O2 C38 1.410(1). O1 Zr1 O2 91.63(4), Zr1 O1 C21 143.57(8), Zr1 O2 C38 149.10(8).

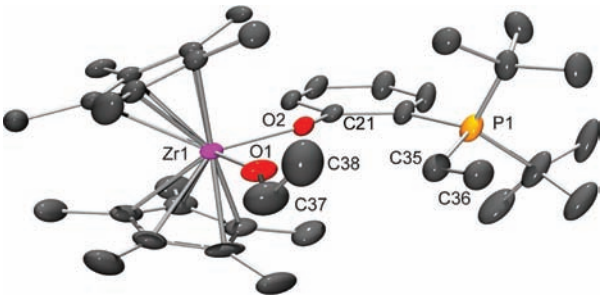
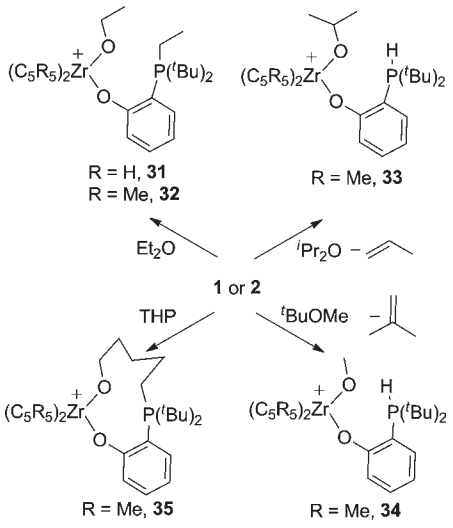


Figure 17. POV-ray representation of the molecular structure of **32**. All hydrogen atoms, solvent, and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bonds length (Å) and angles (deg): Zr1 O2 2.069(2), Zr1 O1 1.968(2), O1 C37 1.421(5). O2 Zr1 O1 94.73(9), Zr1 O2 C21 146.5(2), Zr1 O1 C37 155.7(3).

Scheme 6. Reaction of 1 and 2 with Ethers



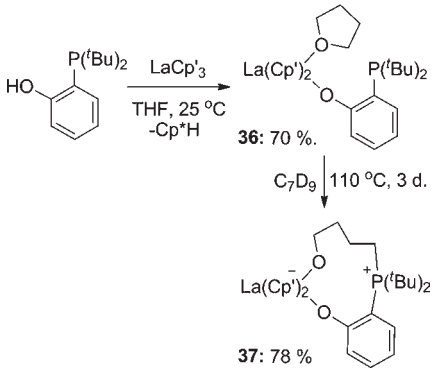
were obtained when we sought to investigate the reaction of **1** and **2** with diethyl ether, expecting this would allow isolation of the simple ether adducts. Treatment of a chlorobenzene solution of **2** with excess diethyl ether leads initially to NMR data consistent with the simple diethyl ether adduct of **2**. However, after ca. 3 days at room temperature, this converts quantitatively (>99% by NMR) to **32** (Scheme 6 and Figure 17). As in the case of THF ring-opening, compound **1** reacts in a similar manner but much more slowly, possibly for analogous reasons to those suggested previously. Following the reaction by NMR spectroscopy indicated that treatment of **1** with excess diethyl ether gives an association complex **1**·OEt_2; the coordinated ether is rather labile, and attempted isolation of this product by removal of the solvent gave only **1**. Only after monitoring a sample by $^{31}P\{^1H\}$ NMR spectroscopy over the course of ca. 1 month did a new singlet resonance at 45 ppm form, consistent with the cleaved ether product **31**. Precipitation of light yellow crystals allowed unambiguous characterization of **31** by X-ray diffraction (see the Supporting Information). Both **32** and **31** represent rare examples of species in which the ether C−O bond has been cleaved, and are distinct from superficially similar C−O cleavage reactions by other Zr(II)[66] and Zr(IV) species.[67] This represents a rare S_N2 type reaction where the nucleofugacity of ethoxide appears to be drastically increased by the presence of the electron deficient and oxophillic zirconium center, and draws parallels to the well-known reaction of BCl_3 with alkyl ethers to give $B(OR)Cl_2$ and alkyl chlorides[68] and the reaction of $[Cp_2Zr(THF)N(^tBu)][BPh_4]$ with allylic ethers.[69] It is noteworthy, and indeed crucial to the concept we propose here, that related zirconocene complexes which do not contain a pendant phosphine[70−73] form only the expected simple diethyl ether adducts; a Lewis basic phosphine and electrophilic zirconium center are both required for activation to occur.

This powerful new reactivity for compound **2** in particular led us to investigate if bulkier alkyl ethers could be cleaved in the same way (Scheme 6). No reaction is observed when diisopropyl ether is added to **2** at room temperature. However, after 4 days at 100 °C, 38% conversion to the unexpected product **33** is observed by in situ ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy and ESI-MS. We speculate that this product arises from similar elimination mechanisms to those described in section 2.5. The facile elimination pathway for this derivative is presumably being driven by relief of steric congestion from the bulkier tetraalkylphosphonium intermediate. Methyl *tert*-butyl ether (MTBE) reacts in a similar fashion: addition of MTBE to **2** and heating in sealed tube at 60 °C for 16 h gives >98% conversion to **34** with isobutene as the elimination side-product. Finally, reaction of **2** with the unstrained 6-membered heterocycle tetrahydropyran (THP) ring-opens this cyclic ether to **35** in an analogous fashion to THF in 100% conversion after ca. 48 h (X-ray structure in the Supporting Information).

The steric and electronic similarities that exist between cationic group 4 and isolobal neutral group 3 complexes has led to exciting discoveries in polymerization and C−H activation chemistry.[74] We hypothesized that neutral group 3 analogues of **1** and **2** would express a similar analogy in their reactivity to main group FLPs. Our preliminary investigations have been frustrated to some extent by the dearth of reliable methods for obtaining complexes free from coordinating solvents such as THF. However, we reasoned that the isolation of THF adducts would at least allow us to explore the FLP-type ring-opening chemistry previously described. Such THF adducts were obtained by protonolysis of MCp_3 compounds[75,76] with phosphino-alcohols in THF.

For example, addition of *t*-$Bu_2P(C_6H_5)OH$ to Cp'_3La in THF gives **36** as a highly sensitive off white solid (Scheme 7). The absence of La−P interaction is inferred from the minor

Scheme 7. Synthesis of the Related Neutral La Compound 36 and Subsequent Thermolysis to Give the THF Ring-Opening Product, 37



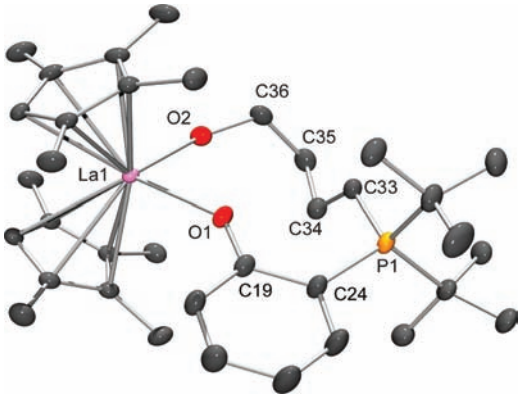
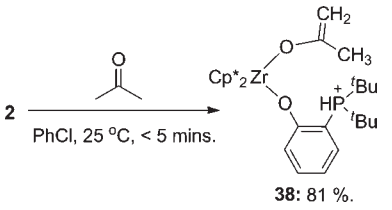


Figure 18. POV-ray representation of the molecular structure of **37**. All hydrogen atoms and borate anion have been omitted for clarity. Thermal ellipsoid is drawn at the 50% probability level. Solvent molecules have been omitted for clarity. Selected bonds length (Å) and angles (deg): La1 O1 2.3924(1), La1 O2 2.2014(1), C19 O1 1.3026, P1 C24 1.7928, P1 C33 1.8153(1), O2 C36 1.3902. La1 O1 C19 143.67, O1 La1 O2 92.97, C33 P1 C24 113.05, P1 C24 C19 123.12, C24 C19 O1 123.34.

$^{31}P\{^{1}H\}$ NMR shift upon protonolysis and is almost identical to that observed in the neutral Zr precursors.[20] The presence of the expected 1 equiv of coordinated THF is confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Attempts to remove the THF by vacuum or heating were unsuccessful. Compound **36** proved to be surprisingly stable in solution with respect to ring-opening of coordinated THF by the pendant phosphine. However, after ca. 3 days at 110 °C, 100% conversion to the ring-opened product **37** (Figure 18) was observed. This markedly differing stability is in direct contrast to **2** which reacts within seconds, and even with **1** which reacts within days at room temperature; however, it does confirm the analogy to the Zr system and indeed main group FLPs.

2.8. Reactivity with Acetone. It has been shown that coordination of a remote functionality to the Lewis acid site in an FLP can increase the acidity of conjugatively linked protons to such an extent that they may be deprotonated by relatively weak bases.[34] An ideal candidate for these reactions is ketones possessing α-protons. We envisaged that, upon coordination of the carbonyl-oxygen in acetone, the already relatively acidic C−H protons (pK_a ~26.5)[77] may be deprotonated by the proximal

Scheme 8. Synthesis of Compound 38



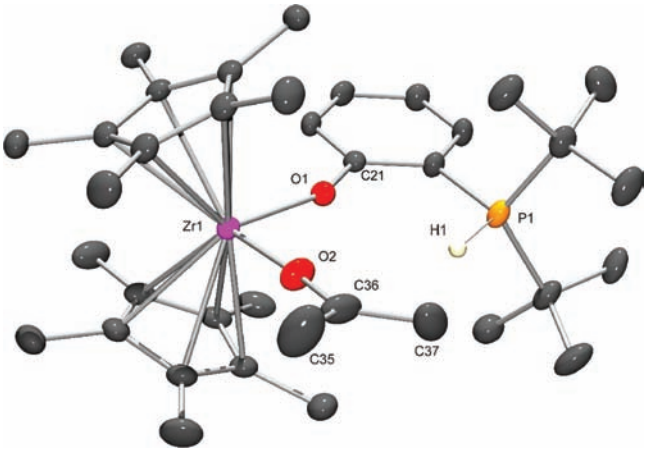


Figure 19. POV-ray representation of the molecular structure of **38**. All hydrogen atoms, solvent, and borate anion have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1 O1 2.076(1), O1 C21 1.326(2), Zr1 O2 1.986(1), O2 C36 1.349(2), C36 C35 1.378(3), C36 C37 1.456(3). O1 Zr1 O2 94.35(5), Zr1 O1 C21 154.96(9), Zr1 O2 C36 174.7(1), O2 C36 C35 121.8(2), O2 C36 C37 115.0(2), C35 C36 C37 123.2(2).

phosphine. In fact, upon treating **2** with a slight excess of acteone, the anticipated reaction occurred immediately and quantitatively to yield the Zr-enolate **38** and phosphonium center (Scheme 8), which was subsequently isolated and characterized crystallographically (Figure 19).

