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Cationic Group 4 Metallocene–(*o*-Phosphanylaryl)oxido Complexes: Synthetic Routes to Transition-Metal Frustrated Lewis Pairs

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Synthetic routes to cationic group 4 metallocene–(*o*-phosphanylaryl)oxido compounds of the type $[Cp^R_2M(O\text{^}PR_2)]$-[WCA] (M = Ti, Zr, Hf; WCA = weakly coordinating anion) are described. The neutral mono-methyl complexes $[Cp^R_2ZrMe(O\text{^}PR_2)]$ **1**–**6** [Cp^R = Cp (**1**–**3**) or Cp* (**4**); $O\text{^}PR_2$ = *o*-$OC_6H_4(PtBu)_2$ (**1** and **4**), $OCMe_2CH_2(PtBu)_2$ (**2**) or $OC(CF_3)_2CH_2(PtBu)_2$ (**3**)] are prepared by protonolysis of $[Cp^R_2ZrMe_2]$ by the parent alcohol. The remaining methyl group in such complexes is best removed by protonolysis with [DTBP]-$[B(C_6F_5)_4]$ (DTBP = 2,6-di-*tert*-butylpyridinium) to yield the desired cationic complexes **7** and **8** in the case of **1** and **4**. In the case of **2** and **3**, this method leads to side reactions. Treatment with $B(C_6F_5)_3$ yields the desired cations in all cases; however, side reactions with the generated $[MeB(C_6F_5)_3]$ anion in subsequent reactions leads to problems. Hafnium analogues may be synthesised by similar routes. In the case of titanium, a different method must be adopted: chloride abstraction using $[Et_3Si][B(C_6F_5)_4]$ from the parent complex $[Cp_2TiCl(O\text{^}PR_2)]$. Such cationic group 4 metallocene–(*o*-phosphanylaryl)oxido compounds exhibit reactivity that is best described by the frustrated Lewis pair concept.

Introduction

Solution-phase combinations of sterically hindered Lewis acid–Lewis base pairs, so-called frustrated Lewis pairs (FLPs), have been the subject of recent interest, particularly because of the high latent reactivity of such species in the activation of small molecules. Initial studies have 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 phosphane and fluorinated borane systems [such as $PtBu_3/B(C_6F_5)_3$] first reported by Stephan and Ménard 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.[6,7] 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] 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.[14,15]

We have been exploring the chemistry of cationic zirconocene–(*o*-phosphanylaryl)oxido complexes as analogues of linked main-group frustrated Lewis pairs in which the Lewis acidic borane component is replaced with an electrophilic transition-metal centre. Our initial results have established the analogy with main-group frustrated pairs,[16,17] but also demonstrated additional reactivity, for example, the catalytic dehydrogenation of amine–boranes,[17] a reaction only demonstrated in a stoichiometric sense with main-group FLP systems.[18,19] It is our view that combining the ability of transition-metal complexes in catalysis with the capability of FLPs to activate substrate molecules by means of ditopic activation offers exciting possibilities for exploitation in new activation pathways and reactivity patterns.

Establishing clean and robust protocols for the synthesis of the target cationic group 4 metallocene–(*o*-phosphanylaryl)oxido complexes was identified as a critical issue in going on to fully exploit these species. In this article, we explore several routes that highlight the crucial factors in isolating these novel complexes.

Results and Discussion

Our general synthetic strategy was to access neutral precursor compounds of the type $[Cp^R_2Zr(Me)(O\text{^}PR_2)]$ [Cp^R = cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*)] using the range of phosphanyl alcohols $HO\text{^}PR_2$ we reported recently as synthons for linked phosphanyl borinate ester frustrated Lewis pairs.[20] There then exists the plethora of synthetic methods developed for cationic group 4 metallocene polymerisation catalysis to abstract the methyl ligand and yield the target $[Cp^R_2Zr(O\text{^}PR_2)]^+$ fragments.

Synthesis of Neutral Complexes $[Cp^R_2Zr(Me)(O\text{^}PR_2)]$ (1–6)

The protonolysis of $[Cp_2ZrMe_2]$ by alcohols,[21–24] even phosphanyl alcohols,[25] has already been reported. Using

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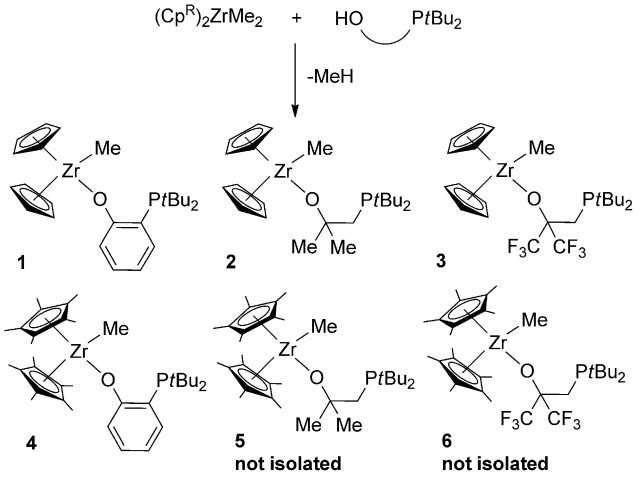
this approach, the neutral precursors **1**–**3** were prepared in good yield (Scheme 1). In all three cases, reaction of the appropriate phosphanyl alcohol with [Cp_2ZrMe_2] in 1:1 stoichiometry proceeded at ambient temperature to selectively give the mixed alkyl/alkoxy zirconocene species.



Scheme 1. Synthesis of **1**–**6**.