3. CONCLUSIONS

We have extended the concept of frustrated Lewis pairs (FLPs) from the main group to transition metal systems. The analogy to FLPs provides a coherent and useful paradigm in rationalizing the reactivity of cationic zirconocene−phosphinoaryloxide complexes. We consider these complexes to be FLPs where the usual main group Lewis acid (typically a fluorinated aryl borane) is replaced by a zirconocene fragment. Our complexes mirror the reactivity of main group systems for the heterolytic cleavage of dihydrogen, activation of CO_2, alkenes, alkynes and aldehydes, and the ring-opening of THF. However, they also go beyond the main group systems reported to date in accessing more powerful reactivity, such as the stepwise reduction of CO or CO_2 under mild conditions, the cleavage of aliphatic C−Cl or even C−F bonds, and the cleavage of C−O bonds in noncyclic ethers. It should be noted that such reactivity is not observed in the absence of the integrated Lewis base phosphine fragment. In many cases, we have been struck by the good thermodynamic stability of what appear to be potentially labile species, for example, the robust Zr-CO complex **13**, albeit in the presence of other substrates these species are highly kinetically

dx.doi.org/10.1021/ja207936p |J. Am. Chem. Soc. 2011, 133, 18463–18478

labile. As expected, the specific reactivity patterns observed are a function of the substitution patterns of both the zirconocene and phosphine moieties of our complexes; in general, more sterically encumbered species have the higher intrinsic activity. We suggest the remarkable reactivity of these species in small molecule activation, combined with the catalytic reactivity for amine borane dehydrogenation (as opposed to only stoichiometric reaction for main group systems), offers exciting possibilities which we continue to explore.

4. EXPERIMENTAL SECTION

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of argon using standard Schlenk-line and glovebox (M-Braun, O_2 < 0.1 ppm, H_2O < 0.1 ppm) techniques, and all glassware was oven-dried (200 °C) overnight and allowed to cool under vacuum prior to use. The compounds $Cp^*_2ZrMe_2$,[78] $CpCp^*ZrMe_2$,[78] *t*-$Bu_2P(C_6H_4)OH$,[79] *i*-$Pr_2P(C_6H_4)OH$,[80] $[DTBP][B(C_6F_5)_4]$,[20] **1**, **2**, and **6**[20] were prepared according to the literature. Cp'_3La was purchased from Strem and sublimed before use. Solvents were purified and predried using an Anhydrous Engineering column purification system[81] and then vacuum transferred from the appropriate drying agent (K/benzophenone for aromatic and ethers, CaH_2 for hydrocarbons and chlorinated solvents) prior to use. NMR spectra were recorded using a JEOL ECP 300 MHz spectrometer and Varian 400 and 500 MHz spectrometers (using the appropriate deuterated solvent, purchased from Cambridge Isotope Laboratories or Sigma-Aldrich and purified by vacuum transfer from the appropriate desiccant) and referenced to an appropriate standard (residual solvent signal for ^1H, $BF_3 \cdot OEt_2$ for ^{11}B, 85% H_3PO_4 for ^{31}P, and $FCCl_3$ for ^{19}F NMR). Spectra of air and moisture sensitive compounds where recorded using sealable J-Youngs tap NMR tubes. Microanalysis was carried out by the Microanalytical Laboratory, University of Bristol using a Carlo Elba spectrometer.

2-(Dimesityl)phosphinophenol. 2-(Dimesityl)phosphinophenol was prepared in a analogous fashion to a previously reported procedure for *i*-$Pr_2P(C_6H_4)OH$[80] from *o*-methoxymethylphenol in two steps (5 mmol scale). White solid, recrystallized from DCM/hexane at −20 °C. Yield: 59%. ^1H NMR (400 Hz, toluene-d_8): δ 7.14 (ddd, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.7 Hz, $\underline{H}_{C5}$), 7.00 (tm, 1H, $^3J_{HH}$ = 7.3 Hz, $\underline{H}_{C3}$), 6.84 (overlapping ddd, 1H, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, $\underline{H}_{C4}$), 6.67 (d, 4H, J_{HH} = 3.2 Hz, *m*-$\underline{H}$), 6.47 (tm, 1H, $^3J_{HH}$ = 7.3 Hz, $\underline{H}_{C6}$), 6.14 (s, 1H, O$\underline{H}$), 2.17 (s, 12H, *p*-C$\underline{H}_3$), 2.07 (s, 6H, *p*-C$\underline{H}_3$. $^{13}C\{^1H\}$ (100 Hz, toluene-d_8): δ 164.8 (d, $^2J_{CP}$ = 20.6 Hz, $\underline{C}1$), 147.5 (d, $^2J_{CP}$ = 15.00 Hz, *o*-$\underline{C}$), 143.1 (s, *p*-$\underline{C}$), 135.2 (d, $^3J_{CP}$ = 3.9 Hz, *m*-$\underline{C}$), 135.9 (s, $\underline{C}3$), 133.5 (d, $^1J_{CP}$ = 9.7 Hz, *i*-$\underline{C}$), 138.7 (d, $^2J_{CP}$ = 2.7 Hz, $\underline{C}5$), 126.6 (d, $^3J_{CP}$ = 4.3 Hz, $\underline{C}2$), 125.4 (d, $^3J_{CP}$ = 1.6 Hz, C6), 120.5 (s, $\underline{C}4$), 27.4 (d, J_{CP} = 16.5 Hz, *o*-$\underline{C}H_3$), 25.5 (s, *p*-$\underline{C}H_3$). $^{31}P\{^1H\}$ (161 Hz, toluene-d_8): δ −43.16 (s). ESI MS: 363.19 [M + H]. Elemental Analysis: Calcd: C, 79.53; H, 7.51. Found: C, 79.56; H, 7.80.

Compound 3. $CpCp^*ZrMe_2$ (23.1 mg, 0.1 mmol) and *t*-$Bu_2P(C_6H_5)OH$ (23.8 mg, 0.1 mmol) were loaded into an NMR tube fitted with a Teflon needle valve and dissolved in toluene-d_8 (0.7 mL), immediately resulting in the slow evolution of gas as the reagents dissolved. The tube was removed after gas evolution subsided (ca. 16 h), and the relevant NMR spectra of the neutral precursor acquired. (Not isolated, quantitative by NMR.) ^1H NMR (400 Hz toluene-d_8): δ 7.62 (dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.0 Hz, $\underline{H}_{C6}$), 7.15 (ddd, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.7 Hz $\underline{H}_{C3}$), 6.76 (dt, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, $\underline{H}_{C4}$), 6.52 (ddd, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 6.4 Hz, $^4J_{HH}$ = 1.2 Hz $\underline{H}_{C5}$), 5.83 (s, 5H, $C_5\underline{H}_5$), 1.79 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.27 (d, $^3J_{HP}$ = 11.3 Hz, 9H, $C(C\underline{H}_3)_3$), 1.26 (d, $^3J_{HP}$ = 11.3 Hz, 9H, $C(C\underline{H}_3)_3$), 0.35 (d, J_{HP} = 0.7 Hz, 3H, Zr CH_3). $^{13}C\{^1H\}$ (100 Hz, toluene-d_8): δ 169.9 (d, $^2J_{CP}$ = 24.1 Hz, $\underline{C}1$), 136.1 (d, $^3J_{CP}$ = 3.9 Hz, $\underline{C}6$), 130.3 (s, $\underline{C}5$), 125.5 (d, $^2J_{CP}$ = 24.9 Hz, $\underline{C}3$), 119.7 (d, $^3J_{CP}$ = 3.1 Hz, $\underline{C}4$), 117.9 (s, $\underline{C}2$), 118.4 (s, $\underline{C}_5(CH_3)_5$), 111.6 (s, $\underline{C}_5H_5$), 32.5 (d, $^1J_{CP}$ = 25.7 Hz, $\underline{C}(CH_3)_3$), 32.4 (d, $^1J_{CP}$ = 25.7 Hz, $\underline{C}(CH_3)_3$), 31.1 (d, $^2J_{CP}$ = 16.4 Hz, $C(\underline{C}H_3)_3$), 30.9 (d, $^2J_{CP}$ = 16.4 Hz, $C(\underline{C}H_3)_3$), 30.2 (d, J_{CP} = 9.3 Hz,, $Zr\underline{C}H_3$), 11.6 (d, J_{CP} = 1.6 Hz, $C_5(\underline{C}H_3)_5$). $^{31}P\{^1H\}$ (161 Hz, toluene-d_8): δ 9.20 (s).

The tube was returned to the glovebox and combined with a chlorobenzene solution $[(DTBP)H][B(C_6F_5)_4]$ (78.4 mg, 0.09 mmol), resulting in orange solution and gas evolution. The solution was allowed to stand for 16 h and analyzed by ^{31}P NMR which showed quantitative conversion to **3**. The tube was again returned to the glovebox and then layered with hexanes and allowed to stand for a further 16 h, precipitating an orange oil. Decanting the supernatant and washing the residue with several portions of hexanes before drying in vacuo afforded an amorphous yellow solid. Yield: 97.9 mg, 0.081 mmol, 90%. ^1H NMR (500 Hz, chlorobenzene/benzene-d_6, 5:1): $\underline{H}_{C3}$, $\underline{H}_{C4}$, and $\underline{H}_{C6}$ aromatic signals are obscured by chlorobenzene signals and could not be unambiguously identified. δ 6.41 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 4.9 Hz, 1H, $\underline{H}_{C5}$), 5.76 (s, 5H, $C_5\underline{H}_5$), 1.78 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.11 (br. d, $^3J_{HP} \sim 55$ Hz, 18H, $C(C\underline{H}_3)_3$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/benzene-d_6, 5:1): δ 53.34. $^{13}C\{^1H\}$ (125 Hz, 500 Hz, chlorobenzene/benzene-d_6, 5:1): δ 168.0 (d, $^2J_{CP}$ = 15.2 Hz, $\underline{C}1$), 133.9 (s, $\underline{C}4$), 133.6 (d, $^4J_{CP}$ = 2.9 Hz, $\underline{C}5$), 123.2 (s, d, $^3J_{CP}$ = 3.9 Hz, $\underline{C}6$), 122.4 (d, $^1J_{CP}$ = 21.5 Hz, $\underline{C}2$), 120.9 ($\underline{C}_5(CH_3)_5$), 117.9 (d, $^1J_{CP}$ = 4.9 Hz, $\underline{C}3$), 116.6 (s, $\underline{C}_5H_5$), 32.1 (br.s, $\underline{C}(CH_3)_3$), 29.8 (br. s, $C(\underline{C}H_3)_3$), 12.8 (s, $C_5(\underline{C}H_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/benzene-d_6, 5:1): δ 53.3 (s). ESI MS: 527.2 [M]. Elemental Analysis: Calcd: C, 52.70; H, 3.50. Found: C, 52.71; H, 3.90.

Compound 4. Compound **4** was prepared in an analogous fashion to **2** (0.07 mmol scale). Orange crystals were grown from a chlorobenzene solution layered with hexane. Yield: 77.5 mg, 0.062 mmol, 89%. ^1H NMR (500 Hz, chlorobenzene/toluene-d_8, 5:1): $\underline{H}_{C3}$, $\underline{H}_{C4}$, and $\underline{H}_{C6}$ aromatic signals are obscured by chlorobenzene signals and could not be unambiguously identified. δ 6.45 (ddd, 1H, $^3J_{HH}$ = 8.26 Hz, $^4J_{HH}$ = 4.5 Hz, J_{HP} = 1.1 Hz, $\underline{H}_5$, 1H, $\underline{H}c_5$), 2.49 (sept, $^3J_{HH}$ = 7.34 Hz, 1H, $C\underline{H}(CH_3)_2$), 2.48 (sept, $^3J_{HH}$ = 7.34 Hz, 1H, $C\underline{H}(CH_3)_2$), 1.57 (s, 30H, $C_5(C\underline{H}_3)_5$), 0.96 (dd, $^3J_{HP}$ = 14.9, $^3J_{HH}$ = 7.34 Hz, 6H, $CH(C\underline{H}_3)_2$), 0.95 (dd, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.34 Hz, 6H, $CH(C\underline{H}_3)_2$). $^{13}C\{^1H\}$ (125 Hz, chlorobenzene/toluene-d_8, 5:1): δ 166.7 (d, $^2J_{CP}$ = 16.6 Hz, $\underline{C}1$), 133.8 (s, $\underline{C}5$), 133.2 (s, $\underline{C}4$), 122.6 (d, $^3J_{CP}$ = 3.9 Hz, $\underline{C}6$), 121.7 (d, $^1J_{CP}$ = 28.4 Hz, $\underline{C}2$), 119.7 (d, $^2J_{CP}$ = 5.9 Hz, $\underline{C}3$), 127.16 (s, $\underline{C}_5(CH_3)_5$), 26.8 (d, $^1J_{CP}$ = 11.7 Hz, $\underline{C}H(CH_3)_2$), 21.4 (d, $^1J_{CP}$ = 2.0 Hz, $CH(\underline{C}H_3)_2$), 20.4 (d, $^2J_{CP}$ = 4.9 Hz, $CH(\underline{C}H_3)_2$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8 5:1): δ 23.88 (s). ESI MS: 569.25 [M]. Elemental Analysis: Calcd: C, 62.60; H, 8.17. Found: C, 62.27; H, 8.31.

Compound 5. In this instance, the neutral precursor was prepared in an identical fashion to that previously reported[20] from $Cp^*_2ZrMe_2$ (195 mg, 0.5 mmol) and $Mes_2P(C_6H_5)OH$ (181.2, 0.5 mmol). Yield: 339.5 mg, 0.46 mmol, 92%. ^1H NMR (400 Hz, toluene-d_8): δ 7.15 (ddd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 1.7 Hz, $\underline{H}_{C6}$), 7.06 (tm, 1H, $^3J_{HH}$ = 7.3 Hz, $\underline{H}_{C4}$), 6.73 (d, 4H, J_{HH} = 2.5 Hz, *m*-$\underline{H}$), 6.54 (tm, 1H, $^3J_{HH}$ = 7.58 Hz, $\underline{H}_{C3}$), 6.47 (tm, 1H, $^3J_{HH}$ = 6.11 Hz, $\underline{H}_{C5}$), 2.36 (s, 12H, *p*-C$\underline{H}_3$), 2.13 (s, 6H, *p*-C$\underline{H}_3$), 1.78 (s, 30H, $C_5(C\underline{H}_3)_5$), −0.03 (s, 3H, $ZrC\underline{H}_3$). $^{13}C\{^1H\}$ (100 Hz, toluene-d_8): δ 167.3 (d, $^2J_{CP}$ = 23.4 Hz, $\underline{C}1$), 144.0 (d, $^3J_{CP}$ = 16.4 Hz, *i*-$\underline{C}$), 137.5 (s, *o*-$\underline{C}$), 134.4 (s, *p*-$\underline{C}$), 132.6 (d, $^2J_{CP}$ = 21.8 Hz, $\underline{C}3$), 130.5 (d, $^3J_{CP}$ = 3.1 Hz, *m*-$\underline{C}$), 129.3 (s, $\underline{C}5$), 125.6 (d, $^3J_{CP}$ = 11.7 Hz, $\underline{C}6$), 120.7 (d, $^3J_{CP}$ = 11.7 Hz, $\underline{C}4$), 118.7 (s, $\underline{C}2$), 118.6 (s, $\underline{C}_5(CH_3)_5$), 33.8 (d, J_{CP} = 8.6 Hz, $Zr\underline{C}H_3$), 23.7 (d, J_{CP} = 16.4 Hz, *o*-$\underline{C}H_3$), 20.9 (s, *p*-$\underline{C}H_3$), 11.5 (s, $C_5(\underline{C}H_3)_5$). $^{31}P\{^1H\}$ (161 Hz, toluene-d_8): δ −26.8 (s). ESI MS: 737.35 [M + H]. Elemental Analysis: Calcd (1:1 hexane solvate): C, 74.31; H, 8.93. Found: C, 74.55; H, 8.90.

The neutral precursor (36.9 mg, 0.05 mmol) prepared above was activated and isolated in an analogous fashion to **2** except the compound was obtained as a deep red oil that could not be solidified despite repeated precipitation into hexanes. Yield: 69.7 mg, 0.046 mmol, 92%. ^1H NMR (500 Hz chlorobenzene/toluene-d_8, 5:1): $\underline{H}_{C3}$ and $\underline{H}_{C4}$ aromatic signals are obscured by chlorobenzene signals and could not

be unambiguously identified. 6.73 (d, 4H, J_{HH} = 3.1 Hz, *m*-H), 6.64 (t, 1H, $^3J_{HH}$ = 7.55 Hz, H_{C6}), 6.09 (pseudo t, 1H, $^3J_{HH}$ = 6.8 Hz, H_{C5}), 2.17 (s, 12H, *p*-CH_3), 2.16 (s, 6H, *p*-CH_3), 1.64 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ (100 Hz, toluene-d_8): δ 166.2 (d, $^2J_{CP}$ = 24.3 Hz, C1), 143.8 (d, $^3J_{CP}$ = 15.7 Hz, *i*-C), 139.2 (s, *o*-C), 135.6 (s, C6), 135.6 (s, *p*-C), 129.4 (d, $^3J_{CP}$ = 2.6 Hz, *m*-C), 129.3 (s, $C_5(CH_3)_5$), 125.3 (d, $^2J_{CP}$ = 13.7 Hz, C3), 121.8 (s, C2), 122.6 (s, C4), 119.6 (s, C5), 23.7 (d, J_{CP} = 15.0 Hz, *o*-CH_3), 21.2 (s, *p*-CH_3), 12.07 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8 5:1): δ −32.9 (s). ESI-MS not observed. Satisfactory elemental analysis could not be obtained. We attribute the depleted C and H determinations to be due to traces of chlorobenzene that remain occluded in the oil. Calcd: C, 55.28; H, 4.13. Found: C, 55.12; H, 4.25.

Compound 8. A sample of **3** dissolved in chlorobenzene (~0.7 mL) in a NMR tube equipped with a Teflon needle valve was connected to a Schlenk line and subjected to three freeze−pump−thaw degassing cycles then backfilled with 1 bar hydrogen at room temperature via liquid nitrogen trap. The solution immediately changed color to orange to yellow. The relevant spectra were recorded *in situ.* since attempts to isolate the material resulted in quantitative recovery of **3**. ^1H NMR (500 Hz, chlorobenzene/benzene-d6, 5:1): H_{C3}, H_{C4}, and H_{C6} aromatic signals are obscured by chlorobenzene signals and could not be unambiguously identified. 6.61 (br. s, 1H, Zr-H), 6.28 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 4.6 Hz, H_5, 1H, H_{C5}), 5.69 (s, 5H, C_5H_5), 1.77 (s, 15H, $C_5(CH_3)_5$), 0.90 (br. d, $^3J_{HP}$ = 17.2 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, 500 Hz, chlorobenzene/benzene-d_6, 5:1): δ 168.4 (s, C1), 137.7 (s, C3), 131.3 (s, C6), 121.4 (s, C5), 120.9 ($C_5(CH_3)_5$), 120.5 (d, $^3J_{CP}$ = 11.8 Hz, C4), 110.8 (s, C_5H_5), 100.2 (d, $^1J_{CP}$ = 72.4 Hz, C2), 34.6 (d, $^1J_{CP}$ = 36.2 Hz, $C(CH_3)_2$), 34.4 (d, $^1J_{CP}$ = 34.2 Hz, $C(CH_3)_2$), 27.7 (br. s, $C(CH_3)_2$), 27.5 (br. s, $C(CH_3)_2$), 12.75 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/benzene-d_6, 5:1): δ 19.61.

Compound 9. Compound **9** was prepared in an identical fashion to **6**[20] using **5** (instead of **2**) (30.3 mg, 0.02 mmol). The product could not be isolated in pure form, since exposure to vacuum resulted in some decomposition to **5**, and thus, only in situ NMR data of the major species are presented. ^1H NMR (chlorobenzene/toluene-d_8, 5:1): H_{C3} aromatic signals are obscured by chlorobenzene signals and could not be unambiguously identified. δ 7.80 (d, 1H, $^2J_{HP}$ = 484.4 Hz), 7.02 (m, 1H, H_{C5}), 6.42 (d, 4H, J_{HH} = 4.9 Hz, *m*-H), 6.37 (dt, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 2.4 Hz, H_{C4}), 6.07 (t, 1H, $^3J_{HH}$ = 7.63 Hz, H_{C6}), 1.81 (s, 12H, *p*-CH_3), 1.71 (s, 6H, *p*-CH_3), 1.41 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ (100 Hz, chlorobenzene/toluene-d_8, 5:1): δ 167.3 (s, C1), 146.5 (d, $^3J_{CP}$ = 2.9 Hz, *i*-C), 143.8 (s, $^3J_{CP}$ = 9.8 Hz *o*-C), 137.1 (s, *p*-C), 133.9 (s, C3), 132.1 (d, $^3J_{CP}$ = 11.8 Hz, *m*-C), 129.7 (s, C6), 121.8 (s, C5), 120.0 (d, $^3J_{CP}$ = 13.7 Hz, C4), 119.6 (s, $C_5(CH_3)_5$), 101.7 (d, $^1J_{CP}$ = 90 Hz, C2), 21.6 (d, J_{CP} = 7.8 Hz, *o*-CH_3), 20.6 (s, *p*-CH_3), 11.3 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8, 5:1): δ −27.33 (s, minor 10%), −29.23 (s, major 90%). ESI MS: not observed.