The reaction times varied slightly and reflect the acidity of the parent alcohol but were generally complete within hours at ambient temperature. The same methodology was applied to pentamethylcyclopentadienyl analogues **4**–**6** using [$Cp^*_2ZrMe_2$]. In the case of **4**, the significantly more crowded and less electrophilic metal centre required longer reaction times and heating to drive the reaction to completion. Compounds **5** and **6** could not be isolated cleanly, being accompanied by several side- and decomposition products. All of the isolated compounds are highly air- and moisture-sensitive crystalline solids but showed no signs of decomposition in the solid state or in solution when kept under an inert atmosphere. Single crystals of **2**–**4** were obtained; the X-ray crystal structures (see Figures 1, 2, and 3) are all very similar (Table 1) and in each case the compounds adopt the expected pseudotetrahedral geometry with respect to the central Zr atom. All the Zr1–C1 distances, C1–Zr1–O1 and Cp–Zr1–Cp tilt angles (represented by ϕ and θ, respectively) are within the normal range for d^0 metallocenes.[26] The subtle variations between the structures are best explained by the varying steric environments between these different derivatives. The NMR spectra of these compounds supports the expectation that the phosphanes are not coordinated to the zirconium centres to any extent in solution. In spite of this, for compound **4** detectable $J_{H,P}$ and $J_{C,P}$ couplings were observed in the Zr–Me and Cp–Me groups by $^{13}C\{^1H\}$ and ^1H NMR spectroscopy; these couplings are best explained by through-space couplings that result from the relatively short contacts (Figure 3), as opposed to through-bond couplings that have been noted in similar cases where Zr–P is known to be present both in solution and in the solid state.[27]

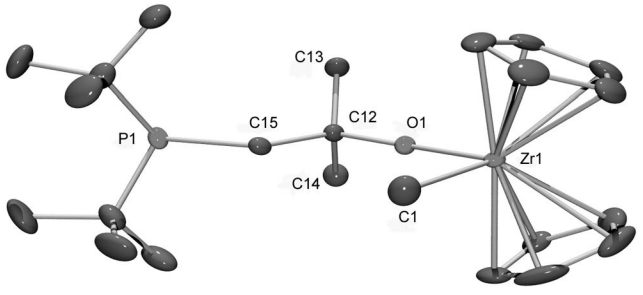


Figure 1. POV-ray representation of the molecular structure of **2**. All hydrogen atoms and the borate anion have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bonds lengths and angles are given in Table 1.

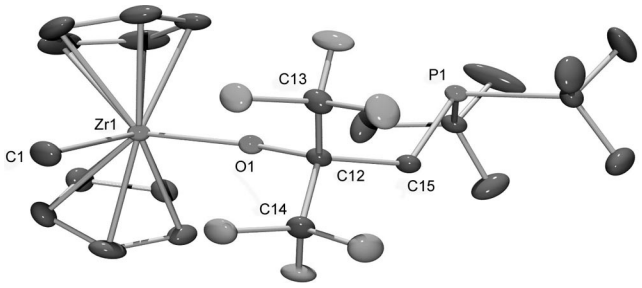


Figure 2. POV-ray representation of the molecular structure of **3**. All hydrogen atoms and the borate anion have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

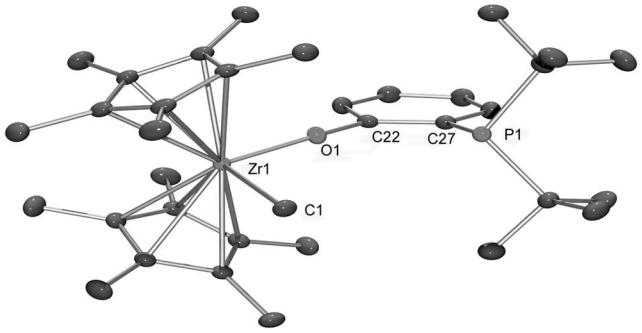
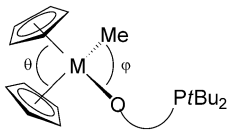


Figure 3. POV-ray representation of the molecular structure of **4**. All hydrogen atoms and the borate anion have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. Comparison of some relevant structural parameters for **2**–**5**.



	Zr1–O1 [Å]	Cp–Zr1 [Å][a]	Zr1–C1 [Å]	Zr1–O1–C [°]	θ [°]	ϕ [°]
2	1.919(2)	2.245	2.300(3)	169.6(2)	129.41	94.02(9)
3	1.9923(9)	2.300	2.280(2)	165.78(8)	130.36	98.01(5)
4	1.955(1)	2.299	2.296(2)	172.9(1)	132.74	92.16(6)

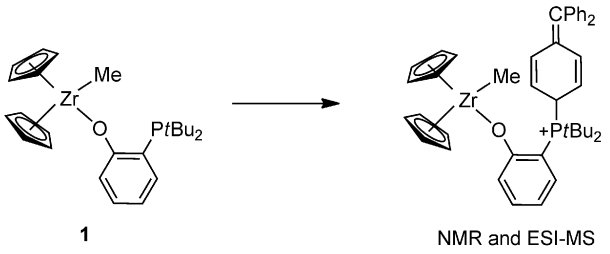
[a] Mean of the two Cp–Zr1 centroid distances.

Synthesis of the Cationic Species $[Cp^R_2Zr(O\text{^}PR_2)]^+$

Thanks to the ubiquity of zirconocene cations in olefin polymerization chemistry, there are many synthetic methodologies available to prepare such compounds. In every case, the cationic metals are stabilized by the inclusion of a weakly coordinating anion (WCA). In general, this class of anions has proved essential in the isolation of many highly electrophilic main-group [28,29] and transition-metal compounds.[30,31] The most common approach involves removal of the R ligand from a $[Cp_2ZrR_2]$ species. Protonolysis of the kinetically labile Zr–alkyl bond by weak ammonium acids[32] is widely used but is reliant on the poor donor qualities of the amine liberated upon protonolysis. These seemingly innocent byproducts are often overlooked, but recently have been shown to have a profound influence on the reactivity of these cations.[33,34] The presence of potentially reactive byproducts post-activation can be avoided by employing the powerful carbocationic Lewis acid $[CPh_3]^+$ to abstract methide or hydride from $[Cp_2ZrR_2]$. The comparatively inert $HCPh_3$ or $MeCPh_3$ byproducts are not known to coordinate to the cationic metal and are easily removed.[35] In a similar way, neutral Lewis acids such as $B(C_6F_5)_3$ may be used to abstract hydride or methide. The resulting ion pairs $[Cp_2ZrR][RB(C_6F_5)_3]$ are often in equilibrium with the zwitterionic complexes, $[Cp_2ZrR(\mu\text{-}R)B(C_6F_5)_3]$, in which the alkyl (or hydride) ligand is only partially dissociated. The position of this equilibrium depends on the ligand set but is also shown to be highly solvent-dependent.[36] We have previously reported the viability of the protonolysis route with our species,[17] although in place of the standard ammonium acid $[PhNMe_2H][B(C_6F_5)_4]$, the novel reagent $[DTBP(H)][B(C_6F_5)_4]$ (DTBP = 2,6-di-*tert*-butylpyridinium) was prepared to avoid the issue of possible coordination of $PhNMe_2$.[37] Although this worked well for the zirconocene derivatives tested to date, it has drawbacks as a methodology since the synthesis of $[DTBP(H)][B(C_6F_5)_4]$ starting from C_6F_5Br is tedious and potentially dangerous.[38,39] For this chemistry, the reagent must also be obtained in impeccable purity, which was only possible by multiple precipitations from compatible solvents (fluorobenzene). Another inherent problem is the very similar solubility of the reagent to the products, making purification challenging in the event of incomplete reaction. We were therefore interested in exploring the use of the more convenient, commercially available reagents for generating such cations.

Activation with $[CPh_3][B(C_6F_5)_4]$

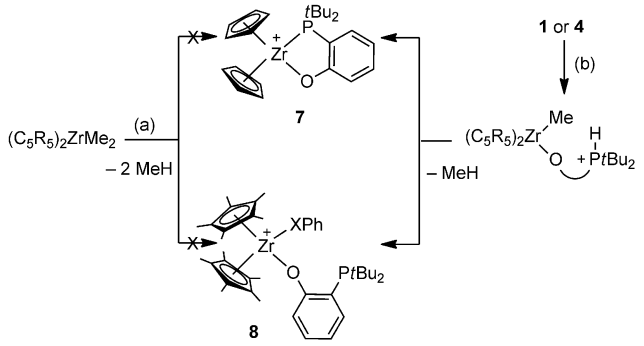
The initial investigations into the generation of the cationic species focused on methide abstraction with $[CPh_3][B(C_6F_5)_4]$. Unfortunately, a persistent side reaction accompanied the formation of the desired metal cations, which proved difficult to purify. We suggest this competing reaction occurs between the pendant phosphane and $[CPh_3]^+$, the product of which was assigned on the basis of the $^{31}P\{^1H\}$ NMR spectrum and ESI-MS of the reaction mixture. An analogous reaction has been noted to occur between $[CPh_3]^+$ and related tertiary phosphanes, and it appears that when adduct formation is precluded by steric hindrance, rapid S_NAr occurs at the *para* position to give zwitterionic products (Scheme 2).[40]



Scheme 2. Side-product formation.

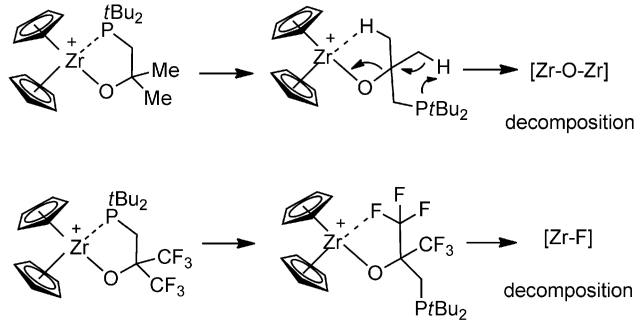
Activation by Protonolysis

The apparent incompatibility of $[CPh_3][B(C_6F_5)_4]$ and phosphane components in these systems promoted further investigation of routes based on protonolysis. Attempts were made to generate the desired complexes by means of a one-pot procedure from the appropriate $[(C_5R_5)_2ZrMe_2]$ reagent and the pre-formed phosphonium salt of the phosphanyl alcohol (Scheme 3). This route is particularly attractive since only the phosphane Lewis base is present at the end of the reaction and the byproduct is methane. Unfortunately, this method did not give clean reactions and was abandoned in favour of more traditional, controlled approaches based on protonation of the remaining alkyl group of the pre-formed mixed alkyl/alkoxide complexes. In chlorobenzene solvent, activation with $[DTBP(H)][B(C_6F_5)_4]$ furnishes the desired cations from **1** and **4** almost instantaneously and cleanly; as previously reported, the Cp compound **7** contains a Zr–P bond, whereas the Cp* analogue **8** has no Zr/P interaction and is isolated as the chorobenzene adduct. With a view to generating solvent-ligand-free cations, a brief survey of the activation of **4** in other solvents was carried out (Scheme 3). The protonolysis of **4** proceeded smoothly in PhF and PhBr by $^{31}P\{^1H\}$ NMR spectroscopy resulting in the appropriate halobenzene adducts **8**. However, no reaction in benzene or toluene solvent even at 100 °C was apparent. Although solubility issues may also be important, this suggests that the loss of methane by protonolysis is an associative process and that an incoming ligand, even a very weak halobenzene donor, is essential for reactivity. In this regard, it is noteworthy that compound **1** reacts smoothly to generate **7**, in which the internal phosphane donor can coordinate, even in benzene, in which the resulting product is only sparingly soluble. In all successful cases, it seems likely that this reaction proceeds through the initial protonation of the phosphane-moiety to generate a phosphonium intermediate, which then acts as an internal acid for the associative methane-loss step.