Compound 10. A sample of **2** (27.8 mg, 0.02 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. The tube was removed, connected to a Schlenk line via a three way valve connected to a regulated 1 bar supply of CO_2 via a −78 °C trap. The tube was subjected to three freeze−pump−thaw degassing cycles, refilling with CO on the last cycle once the tube had warmed to room temperature. Upon shaking, the solution immediately became bright red. The tube was again degassed and then returned to the glovebox. The solution was layered with hexane precipitating large yellow blocks. Yield: 25.2 mg, 0.0191 mmol, 96%. ^1H NMR (500 Hz chlorobenzene/toluene-d_8, 5:1): δ 7.22 (m, 2H, H_{C5} and H_{C3}), 6.74 (partial m, H_{C4}), 6.44 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.2 Hz $^4J_{HH}$ = 0.9 Hz, H_{C6}), 1.61 (s, 30H, $C_5(CH_3)_5$), 1.18 (d, $^3J_{HP}$ = 15.9 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, chlorobenzene/toluene-d_8, 5:1): δ 169.3 (s, C1), 161.9 (d, $^1J_{CP}$ = 85.1 Hz, ZrOC(O)P), 137.5 (s, C5), 128.9 (d, $^2J_{CP}$ = 8.8 Hz, C3), 126.2 (s, $C_5(CH_3)_5$), 123.5 (d, $^3J_{CP}$ = 7.8 Hz, C6), 119.7 (d, $^3J_{CP}$ = 9.8 Hz, C4), 117.6 (s, C_5H_5), 104.5 (d, $^1J_{CP}$ = 49.9 Hz, C2), 38.6 (d, $^1J_{CP}$ = 26.4 Hz, $C(CH_3)_3$), 28.9 (s, $C(CH_3)_3$), 11.2 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8, 5:1): δ 37.02 (s). ESI-MS: 615.29 [M − CO_2 + H_2O]. Elemental Analysis (1:1 PhCl solvate from crystal structure): Calcd: C, 54.42; H, 4.00. Found: C, 54.78; H, 4.36.

Compound 11. An identical procedure to **10** using **1** instead of **2** (45.5 mg, 0.04 mmol) was followed, giving pale yellow blocks. Yield: 42.7 mg, 0.0361 mmol, 73%. ^1H NMR (500 Hz fluorobenzene/toluene-d_8, 5:1): H_{C4} aromatic signal is obscured by fluorobenzene signals and could not be unambiguously identified. δ 7.33 (overlapping ddt, 1H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.22 Hz, H_{C5}), 7.04 (partial m, H_{C3}), 6.48 (ddd, 1H, $^3J_{HH}$ = 8.31 Hz, $^3J_{HH}$ = 6.6 Hz $^4J_{HH}$ = 0.98 Hz, H_{C6}), 6.02 (s, C_5H_5), 1.16 (d, $^3J_{HP}$ = 15.9 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, fluorobenzene/benzene-d_{68}, 5:1): δ 169.9 (d, $^2J_{CP}$ = 1.5 Hz, C1), 164.7 (d, $^1J_{CP}$ = 94.4 Hz, ZrOC(O)P), 137.4 (d, $^4J_{CP}$ = 2.9 Hz, C5), 134.6 (d, $^2J_{CP}$ = 4.9 Hz, C3), 122.2 (d, $^3J_{CP}$ = 7.3 Hz, C6), 121.2 (d, $^3J_{CP}$ = 10.3 Hz, C4), 117.6 (s, C_5H_5), 105.4 (d, $^1J_{CP}$ = 58.7 Hz, C2), 37.4 (d, $^1J_{CP}$ = 27.4 Hz, $C(CH_3)_3$), 27.8 (s, $C(CH_3)_3$). $^{31}P\{^1H\}$ (161 Hz, fluorobenzene/toluene-d_8 5:1): δ 37.02 (s). ESI-MS: 489.15 [M − CO_2 + O_2]. Elemental Analysis: Calcd: C, 49.80; H, 2.73. Found: C, 49.79; H, 2.78.

Compound 12. A sample of **6** (64.0 mg, 0.05 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a colorless solution. The tube was removed, connected to a Schlenk line and subjected to three freeze−pump−thaw degassing cycles and then backfilled with 1 bar carbon dioxide at room temperature via trap cooled to −40 °C. After ca. 5 min, a white precipitate began to form. The $^{31}P\{^1H\}$ NMR spectrum of the supernatant revealed 100% conversion of **6**. The sample was degassed and then returned to the glovebox and poured into hexane (1 mL). The resulting white powder was collected on a frit and washed with several portions of hexane before drying in vacuo. Crystals suitable for X-ray diffraction were grown from a DCM solution layered with hexane at room temperature. Yield: 39 mg, 0.029 mmol, 59%. ^1H NMR (500 MHz, DCM-d_2): δ 8.76 (d, J_{HP} = 2.4 Hz, 1H, OC(O)H), 7.77 (d, 1H, $^1J_{HP}$ = 492.2 Hz, P-H), 7.54 (t, 1H, $^3J_{HH}$ = 8.2 Hz, H_{C5}), 7.39 (ddd, 1H, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, H_{C3}), 7.00 (dt, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HP}$ = 2.2 Hz, H_{C4}), 6.57 (ddd, 1H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 0.7 Hz, H_{C6}), 1.95 (s, 30H, $C_5(CH_3)_5$), 1.52 (br. d, $^3J_{HP}$ = 16.7 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 MHz, DCM-d2): δ 167.6 (s, C1), 166.6 (s, OC(O)H), 133.5 (s, C5), 133.3 (d, $^2J_{CP}$ = 6.9 Hz, C3), 124.8 (s, $C_5(CH_3)_5$), 123.8 (d, $^3J_{CP}$ = 6.4 Hz, C6), 119.9 (d, $^3J_{CP}$ = 10.8 Hz, C4), 102.4 (d, $^1J_{CP}$ = 73.9 Hz, C2), 37.2 (d, $^1J_{CP}$ = 37.2 Hz, $C(CH_3)_3$), 28.5 (s, $^2J_{CP}$ = 1.5 Hz, $(C(CH_3)_3)$, 12.2 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (121 Hz, DCM-d_2): δ 14.78 (s). ESI-MS: 643.29 [M]. Elemental Analysis: Calcd: C, 53.52 H, 4.11. Found: C, 53.48; H, 4.34.

Compound 13. A sample of **6** (69.5 mg, 0.05 mmol) (compound **2** may also be conveniently used in the same manner) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. The tube was removed, connected to a Schlenk line via a three way valve connected to a regulated 1 bar supply of CO. The tube was subjected to three freeze−pump−thaw degassing cycles, refilling with CO on the last cycle once the tube had warmed to room temperature. Upon shaking, the solution immediately became bright red. The tube was again degassed and then returned to the glovebox. The solution was layered with hexane, precipitating large red blocks. Yield: 64.0 mg, 0.049 mmol, 98%. ^1H NMR (400 Hz chlorobenzene/toluene-d_8, 5:1): H_{C3} and H_{C4} aromatic signals are obscured by chlorobenzene signals and could not be unambiguously identified. δ 7.51 (dt, 1H, $^3J_{HH}$ = 7.69 Hz, $^4J_{HH}$ = 1.83 Hz, H_{C6}), 6.09 (ddd, 1H, $^3J_{HH}$ = 8.06 Hz, $^3J_{HH}$ = 5.13 Hz $^4J_{HH}$ = 1.10 Hz, H_{C5}), 1.66 (s, 30H, $C_5(CH_3)_5$), 1.08 (d, $^3J_{HP}$ = 12.05 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, chlorobenzene/toluene-d_8, 5:1): δ 195.1 (s, ZrCO), 165.9 (d, $^3J_{CP}$ = 22.0 Hz, C1),

136.9 (s, C6), 126.1 (s, $C_5(CH_3)_5$), 122.5 (d, $^2J_{CP}$ = 23.5 Hz, C3), 121.4 (s, C2), 121.1 (s, C4), 118.5 (d, $^4J_{CP}$ = 3.4 Hz, C5), 33.1 (d, $^1J_{CP}$ = 20.1 Hz, $C(CH_3)_2$), 30.9 (d, $^2J_{CP}$ = 14.2 Hz, $C(CH_3)_2$), 11.3 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8 5:1): δ 5.63. ESI-MS: 615.29 [M − CO + H_2O]. Elemental Analysis: Calcd: C, 54.26; H, 4.01. Found: C, 54.25; H, 4.29.

Compound 14. *Method A.* **2** (69.5 mg, 0.05 mmol) was dissolved in chlorobenzene (0.3 mL) then loaded into a high pressure NMR tube fitted with a Teflon needle valve giving a bright orange solution. The tube was removed, connected to a Schlenk line, and subjected to three freeze−pump−thaw degassing cycles and then backfilled with 10 bar carbon monoxide/hydrogen (50:50) at room temperature via a column (10 × 1 cm) of freshly activated powdered molecular sieves. The solution immediately changed color to pale green. Once the reaction was deemed complete by $^{31}P\{^1H\}$ NMR (ca. 14 days), the sample was degassed, returned to the glovebox, and transferred to a standard NMR tube where toluene-d_8 (0.3 mL) was added. The tube was sealed and removed, and the relevant spectra were acquired. The sample was returned to the glovebox and layered with hexane. The colorless crystals were separated from the supernatant via decantation and then washed with hexane and dried in vacuo. Yield: 56 mg, 0.043 mmol, 86%. ^1H NMR (500 Hz chlorobenzene/toluene-d_8, 1:1): δ 7.23 (m, 1H, H_{C5}), H_{C3} obscured by chlorobenzene ^{13}C satellites, 7.19 (tm, 1H, $^3J_{HH}$ = 7.0 Hz, H_{C4}), 6.67 (tm, 1H, $^3J_{HH}$ = 8.24 Hz, H_{C6}), 6.50 (dd, 1H, $^3J_{HH}$ = 8.55 Hz, $^4J_{HH}$ = 5.18 Hz H_{C3}), 5.19 (br. s., 2H, OCH_2P), 1.63 (s, 30H, $C_5(CH_3)_5$), 1.63 (d, $^3J_{HP}$ = 14.6 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, chlorobenzene/toluene-d_8, 1:1): δ 168.4 (d, $^2J_{CP}$ = 1.6 Hz, C1), 135.6 (s, C5), 124.4 (d, $^2J_{CP}$ = 8.8 Hz, C3), 123.9 (s, $C_5(CH_3)_5$), 129.0 (s, C6), 118.9 (d, $^3J_{CP}$ = 10.8 Hz, C4), 103.1 (d, $^1J_{CP}$ = 59.7 Hz, C2), 64.6 (d, $^1J_{CP}$ = 40.1 Hz,OCH_2P), 37.6 (d, $^1J_{CP}$ = 31.3 Hz, $C(CH_3)_3$), 28.5 (s, $C(CH_3)_3$), 11.5 (s, $C_5(CH_3)_5$).$^{31}P\{^1H\}$ (161 Hz, chlorobenzene/toluene-d_8, 1:1): δ 40.2 (s). ESI-MS: 627.29 [M]. Elemental Analysis: Calcd: C, 54.18; H, 4.16. Found: C, 54.39; H, 4.00.

Method B. Paraformaldehyde (ca. 30 mg) was decomposed at 120 °C under a 10^{-3} Torr static vacuum and collected in a liquid nitrogen trap via a glass sinter (porosity 4). The trap was then connected to an NMR tube containing **2** (27.8 mg, 0.02 mmol) and subjected to three freeze−pump−thaw degassing cycles. After the last cycle, the NMR tube was allowed to remain frozen and fully submersed in liquid nitrogen and then opened to the trap. Upon slow warming to ambient conditions, excess formaldehyde gas was vacuum transferred to the NMR tube. The tube was then allowed to warm to ambient where the color changed from orange to yellow. Following the reaction by $^{31}P\{^1H\}$ NMR revealed ca. 60% conversion to **14** after 30 min, ca. 20% unidentified species (s, 23.49; s, 23.04; s, 21.86; s, 21.52), and unreacted **2.**

Compound 15. A sample of **2** (27.8 mg, 0.02 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess phenylacetylene (ca. 3 drops) was added, immediately giving a pale green solution. The ^{31}P and $^{31}P\{^1H\}$ NMR spectra of the colorless solution revealed >99% conversion of **3**. The sample was returned to the glovebox, layered with hexane, and allowed to stand for 16 h, precipitating large pale green needles. The supernatant was decanted, and the solids washed with hexane before drying in vacuo. Yield: 24.8 mg, 0.018 mmol, 90%. ^1H NMR (500 MHz DCM-d_2): δ 7.51 (m, 2H, H_{C5} and H_{C3}), 7.32 (m, 5H, H_{Ar}), 6.95 (overlapping ddd, 1H, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HP}$ = 2.8 Hz, H_{C4}), 6.65 (d, 1H, $^1J_{HP}$ = 471.5 Hz, P-H), 6.58 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.2 Hz, H_{C6}), 2.04 (s, 30H, $C_5(CH_3)_5$), 1.36 (d, $^3J_{HP}$ = 17.0 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 MHz, DCM-d_2): δ 167.7 (s, C1), 137.0 (d, $^4J_{CP}$ = 2.45 Hz, C5), 132.9 (d, $^2J_{CP}$ = 7.8 Hz, C3), 132.2 (s, *o*-C), 130.4 (s, *p*-C), 129.3 (s, *m*-C), 128.7 (s, *i*-C), 127.1 (s, PhCCZr), 125.6 (s, PhCCZr), 123.3 (d, $^3J_{CP}$ = 6.9 Hz, C6), 122.8 (s, $C_5(CH_3)_5$), 119.9 (d, $^3J_{CP}$ = 11.7 Hz, C4), 101.4 (d, $^1J_{CP}$ = 73.9 Hz, C2), 35.0 (d, $^1J_{CP}$ = 36.7 Hz, $C(CH_3)_3$), 28.5 (s, $C(CH_3)_3$), 12.6 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (121 Hz, DCM-d_2): δ 20.49 (s). ESI-MS: 699.33 [M]. Elemental Analysis: Calcd: C, 57.44 H, 4.24. Found: C, 57.83; H, 4.08.

Compound 16. Conpound **16** was prepared in a analogous fashion to **15** but not isolated. $^{31}P\{^1H\}$ (121 Hz, unlocked, PhCl): δ 20.25. ^{31}P (121 Hz, unlocked, PhCl): δ 20.23 (d, $^1J_{PH}$ = 481.95 Hz). ESI-MS: 559.17 [M].

Compound 17. Compound **17** was prepared in a analogous fashion to **15** but not isolated. $^{31}P\{^1H\}$ (121 Hz, unlocked, PhCl): δ −29.95. ^{31}P (121 Hz, unlocked, PhCl): δ −29.95 (d, $^1J_{PH}$ = 513.59 Hz). ESI-MS: 825.25 [M].

Compound 18. A sample of **2** (55.6 mg, 0.04 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. The tube was removed, connected to a Schlenk line via a three way valve connected to a regulated 1 bar supply of ethene. The tube was subjected to three freeze−pump−thaw degassing cycles, refilling with ethene on the last cycle once the tube had warmed to room temperature. Upon shaking, the solution immediately became pale green. The tube was again degassed and then returned to the glovebox. The solution was layered with hexane, precipitating colorless needles. Yield: 39.2 mg, 0.03 mmol, 75%. ^1H NMR (500 MHz, DCM-d_2): δ 7.48 (t, 1H, $^3J_{HH}$ = 8.2 Hz, H_{C5}), 7.35 (ddd, 1H, $^3J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HP}$ = 1.8 Hz, H_{C3}), 6.95 (t, 1H, $^3J_{HH}$ = 7.93 Hz, H_{C4}), 6.65 (ddd, 1H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 1.2 Hz, H_{C6}), 3.10 (br. d, 2H, $^2J_{HP}$ = 54.2 Hz, $ZrCH_2CH_2P$), 1.97 (br. s, 15H, $C_5(CH_3)_5$), 1.77 (br. s, 15H, $C_5(CH_3)_5$), 1.70 (br. s, 9H, $C(CH_3)_3$), 1.50 (d, $^3J_{HP}$ = 17.0 Hz, 2H, $ZrCH_2CH_2P$), 1.28 (br. s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 MHz, DCM-d_2): δ 170.4 (s, C1), 135.9 (d, $^2J_{CP}$ = 1.9 Hz, C5), 135.3 (d, $^3J_{CP}$ = 5.9 Hz, C3), 124.4 (d, $^3J_{CP}$ = 7.8 Hz, C6), 122.2 (s, $C_5(CH_3)_5$) 119.2 (d, $^3J_{CP}$ = 9.8 Hz, C4), 100.9 (d, $^1J_{CP}$ = 76.3 Hz, C2), 37.6 (br. m, $C(CH_3)_3$), 31.1 (br. s, $C(CH_3)_3$), 28.1 (br. s, $C(CH_3)_3$), 28.8 (d, $^1J_{CP}$ = 6.9 Hz, $ZrCH_2CH_2P$), 21.7 (d, $^1J_{CP}$ = 36.2 Hz, $ZrCH_2CH_2P$), 11.9 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (121 Hz, DCM-d_2): δ 45.07. ESI-MS: 625.31 [M]. Elemental Analysis: Calcd: C, 55.13; H, 4.40. Found: C, 55.49; H, 4.68.

Compound 20. Samples of $[Cp^*_2Zr(Me)O(C_6H_4)P^tBu_2]$ (49.1 mg, 0.08 mmol) and $[DTBP][B(C_6F_5)_4]$ (69.7 mg, 0.08 mmol) were weighed into two vials, dissolved in DCM (1 mL), and mixed, immediately precipitating a white solid. After standing overnight, the solids had dissolved, and the $^{31}P\{^1H\}$ NMR spectra of the pale green solution revealed >99% conversion to **19**. The sample was returned to the glovebox and poured into hexane, and the resulting white solids were collected on a frit and then washed with several portions of hexanes before drying in vacuo. Large green crystals suitable for X-ray diffraction were grown by layering a concentrated DCM solution with hexane. Yield: 93.3 mg, 0.079 mmol, 99%. Compound **20** may also be conveniently obtained by dissolution of **2** in DCM. ^1H NMR (500 Hz, DCM-d_2): δ 7.50 (tm, 1H, $^3J_{HH}$ = 8.0 Hz, H_{C5}), 7.46 (ddd, 1H, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 8.2 Hz, J_{HP} = 1.6 Hz, H_{C3}), 6.97 (tm, 1H, $^3J_{HH}$ = 8.1 Hz, H_{C4}), 6.16 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.5 Hz, J_{HP} = 0.9 Hz, H_{C6}), 4.64 (d, 2H, $^2J_{HP}$ = 5.8 Hz, PCH_2Cl), 1.95 (s, 30H, $C_5(CH_3)_5$), 1.60 (d, $^3J_{HP}$ = 15.9 Hz, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125 Hz, DCM-d_2): δ 168.0 (s, C1), 136.3 (d, $^4J_{CP}$ = 2.9 Hz, C5), 135.1 (d, $^2J_{CP}$ = 6.9 Hz, C3), 126.1 (d, $^3J_{CP}$ = 7.8 Hz, C6), 125.4 (s, $C_5(CH_3)_5$), 119.3 (d, $^3J_{CP}$ = 10.9 Hz, C4), 101.2 (d, $^1J_{CP}$ = 66.5 Hz, C2), 39.6 (d, $^1J_{CP}$ = 32.3 Hz, $C(CH_3)_3$), 31.7 (d, $^1J_{CP}$ = 43.0 Hz, PCH_2C), 29.0 (s, $C(CH_3)_3$), 12.6 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ (161 Hz, DCM-d_2): δ 41.5 (s). ESI-MS: 681.23 [M]. Elemental Analysis (DCM/hexane 1:1 solvate from crystal structure): Calcd: C, 51.67; H, 4.60. Found: C, 51.53; H, 4.85.

Compound 21. A sample of **1** (0.05 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess ^{n}PrCl (ca. 3 drops) was added, immediately causing the solution to turn pale green. The ^{31}P and $^{31}P\{^1H\}$ NMR spectra revealed >99% conversion of **1**. The NMR of the reaction mixture after standing overnight showed a 9:1

mixture of **21**:**27**. Attempts to crystallize the reaction mixture led only to the isolation of pale green oils that were found to be mixtures of **21** and **27**. $^{31}P\{^{1}H\}$ (121 Hz, unlocked, PhCl): δ 42.87. ESI-MS: 535.21 [M].

Compound 22. Compound **22** was prepared in a similar manner to **21** using ^{n}PrCl and **2** (0.02 mmol). The NMR of the reaction mixture after standing overnight showed a 9:1 mixture of **28**:**22**. Attempts to crystallize the reaction mixture led only to the isolation of pale green oils that were found to be mixtures of **28** and **22**. $^{31}P\{^{1}H\}$ (121 Hz, unlocked, PhCl): δ 42.63. ESI-MS: 675.30 [M].

Compound 23. Compound **23** was prepared in a similar manner to **21** using ^{i}PrCl and **1** (0.02 mmol). The NMR of the reaction mixture after standing overnight showed a 10:1 mixture of **23**:**27**. Attempts to crystallize the reaction mixture led only to the isolation of pale green oils that were found to be mixtures of **23** and **27**. $^{31}P\{^{1}H\}$ (121 Hz, unlocked, PhCl): δ 51.80. ESI-MS: 535.21 [M].

Compound 24. Compound **24** was prepared in an analogous manner to **21** using excess ^{i}PrCl (0.05 mmol). The NMR of the reaction mixture after standing overnight showed a 15:1 mixture of **24**:**28**. Pale green crystals were obtained after three recrystallizations from DCM solutions layered with hexane. Yield: 24.0 mg, 0.0177 mmol, 35%. ^{1}H NMR (500 MHz DCM-d_2): δ 7.46 (pseudo t, 1H, $^{3}J_{HH}$ = 8.4 Hz, $\underline{H}_{C5}$), 7.36 (overlapping dd, 1H, $^{3}J_{HH}$ = 7.47 Hz, J_{HP} = 1.47 Hz $\underline{H}_{C3}$), 7.15 (overlapping dd, 1H, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 2.6 Hz, $\underline{H}_{C4}$), 6.06 (dd, 1H, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 4.9 Hz, $\underline{H}_{C6}$), 3.67 (sept, 1H, $^{3}J_{HH}$ = 7.6 Hz, $CH(\underline{C}H_3)_2$), 1.95 (s, 30H, $C_5(\underline{C}H_3)_5$), 1.62 (partial dd, $^{3}J_{HP}$ = 15.7 Hz, $^{3}J_{HH}$ = 7.6 Hz, 6H, $CH(\underline{C}H_3)_2$), 1.56 (d, $^{3}J_{HP}$ = 15.4 Hz, 18H, $C(\underline{C}H_3)_3$). $^{13}C\{^{1}H\}$ (125 MHz DCM-d_2): δ 167.9 (s, $\underline{C}1$), 135.4 (d, $^{2}J_{CP}$ = 3.1 Hz, $\underline{C}5$), 130.6 (d, $^{3}J_{CP}$ = 7.8 Hz, $\underline{C}3$), 124.7 (d, $^{3}J_{CP}$ = 3.1 Hz, $\underline{C}4$), 119.0 (d, $^{4}J_{CP}$ = 10.9 Hz, $\underline{C}6$), 115.5 (s, $\underline{C}_5H_5$), 103.6 (d, $^{1}J_{CP}$ = 66.2 Hz, $\underline{C}2$), 39.5 (d, $^{1}J_{CP}$ = 31.1 Hz, $\underline{C}(CH_3)_3$), 29.1 (s, $C(\underline{C}H_3)_3$), 24.9 (d, $^{1}J_{CP}$ = 35.0 Hz, $CH(\underline{C}H_3)_2$), 20.8 (br. s, $CH(\underline{C}H_3)_2$), 12.6 (s, $C_5(\underline{C}H_3)_5$). $^{31}P\{^{1}H\}$ (121 Hz, DCM-d_2): δ 51.24. ESI-MS: 675.30 [M]. Satisfactory elemental analysis could not be obtained. We attribute the depleted C and H determinations to be due to traces of elimination product (evident in ESI-MS and NMR) that could not fully be removed despite recrystallization. Calcd: C, 54.01; H, 4.38. Found (average of five determinations): C, 53.50; H, 4.51.