Scheme 3. Attempted (left) and successful (right) synthesis of **7** and **8** by protonolysis of **1** and **4**. Reagents and conditions: (a) [*t*Bu$_2$PH^OH][B(C$_6$F$_5$)$_4$] (0.98 equiv.), PhF, 25–100 °C, 1–16 h; (b) [DTBP(H)][B(C$_6$F$_5$)$_4$] (0.98 equiv.), PhX (X = F, Cl or Br), 25–100 °C, 1–16 h.

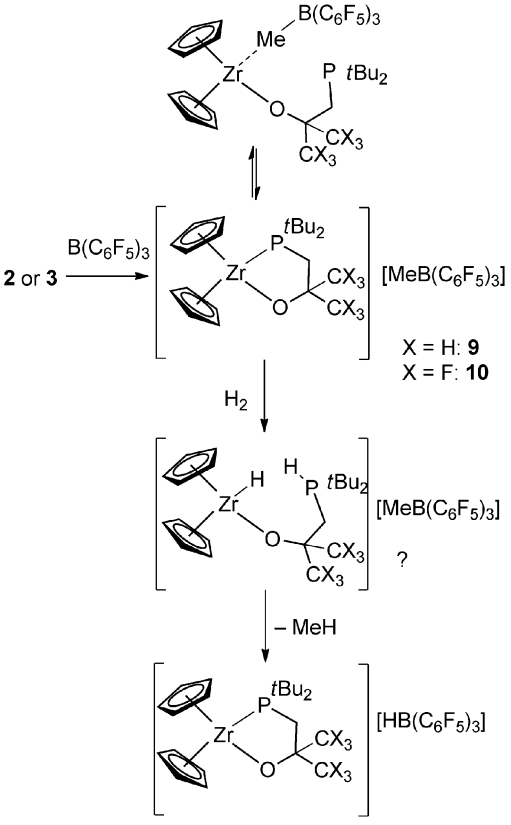
Activation of **2** and **3** by means of the same procedure was not straightforward. In both cases, it was possible to tentatively assign species as the anticipated cationic analogues of **7**. However, these compounds contain persistent impurities that could not be removed by standard purification methods. Jordon et al. have noted the decomposition of the related species [Cp$_2$ZrO*t*Bu][B(C$_6$F$_5$)$_4$] in chlorobenzene to give [{Cp$_2$Zr(μ-O)$_2$}$_2$] and poly(isobutylene).[22] We propose a similar reaction pathway in this case (Scheme 4). Clearly, the nature of the linker is very important in accessing stable isolable compounds, and our original *o*-phenylene plays a critical role in this regard.



Scheme 4. Possible routes for the decomposition of **2** (top) and **3** (bottom).

Activation with B(C$_6$F$_5$)$_3$

As well as being commercially available and easily purified by sublimation, B(C$_6$F$_5$)$_3$ (and the neutral zirconocene precursors) is highly soluble in hydrocarbon solvents which, combined with the insolubility of the ion-pair products, provides an effective purification route. Addition of solutions of **1** or **4** in toluene or hexane to B(C$_6$F$_5$)$_3$ resulted in the immediate precipitation of a bright yellow oil that was isolated by washing with hexane and drying under vacuum to yield a light yellow powder. When redissolved in PhCl or PhF, the ^{11}B and ^{19}F NMR spectra were consistent with the clean formation of the [MeB(C$_6$F$_5$)$_3$] anion, and ^{31}P{^{1}H} NMR spectra were identical to those of compounds **7** and **8** obtained by protonolysis; this suggests that the desired cations [Cp$_2$Zr(OC$_6$H$_4$P*t*Bu$_2$)][MeB(C$_6$F$_5$)$_3$] (**7a**) and [Cp*$_2$Zr(OC$_6$H$_4$P*t*Bu$_2$)(ClPh)][MeB(C$_6$F$_5$)$_3$] (**8a**) have been formed. The same methodology shows some promise for **2** and **3**, for which NMR spectroscopy signals are consistent with the desired cations **9** and **10**, albeit alongside several side products that persisted during purification. We suggest that a weak interaction with an only partially dissociated methyl group bridging between Zr and B may aid stability compared with the rapid decomposition seen after protonation (Scheme 5).



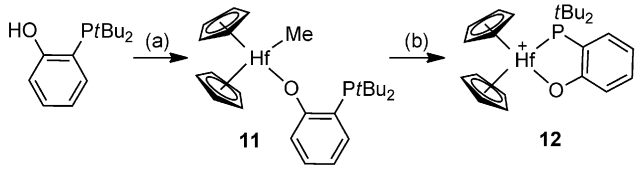
Scheme 5. Proposed heterolytic activation of H$_2$ by **9** and **10** and further reaction with [MeB(C$_6$F$_5$)$_3$] anion.

With this evidence for the cations derived from **2** and **3** in hand, we were interested to explore the reactivity of these species with hydrogen. In many ways, the heterolytic cleavage of hydrogen is the standard reaction for frustrated Lewis pair-type reactivity, and we have previously reported that whilst **7** is apparently inert towards hydrogen at temperatures up to 80 °C, **8** rapidly and irreversibly cleaves the H–H bond. With both **9** and **10** the reaction with hydrogen is not straightforward or clean; however, NMR spectroscopy data is consistent with quantitative formation of the known anion [HB(C$_6$F$_5$)$_3$]. One possibility is a reaction sequence involving methane loss by proton transfer to [MeB(C$_6$F$_5$)$_3$] from a postulated phosphonium cation, followed by hydride abstraction from the Zr–H fragment by

the generated $B(C_6F_5)_3$ (Scheme 5). This unexpected reactivity highlights the crucial role of the anion as well as the zirconocene fragment, but unfortunately rules out the use of $B(C_6F_5)_3$ as an activating agent with these species.