Compound 25. Compound **25** was prepared in a similar manner to **22** using neopentyl chloride (0.02 mmol). The NMR of the reaction mixture after standing overnight showed a 1:4 mixture of **25**:**28**. Attempts to crystallize the reaction mixture led only to the isolation of a pale green powder that was found to be mixtures of **25** and **28**. $^{31}P\{^{1}H\}$ (121 Hz, unlocked, PhCl): δ 55.85. ESI-MS: 703.34 [M].

Compound 26. A sample of **2** (83.4 mg, 0.06 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess 1-fluoropentane (ca. 3 drops) was added, immediately giving a pale green solution and a white precipitate. The $^{31}P\{^{1}H\}$ NMR spectra of the colorless solution revealed >99% conversion of **3** in the supernatant. The sample was returned to the glovebox and poured into hexane, and the resulting white solids were collected on a frit and then washed with several portions of hexanes before drying in vacuo. Yield: 56.6 mg, 0.041 mmol, 69%. ^{1}H NMR (500 Hz, DCM-d_2): δ 7.47 (m, 1H, $\underline{H}_{C5}$), 7.34 (m, 1H, $\underline{H}_{C3}$), 6.92 (tm, 1H, $^{3}J_{HH}$ = 8.1 Hz, $\underline{H}_{C6}$), 6.20 (dd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 5.4 Hz, $\underline{H}_{C4}$), 2.81 (m, 2H, $\underline{H}_a$), 1.95 (partial m, $\underline{H}_b$), 1.92 (s, 30H, $C_5(\underline{C}H_3)_5$), 1.68 (pseudo q, $^{3}J_{HH}$ = 7.7 Hz, 2H, $\underline{H}_d$), 1.52 (d, $^{3}J_{HP}$ = 15.1 Hz, 18H, $C(\underline{C}H_3)_3$), 1.44 (pseudo q, $^{3}J_{HH}$ = 7.4 Hz, 2H, $\underline{H}_c$), 0.99 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $\underline{H}_e$). $^{13}C\{^{1}H\}$ (125 Hz, DCM-d_2): δ 168.6 (s, $\underline{C}1$), 135.6 (d, $^{4}J_{CP}$ = 2.3 Hz, $\underline{C}5$), 135.2 (d, $^{2}J_{CP}$ = 7.0 Hz, $\underline{C}3$), 126.2 (d, $^{3}J_{CP}$ = 8.6 Hz, $\underline{C}6$), 123.7 (s, $\underline{C}_5(CH_3)_5$), 118.5 (d, $^{3}J_{CP}$ = 10.9 Hz, $\underline{C}4$), 103.4 (d, $^{1}J_{CP}$ = 68.5 Hz, $\underline{C}2$), 38.7 (d, $^{1}J_{CP}$ = 35.8 Hz, $\underline{C}(CH_3)_3$), 28.5 (s, $C(\underline{C}H_3)_3$), 33.7 (br. s, $\underline{C}_c$), 26.2 (br. s, $\underline{C}_b$), 23.0 (s, $\underline{C}_d$), 20.1 (d, $^{1}J_{CP}$ = 39.7 Hz, $\underline{C}_a$), 14.2 (s, $\underline{C}_e$), 11.7 (s, $C_5(\underline{C}H_3)_5$). $^{31}P\{^{1}H\}$ (161 Hz, DCM-d_2): δ 43.9 (br. s). ^{19}F (470 Hz, DCM-d_2): δ −207.2 (br. s, Zr−F). ESI-MS: 687.36 [M]. Elemental Analysis: Calcd: C, 55.31; H, 4.64. Found: C, 55.32; H, 4.54.

Compound 27. Prepared in a similar way to **21** using an excess of ^{t}BuCl (3 drops). The sample was layered with hexane and allowed to stand for 16 h precipitating a white microcrystalline solid. The supernatant was decanted, and the solids washed with hexane before drying in vacuo. Yield: 22.0 mg, 0.0188 mmol, 94%. ^{1}H NMR (500 MHz DCM-d_2): δ 7.64 (pseudo t, 1H, $^{3}J_{HH}$ = 8.3 Hz, $\underline{H}_{C5}$), 7.4 (overlapping dd, 1H, $^{3}J_{HH}$ = 7.47 Hz, J_{HP} = 1.47 Hz $\underline{H}_{C3}$), 7.12 (overlapping dd, 1H, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 2.5 Hz, $\underline{H}_{C4}$), 6.73 (d, 1H, $^{1}J_{HP}$ = 476.5 Hz, P-$\underline{H}$), 6.63 (dd, 1H, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 4.9 Hz, $\underline{H}_{C6}$), 6.47 (s, 10H, $C_5\underline{H}_5$), 1.49 (d, $^{3}J_{HP}$ = 17.4 Hz, 18H, $C(C\underline{H}_3)_3$). $^{13}C\{^{1}H\}$ (125 MHz DCM-d_2): δ 167.8 (s, $\underline{C}1$), 137.4 (d, $^{4}J_{CP}$ = 2.0 Hz, $\underline{C}5$), 131.9 (d, $^{2}J_{CP}$ = 7.0 Hz, $\underline{C}3$), 121.2 (d, $^{4}J_{CP}$ = 10.9 Hz, $\underline{C}6$), 119.9 (d, $^{3}J_{CP}$ = 5.5 Hz, $\underline{C}4$), 115.5 (s, $\underline{C}_5H_5$), 102.6 (d, $^{1}J_{CP}$ = 75.5 Hz, $\underline{C}2$), 34.4 (d, $^{1}J_{CP}$ = 35.0 Hz, $\underline{C}(CH_3)_3$), 27.5 (s, $C(\underline{C}H_3)_3$). $^{31}P\{^{1}H\}$ (121 Hz, DCM-d_2): δ 22.50 (s). ESI-MS: 493.11 [M]. Elemental Analysis: Calcd: C, 49.10; H, 2.83. Found: C, 48.99; H, 2.94.

Compound 28. Compound **28** was prepared in a similar manner to **27** using **2** (0.02 mmol.) Yield: 24.2 mg, 0.0184 mmol, 92%. ^{1}H NMR (500 MHz DCM-d_2). δ 7.53 (pseudo t, 1H, $^{3}J_{HH}$ = 7.1 Hz, $\underline{H}_{C5}$), 7.34 (overlapping dd, 1H, $^{3}J_{HH}$ = 7.5 Hz, J_{HP} = 1.5 Hz $\underline{H}_{C3}$), 6.98 (overlapping dd, 1H, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, $\underline{H}_{C4}$), 6.61 (ddd, 1H, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 4.9 Hz, $^{3}J_{HH}$ = 1.0 Hz, $\underline{H}_{C6}$), 6.48 (d, 1H, $^{1}J_{HP}$ = 471.7 Hz, P-$\underline{H}$), 1.96 (s, 30H, $C_5(\underline{C}H_3)_5$), 1.51 (d, $^{3}J_{HP}$ = 16.9 Hz, 18H, $C(\underline{C}H_3)_3$). $^{13}C\{^{1}H\}$ (125 MHz DCM-d_2): δ 167.0 (s, $\underline{C}1$), 136.3 (d, $^{4}J_{CP}$ = 2.0 Hz, $\underline{C}5$), 132.3 (d, $^{2}J_{CP}$ = 7.8 Hz, $\underline{C}3$), 124.23 (s, $\underline{C}_5(CH_3)_5$), 122.6 (d, $^{3}J_{CP}$ = 6.2 Hz, $\underline{C}6$), 119.7 (d, $^{3}J_{CP}$ = 11.7 Hz, $\underline{C}4$), 102.1 (d, $^{1}J_{CP}$ = 76.5 Hz, $\underline{C}2$), 34.8 (d, $^{1}J_{CP}$ = 36.6 Hz, $\underline{C}(CH_3)_3$), 28.2 (s, $C(\underline{C}H_3)_3$), 11.9 (s, $C_5(\underline{C}H_3)_5$). $^{31}P\{^{1}H\}$ (121 Hz, DCM-d_2): δ 21.55 (s). ESI-MS: 635.43 [M]. Elemental Analysis: Calcd: C, 53.00; H, 4.06. Found: C, 53.11; H, 4.16.

Compound 29. A sample of **2** (27.8 mg, 0.02 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess THF (ca. 3 drops) was added, immediately causing the solution to decolorize over the course of ca. 5 min. The $^{31}P\{^{1}H\}$ NMR spectrum of the colorless solution revealed >99% **29**. The sample was returned to the glovebox, layered with hexane, and allowed to stand for 16 h precipitating large colorless crystals. The supernatant was decanted, and the crystals were washed with hexane before drying in vacuo. Yield: 22.1 mg, 0.0162 mmol, 81%. ^{1}H NMR (500 Hz DCM-d_2): δ 7.45 (m, $\underline{H}_{C6}$ and $\underline{H}_{C3}$), 6.88 (ddd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 2.3 Hz J_{HP} = 1.2 Hz, $\underline{H}_{C4}$), 6.32 (ddd, 1H, $^{3}J_{HH}$ = 7.32 Hz, $^{4}J_{HH}$ = 6.0 Hz, J_{HP} = 1.1 Hz, $\underline{H}_{C5}$), 4.46 (t, 1H, $^{3}J_{HH}$ = 5.7 Hz, α-$\underline{H}$), 2.72 (m, 2H, δ-$\underline{H}$), 2.1 (br. m, 2H, γ-$\underline{H}$), 1.93 (s, 30H, $C_5(\underline{C}H_3)_5$), 1.86 (m, 2H, β-$\underline{H}$), 1.49 (d, 18H, $^{3}J_{HH}$ = 14.9 Hz, $C(\underline{C}H_3)_3$). $^{31}P\{^{1}H\}$ (121 Hz, DCM-d_2): δ 42.76. $^{13}C\{^{1}H\}$ (125 Hz, DCM-d_2): δ 169.9 (s, $\underline{C}1$), 135.5 (d, $^{2}J_{CP}$ = 2.9 Hz, $\underline{C}3$), 135.0 (d, $^{3}J_{CP}$ = 6.9 Hz, $\underline{C}6$), 126.7 (d, $^{4}J_{CP}$ = 8.8 Hz, $\underline{C}5$), 122.8 (s, $\underline{C}_5(CH_3)_5$), 117.7 (d, $^{3}J_{CP}$ = 10.76 Hz, $\underline{C}4$), 102.1 (d, $^{1}J_{CP}$ = 69.5 Hz, $\underline{C}2$) 67.3 (s, α-$\underline{C}$), 37.2 (d, $^{1}J_{CP}$ = 37.1 Hz, $\underline{C}(CH_3)_3$), 33.4 (d, $^{3}J_{CP}$ = 14.7 Hz, β-$\underline{C}$), 28.8 (s, $C(\underline{C}H_3)_3$), 21.3 (d, $^{2}J_{CP}$ = 5.9 Hz γ-$\underline{C}$), 19.4 (d $^{1}J_{CP}$ = 41.1 Hz δ-$\underline{C}$), 12.1 (s, $C_5(\underline{C}H_3)_5$). ESI-MS: 669.336 [M]. Elemental Analysis: Calcd: C, 55.16; H, 4.48. Found: C, 55.31; H, 4.48.