Synthesis of $[Cp^R_2Hf(O\text{^}PR_2)]^+$ (12)

To extend this chemistry to the other group 4 elements, the hafnium compound **12** was synthesized in an identical fashion to **7** via the neutral intermediate **11** (Scheme 6).[16] Although both steps proceeded smoothly, extended reaction times were required. Both the solid-state structure and the solution $^{31}P\{^1H\}$ NMR spectra confirmed the presence of the anticipated Hf–P bond. The X-ray structure of **12** (Figure 4) is very similar to that of **7**; it shows the expected pseudotetrahedral geometry at Hf and a puckered five-membered ring with almost identical distances and angles to those in **7**. Of interest is the marginally (ca. 2.5%) contracted Hf–P distance relative to the Zr–P distance in **7**. In light of their similar size, electronegativities and virtually identical Cp–M distances and Cp–M–Cp tilt angles, it is not clear why the Hf–P bond is shorter, although shorter Hf–**L** bonds are often observed in isostructural Zr and Hf complexes.[41,42]



Scheme 6. Synthesis of **11** and **12**. Reagents and conditions: (a) $[Cp_2HfMe_2]$ (1 equiv.), hexanes, 25 °C, 1 d; (b) [DTBP(H)][B-$(C_6F_5)_4$] (0.98 equiv.), PhCl, 25 °C, 2 d.

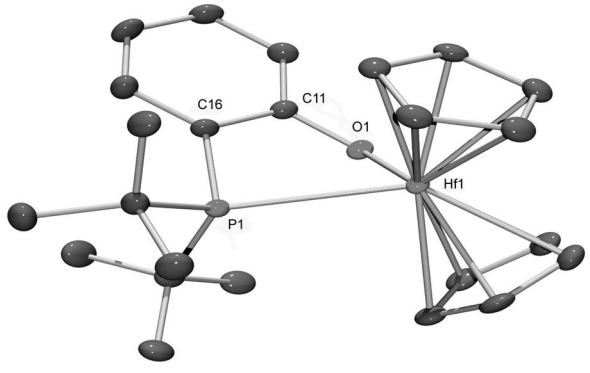
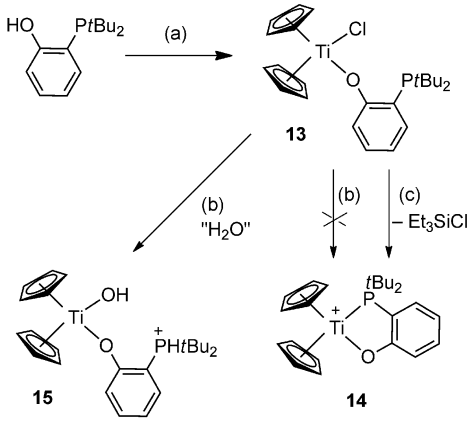


Figure 4. POV-ray drawing of the molecular structure of **12**.[16] Hydrogen atoms and the borate anion have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Hf1–O1 1.989(2), Hf1–P1 2.8209(6), C16–P1 1.824(3), O1–C11 1.366(3), Cp–Hf1 2.185. Angles [°]: O1–Hf1–C11 121.7(2), O1–Hf1–P1 71.16(5), Cp–Hf–Cp 128.07.

Synthesis of $[Cp^R_2Ti(O\text{^}PR_2)]^+$ (14)

For the titanium analogue $[Cp^R_2Ti(O\text{^}PR_2)]^+$ (**14**; R = H), the route analogous to that used for the Zr or Hf derivatives was complicated by the very different reactivity of $[Cp_2TiMe_2]$ (Petasis's reagent).[43] Critically, despite being thermodynamically much less stable than their heavier homologues (particularly in the solid state),[42] the Ti–C bonds are kinetically very robust and do not readily undergo protonolysis. The bonds are so stable that the standard protocol used to synthesize $[Cp_2TiMe_2]$ involves an aerobic, aqueous workup. Only upon extended thermolysis in the presence of alcohols can mixed alkyl/alkoxide compounds be accessed.[44]

In an effort to circumvent these problems, the mixed alkoxy/chloride compound **13** was prepared as an alternative synthon. Complex **13** is very stable and was isolated in high (82%) yield and purity by means of a modification of a published protocol.[25] Halide abstraction using $[Ag(C_6H_6)_3]$-$[B(C_6F_5)_4]$ was then attempted (Scheme 7). Upon mixing solutions of **13** and $[Ag(C_6H_6)_3][B(C_6F_5)_4]$ in chlorobenzene, an encouraging silvery-grey solid was immediately precipitated; however, analysis of the reaction mixture by ^{31}P NMR spectroscopy and ESI-MS revealed an almost quantitative conversion to the water addition product **15** (δ = 21 ppm, d, $^1J_{P,H}$ = 469 Hz, m/z = 433.37) rather than **14**, presumably caused by traces of water carried through from the synthesis of $[Ag(C_6H_6)_3][B(C_6F_5)_4]$. This reagent is prepared in aqueous media and only dried by means of K_2SO_4 and under vacuum.[45] The requirement for stringently anhydrous halide-abstraction reagents led us to the cation $[Et_3Si][B(C_6F_5)_4]$, prepared by reaction with $[CPh_3]$-$[B(C_6F_5)_4]$ in neat Et_3SiH.[28] Addition of this reagent to **13** in PhCl resulted in an immediate colour change from deep red to almost black and the ^{31}P NMR spectrum revealed 80% conversion to **14**. The removal of side products necessitated repeated recrystallisations, thereby resulting in a moderate 30% isolated yield. Crystals suitable for X-ray