Compound 30. An identical procedure to **29** was followed except using **1** and an extended reaction time of ca. 7 days was required for complete conversion. Colorless crystals were obtained. Yield: 24.8 mg, 0.0186 mmol, 93%. ^{1}H NMR (400 MHz DCM-d_2): δ 7.58 (t, 1H, $^{3}J_{HH}$ = 7.2 Hz, $\underline{H}_{C6}$), 7.51 (ddd, 1H, $^{3}J_{HH}$ = 10.8 Hz, $^{3}J_{HH}$ = 8.1 Hz, J_{HP} = 1.59 Hz, $\underline{H}_{C3}$), 6.98 (ddd, 1H, $^{3}J_{HH}$ = 8.19 Hz, $^{4}J_{HH}$ = 2.38 Hz, J_{HP} = 1.10 Hz, $\underline{H}_{C4}$), 6.49 (dd, 1H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 5.6 Hz $\underline{H}_{C5}$), 6.35 (s, 10H, $C_5\underline{H}_5$), 4.22 (t, 1H, $^{3}J_{HH}$ = 6.0 Hz, α-$\underline{H}$), 2.59 (m, 2H, δ-$\underline{H}$), 1.93 (br. m, 2H, γ-$\underline{H}$), 1.84 (m, 2H, β-$\underline{H}$), 1.48 (d, 18H, $^{3}J_{HH}$ = 14.9 Hz, $C(\underline{C}H_3)_3$). $^{31}P\{^{1}H\}$ (161 MHz, DCM-d_2): δ 43.01. $^{13}C\{^{1}H\}$ (100 MHz, DCM-d_2): δ

170.2 (d, $^2J_{CP}$ = 1.6 Hz C1), 136.8 (d, $^2J_{CP}$ = 3.1 Hz, C3), 135.2 (d, $^3J_{CP}$ = 6.23 Hz, C6), 123.3 (d, $^4J_{CP}$ = 7.8 Hz, C5), 118.9 (d, $^3J_{CP}$ = 10.90 Hz, C4), 113.9 (s, C_5H_5), 102.1 (d, $^1J_{CP}$ = 70.1 Hz, C2), 70.3 (s, α-C), 36.8 (d, $^1J_{CP}$ = 37.3 Hz, $C(CH_3)_3$), 31.9 (d, $^3J_{CP}$ = 14.8 Hz, β-C), 28.6 (s, $C(CH_3)_3$), 20.4 (d, $^2J_{CP}$ = 6.2 Hz γ-C), 18.8 (d $^1J_{CP}$ = 42.0 Hz δ-C). ESI-MS: 529.19 [M]. Elemental Analysis: Calc.d: C, 51.62; H, 3.33. Found: C, 51.19; H, 4.69.

Compound 32. A sample of **2** (27.8 mg, 0.02 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in fluorobenzene (0.7 mL) and diethyl ether (20 μL) giving a bright yellow solution. The tube was sealed, removed from the glovebox, and followed by NMR. The procedure was repeated on a preparative scale (278.1 mg, 0.2 mmol) in chlorobenzene. Once the reaction was deemed complete by $^{31}P\{^1H\}$ NMR, the sample was precipitated by layering with hexane. The white microcrystalline precipitate was recrystallized by layering a concentrated DCM solution with hexanes and leaving to stand for 16 h. The supernatant was decanted form the large colorless crystals before drying in vacuo. Yield: 211.2 mg, 0.158 mmol, 79%. ^1H NMR (400 Hz DCM-d_2): δ 7.46 (m, H_{C6} and H_{C3}), 6.89 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.2, J_{HP} = 1.2 Hz H_{C4}) 6.18 (ddd, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 1.0 Hz, H_{C5}) 4.37 (q, 2H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 2.90 (m, 2H, PCH_2CH_3), 1.91 (s, 30H, $C_5(CH_3)_5$), 1.60 (dt, 3H, $^2J_{HP}$ = 16.4 Hz, $^3J_{HH}$ = 7.6 Hz PCH_2CH_3), 1.52 (d, $^3J_{HP}$ = 14.9 Hz, 18H, $C(CH_3)_3$), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3). $^{31}P\{^1H\}$ (161 Hz, DCM-d_2): δ 44.31. $^{13}C\{^1H\}$ (125 Hz, DCM-d_2): δ 168.4 (d, $^2J_{CP}$ = 1.6 Hz, C1), 135.2 (d, $^2J_{CP}$ = 2.3 Hz, C3), 135.1 (d, $^3J_{CP}$ = 7.0 Hz, C6), 126.7 (d, $^4J_{CP}$ = 8.9 Hz, C5), 122.8 (s, $C_5(CH_3)_5$), 117.7 (d, $^3J_{CP}$ = 10.9 Hz, C4), 102.0 (d, $^1J_{CP}$ = 68.9 Hz, C2), 67.0 (s, OCH_2CH_3), 37.8 (d, $^1J_{CP}$ = 36.6 Hz, $C(CH_3)_3$), 29.0 (s, $C(CH_3)_3$), 21.0 (s, OCH_2CH_3), 12.85 (d $^1J_{CP}$ = 56.4 Hz, PCH_2CH_3), 12.74 (s, PCH_2CH_3), 12.3 (s, $C_5(CH_3)_5$). ESI-MS: 671.37 [M]. Elemental Analysis: Calcd: C, 55.07; H, 4.62. Found: C, 55.27; H, 4.74.

Compound 33. Reaction was carried out in an analogous fashion to **32** except using $^iPr_2O$ and an extended reaction time of ca. 4 days and a temperature of 100 °C. The ^{31}P and $^{31}P\{^1H\}$ NMR spectra of the resultant light yellow solution indicated ca. 38% conversion to a new species. $^{31}P\{^1H\}$ NMR (unlocked): δ 18.5. ^{31}P NMR (121 Hz, unlocked, PhCl): δ 18.59 (d, $^1J_{PH}$ = 450 Hz). ESI-MS: 657.33 [M].

Compound 34. A sample of **2** (27.8 mg, 0.02 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess MTBE (ca. 3 drops) was added. The tube was then sealed, removed, and warmed to 60 °C for ca. 16 h. The ^{31}P and $^{31}P\{^1H\}$ NMR spectra of the colorless solution revealed >99% conversion of **3**. The sample was returned to the glovebox, layered with hexane, and allowed to stand for 16 h, precipitating a white microcrystalline solid. The supernatant was decanted, and the solids were washed with hexane before drying under in vacuo. Yield: 17.0 mg, 0.013 mmol, 65%. ^1H NMR (500 MHz DCM-d_2): δ 7.53 (ddd, 1H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.8 Hz, J_{HP} = 1.0 Hz H_{C6}), 7.36 (ddd, 1H, $^3J_{HH}$ = 10.99 Hz, $^4J_{HH}$ = 7.63 Hz, J_{HP} = 1.5 Hz H_{C3}), 6.92 (ddd, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 2.9 Hz, J_{HP} = 0.76 Hz, H_{C4}), 6.67 (ddd, 1H, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 6.0 Hz, J_{HP} = 0.8 Hz H_{C5}), 6.26 (d, 1H, $^1J_{HP}$ = 462.5 Hz, P-H), 4.12 (s, 3H, $ZrOCH_3$), 1.94 (s, 30H, $C_5(CH_3)_5$), 1.53 (d, $^3J_{HP}$ = 16.9 Hz, 18H, $C(CH_3)_3$). $^{31}P\{^1H\}$ (121 Hz, DCM-d_2): δ 23.42. $^{13}C\{^1H\}$ (125 MHz DCM-d_2): δ 168.6 (s, C1), 136.8. (d, $^2J_{CP}$ = 2.0 Hz, C3), 132.4 (d, $^3J_{CP}$ = 8.80 Hz, C6), 123.9 (d, $^4J_{CP}$ = 5.9 Hz, C5), 122.5 (s, $C_5(CH_3)_5$), 118.9 (d, $^3J_{CP}$ = 11.7 Hz, C4), 100.9 (d, $^1J_{CP}$ = 76.3 Hz, C2), 58.1 (s, $ZrOCH_3$), 35.25 (d, $^1J_{CP}$ = 36.2 Hz, $C(CH_3)_3$), 28.7 (s, $C(CH_3)_3$), 12.0 (s, $C_5(CH_3)_5$). ESI-MS: 629.31 [M]. Elemental Analysis: Calcd: C, 54.09; H, 4.31. Found: C, 53.90; H, 4.54.

Compound 35. Reaction was carried out and isolated in an analogous fashion to **29** using **2** (27.8 mg, 0.02 mmol) and an excess of THP (ca. 3 drops) and a reaction time of ca. 2 days. Yield: 20.1 mg, 0.0146 mmol, 73%. ^1H NMR (500 Hz DCM-d_2): δ 7.46 (m, 2H, H_{C6} and H_{C3}), 6.89 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.3 Hz, J_{HP} = 1.2 Hz, H_{C4}), 6.22 (ddd, 1H, $^3J_{HH}$ = 7.32 Hz, $^4J_{HH}$ = 5.95 Hz, J_{HP} = 1.07 Hz, H_{C5}), 4.53 (t, 1H, $^3J_{HH}$ = 5.1 Hz, α-H), 2.57 (m, 2H, ε -H), 2.18 (br. m, 2H, δ-H), 1.92 (s, 30H, $C_5(CH_3)_5$), 1.82 (m, 2H, β-H), 1.66 (m, 2H, γ-H), 1.48 (d, 18H, $^3J_{HH}$ = 15.0 Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ (121 Hz, DCM-d_2): δ 40.31. $^{13}C\{^1H\}$ (125 Hz, DCM-d_2): δ 169.7 (s, C1), 135.3 (d, $^2J_{CP}$ = 2.5 Hz, C3), 134.9 (d, $^3J_{CP}$ = 6.85 Hz, C6), 126.6 (d, $^4J_{CP}$ = 8.3 Hz, C5), 122.7 (s, $C_5(CH_3)_5$), 117.5 (d, $^3J_{CP}$ = 11.3 Hz, C4), 102.2 (d, $^1J_{CP}$ = 69.5 Hz, C2), 71.91 (s, α-C), 37.6 (d, $^1J_{CP}$ = 38.2 Hz, $C(CH_3)_3$), 30.7 (d, $^3J_{CP}$ = 15.2 Hz, β -C), 28.8 (s, $C(CH_3)_3$), 28.5 (s, γ-C), 23.1 (d, $^2J_{CP}$ = 6.4 Hz δ-C), 20.4 (d $^1J_{CP}$ = 42.0 Hz ε-C), 12.1 (s, $C_5(CH_3)_5$). ESI-MS: 683.35 [M]. Elemental Analysis: Calcd: C, 55.47; H, 4.58. Found: C, 55.98; H, 4.90.