Scheme 7. Synthetic routes employed during the synthesis of **14**. Reagents and conditions. (a) $[Cp_2TiCl_2]$ (1 equiv.), Et_2NH (10 equiv.), THF; (b) $[Ag(C_6H_6)_3][B(C_6F_5)_4]$ (1 equiv.), trace H_2O, PhCl, 25 °C, 5 min; (c) $[Et_3Si][B(C_6F_5)_4]$ (0.98 equiv.), PhCl, 25 °C, 5 min.

diffraction were obtained and the identity of **14** was unambiguously confirmed (Figure 5). The expected Ti–P interaction is also implied by the significant $^{31}P\{^{1}H\}$ NMR spectroscopy shift relative to **13** that was observed upon forming the cation. At 2.752 Å, the Ti–P distance is shorter than its second-row cousin **4** by approximately 4%, which is mirrored by the significantly larger down-field shift of the phosphane in the $^{31}P\{^{1}H\}$ NMR spectrum relative to this starting material. A comparison of key structural parameters for the Ti, Zr and Hf compounds **14**, **7** and **12** is given in Table 2.

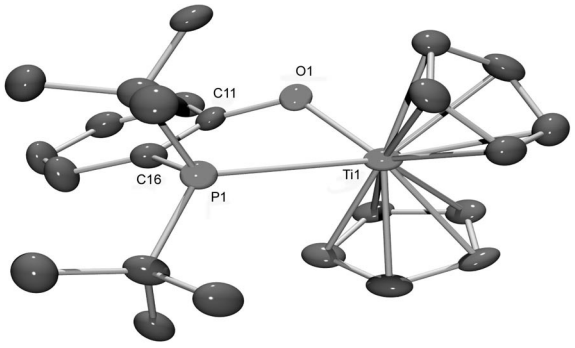


Figure 5. POV-ray drawing of the molecular structure of **14**. All hydrogen atoms and the borate anion have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Ti1–P1 2.785(2), Ti1–O1 1.901(5), O1–C11 1.358(7), C16–P1 1.812(7), Cp–Ti1 2.056. Angles [°]: P1–Ti1–O1 71.5(1), Ti1–O1–C11 122.5(4), O1–C11–C16 119.6(5), C11–C16–P1 113.0(4), C16–P1–Ti1 89.3(2), Cp–Ti–Cp 129.28.

Table 2. Comparison of some relevant structural parameters for **14**, **7** and **12**.

	M–O [Å]	Cp–M [Å][a]	M–O–C [°]	θ [°]	ϕ [°]
14 (Ti)	1.901(5)	2.06	122.5(4)	129.3	71.5(1)
7 (Zr)	1.997(2)	2.20	124.51	128.2	70.18(4)
12 (Hf)	1.989(2)	2.19	121.7(2)	128.1	71.16(5)

[a] Mean of the two M–Cp centroid distances.

Conclusion

A series of neutral and cationic group 4 phosphanylaryloxy–metallocene complexes have been prepared. The methodology chosen to form the cation is critical in obtaining a clean product. In general, protonation of $[Cp^{R}_{2}Zr(Me)(O\text{^}PR_2)]$ by $[DTBP][B(C_6F_5)_4]$ gives the best results. Analogous hafnium compounds are accessed in the same way. $B(C_6F_5)_3$ may also be used but this leads to complications in subsequent reactivity through exchange of the methyl group on the $[MeB(C_6F_5)_3]$ anion formed post-activation. Titanium derivatives require a different route: chloride abstraction from $[Cp^{R}_{2}Ti(Cl)(O\text{^}PR_2)]$ by $[Et_3Si][B(C_6F_5)_4]$. The linker group used in these compounds is critical; *o*-phenoxy moieties give highly air/moisture sensitive but otherwise robust complexes, whereas other linkers lead to side reactions. With reliable synthetic protocols in hand, studies are ongoing to explore the reactivity of these species as transition-metal-containing frustrated Lewis pairs.

Experimental Section

General Remarks: 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. tBu$_2$P(C$_6$H$_4$)OH, tBu$_2$P[CH$_2$C(Me)$_2$]OH, tBu$_2$P[CH$_2$C(CF$_3$)$_2$]OH and [DTBP][B(C$_6$F$_5$)$_4$] were synthesized as described previously by us.[16,20] The standard reagents [Ag(C$_6$H$_6$)$_3$][B(C$_6$F$_5$)$_4$] and [Et$_3$Si][B(C$_6$F$_5$)$_4$] were synthesized by published methods.[46,28] Compounds **1**, **4**, **7** and **8** have been previously reported. Solvents were purified and pre-dried using an Anhydrous Engineering column purification system then vacuum-transferred from the appropriate drying agent (K/benzophenone for aromatics, ethers; CaH_2 for hydrocarbons and chlorinated solvents) prior to use. NMR spectra were recorded using a JEOL ECP 300 spectrometer at 300 MHz, and Varian 400 and 500 spectrometers at 400 and 500 MHz, respectively (using the appropriate deuterated solvent, purchased from Cambridge Isotope Labs or Sigma–Aldrich and purified by vacuum-transfer from the appropriate desiccant) and referenced to an internal standard (residual solvent signal for ^{1}H; $BF_3{\cdot}OEt_2$ for ^{11}B; 85% H_3PO_4 for ^{31}P; and $FCCl_3$ for ^{19}F NMR spectroscopy). Spectra of air- and moisture-sensitive compounds were recorded using sealable J-Youngs tap NMR spectroscopy tubes. Microanalysis was carried out by the Microanalytical Laboratory, University of Bristol, using a Carlo–Elba spectrometer.