Compound 36. A silylated swivel frit apparatus was charged with Cp'_3La (251.3 mg, 0.5 mmol) and THF (5 mL). The resulting yellow suspension was stirred for 10 min to give a fine white suspension. To this, a solution of t-$Bu_2P(C_6H_5)OH$ (119.1, 0.5 mmol) in THF (5 mL) was added dropwise over 30 min. After 10 min, all the solids had dissolved to give a light yellow solution (the reaction was deemed complete by following the $^{31}P\{^1H\}$ spectrum of an identical NMR scale experiment). The flask was removed from the glovebox and connected to a Schlenk line where the solvent was removed in vacuo to leave a light yellow oil which began to crystallize upon prolonged exposure to vacuum. Benzene was vacuum transferred onto the solids, and the resulting yellow solution filtered. The solvent was removed once more to leave a light yellow oil. Pentane (~10 mL) was vacuum transferred onto the solids at −78 °C and then allowed to warm to room temperature giving a light yellow suspension. The solids were stirred at room temperature for 1 h then and collected on a frit and washed by back distillation of the solvent, leaving a white solid that was dried under high vacuum (10^{-3} Torr) for 1 h before being transferred to the glovebox and isolated. A second crop was isolable by cooling the pentane supernatant down to −20 °C. Combined yield: 241.8, 0.35 mmol, 70%. ^1H NMR (400 Hz, toluene-d_8): δ 7.56 (dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.2 Hz, H_{C6}), 7.22 (dt, 1H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.7 Hz, H_{C4}), 6.82 (ddd, 1H, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 5.9 Hz $^4J_{HH}$ = 1.2 Hz, H_{C5}), 6.69 (dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, H_{C3}), 5.67 (s, 2H, $C_2(CH_3)_2C_2(CH_3)_2CH$), 3.90 (m, 4H, α-H_{THF}), 2.14 (s, 12H, $C_2(CH_3)_2C_2(CH_3)_2CH$), 1.97 (s, 12H, $C_2(CH_3)_2C_2(CH_3)_2CH$), 1.49 (m, 4H, β-H_{THF}), 1.23 (d, $^3J_{HP}$ = 11.3 Hz, 18H, $C(CH_3)_3$). $^{31}P\{^1H\}$ (161 Hz, toluene-d_8): δ 15.60 (s). $^{13}C\{^1H\}$ (100 Hz, toluene-d_8): δ 171.0 (d, $^2J_{CP}$ = 24.1 Hz, C1), 135.5 (d, $^3J_{CP}$ = 3.9 Hz, C6), 130.6 (s, C4), 121.7 (d, $^4J_{CP}$ = 3.1 Hz, C5), 122.4 (d, $^1J_{CP}$ = 11.7 Hz, C2), 121.3 (s, $C_2(CH_3)_2C_2(CH_3)_2CH$), 119.3 (s, $C_2(CH_3)_2C_2(CH_3)_2CH$), 115.2 (s, C3), 112.9 (s, $C_2(CH_3)_2C_2(CH_3)_2CH$), 70.7 (s, α-C_{THF}), 32.7 (d, $^1J_{CP}$ = 21.8 Hz, $C(CH_3)_3$), 31.1 (d, $^2J_{CP}$ = 14.8 Hz, $C(CH_3)_3$), 25.2 (s, β-C_{THF}), 13.4 (s, $C_2(CH_3)_2C_2(CH_3)_2CH$), 11.2 (s, $C_2(CH_3)_2C_2(CH_3)_2CH$). Elemental Analysis: Calcd: C, 62.60; H, 8.17. Found: C, 62.27; H, 8.31.

Compound 37. A sample of **36** dissolved in toluene-d_8 (34.5 mg, 0.05 mmol) was heated to 140 °C for ca. 3 days (the reaction was deemed complete by following the $^{31}P\{^1H\}$ spectrum). The relevant NMR spectra were acquired in situ. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into the benzene solution at room temperature. The supernatant was decanted, and the crystals were washed with hexane Yield: 26.9 mg, 0.039 mmol, 78%. ^1H NMR (400 Hz, toluene-d_8): δ 7.19 (tm, 1H, $^3J_{HH}$ = 6.85 Hz, H_{C5}), 6.87 (ddd, 1H, $^3J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 8.1 Hz $^4J_{HH}$ = 1.7 Hz, H_{C3}), 6.81 (ddd, 1H, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 5.9 Hz $^4J_{HH}$ = 1.0 Hz, H_{C6}), 6.87 (overlapping ddd, 1H, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 4.2 Hz $^4J_{HH}$ = 1.2 Hz, H_{C4}), 5.84 (s, 2H, $C(CH_3)C(CH_3)C'(C'H_3)C'(C'H_3)CH$), 4.26 (t, $^3J_{HH}$ = 5.4 Hz, 2H, α-H), 2.61 (m, 2H, δ-H), 2.40 (s, 6H, $C(CH_3)C(CH_3)C'(C'H_3)C'(C'H_3)CH$), 2.38 (s, 6H, $C(CH_3)C(CH_3)C'(C'H_3)C'(C'H_3)CH$), 2.27 (s, 6H, $C(CH_3)C(CH_3)C'(C'H_3)C'(C'H_3)CH$), 2.08 (s, 6H, $C(CH_3)C(CH_3)C'(C'H_3)C'(C'H_3)CH$), 1.83 (m, 2H, γ-H),

1.65 (m, 2H, β-H), 0.86 (d, $^3J_{HP}$ = 14.2 Hz, 18H, C(CH$_3$)$_3$). ^{31}P{^{1}H} (161 Hz, toluene-d_8): δ 45.8 (s). ^{13}C{^{1}H} (100 Hz, toluene-d_8): δ 174.0 (d, $^2J_{CP}$ = 3.4 Hz, C1), 135.0 (d, $^4J_{CP}$ = 2.3 Hz, C5), 133.7 (d, $^2J_{CP}$ = 7.8 Hz, C3,), 126.4 (d, $^3J_{CP}$ = 8.6 Hz, C6), 117.2 (s, C(CH$_3$)C(*C*H$_3$)C′-(C′H$_3$)C′(*C*′H$_3$)CH), 116.5 (s, C(CH$_3$)C(*C*H$_3$)C′(C′H$_3$)C′(*C*′H$_3$)-CH), 110.9 (s, C(CH$_3$)C(*C*H$_3$)C′(C′H$_3$)C′(*C*′H$_3$)CH), 112.8 (d, $^3J_{CP}$ = 11.7 Hz, C4), 97.8 (d, $^1J_{CP}$ = 72.4 Hz, C2), 63.5 (s, α-C), 35.8 (d, $^1J_{CP}$ = 38.9 Hz, C(CH$_3$)$_3$), 35.1 (d, $^3J_{CP}$ = 14.0 Hz, β-C), 27.9 (s, C(CH$_3$)$_3$), 20.9 (d, $^2J_{CP}$ = 6.2 Hz, γ-C), 18.9 (d, $^1J_{CP}$ = 42.0 Hz, δ-C), 13.6 (s, C(CH$_3$)C(*C*H$_3$)C′(C′H$_3$)C′(*C*′H$_3$)CH), 13.5 (s, C(CH$_3$)C-(*C*H$_3$)C′(C′H$_3$)C′(*C*′H$_3$)CH), 11.5 (s, C(CH$_3$)C(*C*H$_3$)C′(C′H$_3$)C′-(*C*′H$_3$)CH), 11.4 (s, C(CH$_3$)C(*C*H$_3$)C′(C′H$_3$)C′(*C*′H$_3$)CH),). ESI-MS: Not observed. Elemental Analysis: Calcd: C, 62.60; H, 8.17. Found: C,62.81; H, 8.10.

Compound 38. A sample of **2** (0.1 mmol) was loaded into an NMR tube fitted with a Teflon needle valve and dissolved in chlorobenzene (0.7 mL) giving a bright orange solution. Excess acetone (ca. 3 drops) was added, immediately giving a pale green solution. The ^{31}P and ^{31}P{^{1}H} NMR spectra of the colorless solution revealed >99% conversion of **2**. The sample was returned to the glovebox, layered with hexane, and allowed to stand for 16 h precipitating large pale green blocks. The supernatant was decanted, and the solids washed with hexane before drying in vacuo. Recrystallization from DCM/hexane afforded colorless blocks. Yield: 21.5 mg, 0.0161 mmol, 81%. ^{1}H NMR (500 MHz, DCM-d_2): δ 7.55 (m, 1H, H$_{C5}$), 7.38 (m, 1H, H$_{C3}$), 6.96 (dt, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 2.0 Hz, H$_{C4}$), 6.58 (m, 1H, H$_{C6}$), 6.56 (d, 1H, $^1J_{HP}$ = 459.5 Hz, P-H), 4.02 (br. s, 1H, CH$_3$C(O)CH*H*), 3.86 (br. s, 1H, CH$_3$C-(O)CH*H*), 1.98 (s, 30H, C$_5$(CH$_3$)$_5$), 1.92 (s, 1H, CH$_3$C(O)CH*H*), 1.52 (br d., $^3J_{HP}$ = 17.0 Hz, 18H, C(CH$_3$)$_3$). ^{31}P{^{1}H} (121 Hz, DCM-d_2): δ 20.05. ^{13}C{^{1}H} (125 MHz, DCM-d_2): δ 167.7 (s, C1), 162.5 (s, CH$_3$C(O)CH*H*), 136.6 (br. s, C5), 132.7 (br. s, C3), 124.4 (br. s, C6), 119.4 (d, $^3J_{CP}$ = 10.8 Hz, C4), 124.0 (s, C$_5$(CH$_3$)$_5$), 100.9 (d, $^1J_{CP}$ = 80.2 Hz, C2), 89.5 (br. s, CH$_3$C(O)CH*H*), 35.5 (br. d, $^1J_{CP}$ = 39.1 Hz, C(CH$_3$)$_3$), 28.6 (s, C(CH$_3$)$_3$), 25.8 (br. s, CH$_3$C(O)CH*H*), 12.3 (s, C$_5$(CH$_3$)$_5$). ESI-MS: 629.30 [M − CH$_3$C(O)CH$_2$ + O$_2$]. Elemental Analysis (1:1 DCM solvate from crystal structure): Calcd: C, 52.73 H, 4.35. Found: C, 52.32; H, 4.46.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The University of Bristol is thanked for funding. Natalie Fey (University of Bristol) is thanked for assistance with calculations.

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