Synthesis of 2: [Cp$_2$ZrMe$_2$] (157.4 mg, 0.63 mmol) and tBu$_2$P[CH$_2$C(Me)$_2$]OH (136.7 mg, 0.63 mmol) were weighed out into two small vials, and each compound was dissolved in hexane (4 mL). The solutions were mixed in a Schlenk flask, including small hexane washes of the vials, which resulted in vigorous gas evolution. The flask was allowed to stand for 16 h and $^{31}P\{^{1}H\}$ NMR spectra of the solution showed >99% conversion to **2**. The flask was removed from the glovebox and cooled in stages to –78 °C, thereby resulting in the precipitation of colourless crystals. The supernatant was removed by using a cannula and the solids were dried under high vacuum for approximately 1 h before being isolated inside the glovebox as colourless crystals; yield 255 mg, 0.56 mmol, 89%. ^{1}H NMR (300 MHz, [D$_8$]toluene): δ = 5.82 (s, 10 H, C$_5$H$_5$), 1.55 (d, $^{2}J_{H,P}$ = 5.1 Hz, 2 H, CH$_2$), 1.22 [s, 6 H, C(CH$_3$)$_2$], 1.11 [d, $^{3}J_{H,P}$ = 10.6 Hz, 18 H, C(CH$_3$)$_3$], 0.27 (s, 1 H, ZrCH$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 Hz, [D$_8$]toluene): δ = 110.8 (s, C$_5$H$_5$), 80.9 [d, $^{2}J_{C,P}$ = 25.7 Hz, C(CH$_3$)$_2$], 37.4 (d, $^{1}J_{C,P}$ = 26.5 Hz, 2 H, CH$_2$), 32.0 (d, $^{3}J_{C,P}$ = 4.6 Hz, CH$_3$), 31.9 [partial d, *C*(CH$_3$)$_3$], 29.6 [d, $^{2}J_{C,P}$ = 13.3 Hz, C(*C*H$_3$)$_3$], 18.81 (s, ZrCH$_3$) ppm. $^{31}P\{^{1}H\}$ NMR (161 MHz, [D$_8$]toluene): δ = 22.0 (s) ppm. ESI-MS: 453.15 [M + H]$^+$. Elemental analysis: calcd. C 60.88, H 8.66; found C 60.58, H 8.73.

Synthesis of 3: Prepared in an analogous fashion to **2** using [Cp$_2$ZrMe$_2$] (297.8 mg, 1.19 mmol) and tBu$_2$P[CH$_2$C(CF$_3$)$_2$]OH (387.5 mg, 1.19 mmol). Colourless crystals; yield 470 mg, 0.84 mmol, 71%. ^{1}H NMR (300 Hz, [D$_8$]toluene): δ = 5.92 (s, 10 H, C$_5$H$_5$), 2.02 (d, $^{2}J_{H,P}$ = 3.3 Hz, 2 H, CH$_2$), 1.04 [d, $^{3}J_{H,P}$ = 11.0 Hz, 18 H, C(CH$_3$)$_3$], 0.54 (s, 1 H, ZrCH$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 Hz, [D$_8$]toluene): δ = 125.16 (q, $^{1}J_{C,F}$ = 291.1 Hz, CF$_3$), 112.3 (s, C$_5$H$_5$), 83.7 [d. sept, $^{2}J_{C,P}$ = 27.4 Hz, $^{2}J_{C,F}$ = 15.3 Hz, C(CF$_3$)$_2$], 32.3 [d, $^{1}J_{C,P}$ = 23.6 Hz, *C*(CH$_3$)$_3$], 30.6 [d, $^{2}J_{C,P}$ =

15.0 Hz, C(CH_3)$_3$], 25.1 (d, $^1J_{C,P}$ = 34.8 Hz, CH_2), 27.9 (br. s, $ZrCH_3$) ppm. ^{19}F NMR (376 Hz, [D$_6$]benzene): δ = –74.4 (d, $^3J_{F,P}$ = 14.6 Hz) ppm. ^{31}P{^{1}H} NMR (161 Hz, [D$_6$]benzene): δ = 16.54 (septet, $J_{P,F}$ = 16.4 Hz) ppm. ESI-MS: sample decomposed. Elemental analysis: calcd. C 49.18, H 5.92; found C 49.14, H 5.99.

Attempted Activation with [CPh$_3$][B(C$_6$F$_5$)$_4$]: Compound **1** (0.05–0.1 mmol) and [CPh$_3$][B(C$_6$F$_5$)$_4$] (0.05–0.1 mmol) were weighed out into two vials, and each compound was dissolved in PhF (1–2 mL). The [CPh$_3$][B(C$_6$F$_5$)$_4$] solution was added dropwise to the solution of the complex over 10 min with rapid stirring, including small PhF washes of the vial. The contents of the vial were transferred to an NMR spectroscopy tube and analysed by ^{31}P{^{1}H} NMR spectroscopy and ESI-MS. The ^{31}P{^{1}H} NMR spectra showed >99% conversion of **1** to a new species assigned as the product of S_NAr at the *para* position in [CPh$_3$]. ^{31}P{^{1}H} NMR (161 Hz, PhF/[D$_8$]toluene): δ = 42.5 (s) ppm. ESI-MS: 717.24 [M]$^+$.

Reaction of 2 and 3 with [DTBP(H)][B(C$_6$F$_5$)$_4$]: Typically, **2** or **3** (0.05–0.1 mmol) and [DTBP(H)][B(C$_6$F$_5$)$_4$] (0.05–0.1 mmol) were weighed out into two vials, and each compound was dissolved in PhF (1–2 mL). The [DTBP(H)][B(C$_6$F$_5$)$_4$] solution was added dropwise to the solution of the complex, including small PhF washes of the vial. The contents of the vial were transferred to an NMR spectroscopy tube and analysed by ^{31}P{^{1}H} NMR spectroscopy and ESI-MS.

For compound **2**, the ^{31}P{^{1}H} NMR spectra of the reaction mixture indicated approximately 90% conversion to **9** (s, 61.7 ppm) along with approximately 10% to a unidentified species (δ = 24.7 ppm, br. s). Attempted isolation of the reaction mixture by repeated precipitation into hexanes or crystallisation at low temperature was unsuccessful. ^{1}H NMR (300 MHz, PhF/[D$_8$]toluene): δ = 5.92 (s, 10 H, C_5H_5), 1.99 (s, CH_2), 1.10 [s, 6 H, C(CH_3)$_2$], 0.90 [d, $^3J_{H,P}$ = 13.1 Hz, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (161 Hz, PhF/[D$_8$]toluene): δ = 61.70 (s) ppm. ESI-MS: (accurate mass) 437.1534 [M]$^+$.

For compound **3**, the ^{31}P{^{1}H} NMR spectra of the reaction mixture indicated approximately 80% conversion to **10** (δ = 62.7 (s) ppm) along with numerous other unidentified species [δ = 45.8 (s), 37.3 (s), 33.03 (s), 23.5 (s) ppm]. Attempted isolation of the reaction mixture by repeated precipitation into hexanes or crystallisation at low temperature were unsuccessful. ^{1}H NMR (300 MHz, PhF/[D$_8$]-toluene): δ = 6.02 (s, 10 H, C_5H_5), 2.01 (br. s, CH_2), 0.93 [d, $^3J_{H,P}$ = 11.6 Hz, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (161 Hz, PhF/[D$_8$]-toluene): δ = 62.7 (s) ppm. ^{19}F NMR (470 Hz, PhF/[D$_8$]toluene): δ = –75.3 ppm (s, CF_3) {data for [B(C$_6$F$_5$)$_4$] anion not reported}. ESI-MS: not observed.

Activation with B(C$_6$F$_5$)$_3$: The same general method was used for **1**, **2**, **3** and **4** and is described here for **1**. B(C$_6$F$_5$)$_3$ (0.05 mmol) and **1** (0.05 mmol) were weighed out into two small vials, and each compound was dissolved in hexane (4 mL). The solutions were mixed in a Schlenk flask, including small hexane washes of the vials, thereby resulting in the precipitation of a yellow oil. The supernatant was decanted and the oil was washed with further portions of hexane before being dried under vacuum to give a tacky yellow solid. NMR spectroscopy revealed both **7a** and **8a** to have identical data to the cation component of **7** and **8**, respectively.

In the case of **2**, an inseparable mixture of products was obtained albeit with some data that can be tentatively assigned to **9**: ^{1}H NMR (300 MHz, PhF/[D$_8$]toluene): δ = 5.90 (s, 10 H, C_5H_5), 1.98 (br. s, CH_2), 1.05 [s, 6 H, C(CH_3)$_2$], 0.95 (br. s, BCH_3), 0.90 [d, $^3J_{H,P}$ = 12.7 Hz, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (161 Hz, PhF/[D$_8$]toluene 5:1): δ = 54 (v br. s) ppm. ^{11}B{^{1}H} NMR (96 Hz, PhF/[D$_8$]toluene): δ = –15.1 (s) ppm. ^{19}F NMR (470 Hz, PhF/[D$_8$]-toluene): δ = –131.8 (d, $^3J_{F,F}$ = 19.1 Hz, 6 F, *ortho*-F), –164.1 (t, $^3J_{F,F}$ = 20.8 Hz, 4 F, *para*-F), –166.6 (m, 6 F, *meta*-F) ppm.

Again for **3**, an inseparable mixture of products was obtained albeit with some data that can be tentatively assigned to **10**: ^{1}H NMR (300 MHz, PhF/[D$_8$]toluene): δ = 6.02 (s, 10 H, C_5H_5), 2.28 (br. s, CH_2), 1.05 [s, 6 H, C(CH_3)$_2$], 1.03 (br. s, BCH_3), 0.87 [d, $^3J_{H,P}$ = 13.2 Hz, 18 H, C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (161 Hz, PhF/[D$_8$]-toluene 5:1): δ = 45 (v br. s) ppm. ^{11}B{^{1}H} NMR (96 Hz, PhF/[D$_8$]-toluene): δ = –15.1 (s) ppm. ^{19}F NMR (470 Hz, PhF/[D$_8$]toluene): δ = –131.8 (d, $^3J_{F,F}$ = 19.1 Hz, 6 F, *ortho*-F), –164.1 (t, $^3J_{F,F}$ = 20.8 Hz, 4 F, *para*-F), –166.6 (m, 6 F, *meta*-F) ppm.

Attempted Activation of Hydrogen with 9 and 10: Both procedures were performed in an identical fashion and only that of **9** is reported here. A solution of **9** in PhF/[D$_8$]toluene was prepared as above in an NMR spectroscopy tube fitted with a Teflon needle valve. The tube was removed, connected to a Schlenk line and subjected to three freeze–pump–thaw degassing cycles then back-filled with 1 bar hydrogen at room temperature by means of a liquid-nitrogen trap. The solution immediately became colourless. The course of the reaction was monitored by NMR spectroscopy and revealed that a complex mixture of products was obtained. After several days a light green oil was observed to separate from solution. A similar set of observations was made using **10**. In both cases, the anion [MeB(C$_6$F$_5$)$_3$] was fully converted into the anion [HB(C$_6$F$_5$)$_3$] after standing overnight: ^{11}B NMR (96 Hz, PhF/[D$_8$]-toluene): δ = –15.1 (d, $^1J_{B,H}$ = 79.9 Hz) ppm. ^{19}F NMR (470 Hz, PhF/[D$_8$]toluene): δ = –134.2 (d, $^3J_{F,F}$ = 20.1 Hz, 6 F, *ortho*-F), –165.0 (t, $^3J_{F,F}$ = 20.4 Hz, 4 F, *para*-F), –167.7 (m, 6 F, *meta*-F) ppm.

Synthesis of Compound 13: [Cp$_2$TiCl$_2$] (248.9 mg, 1.0 mmol) and *t*Bu$_2$P(C$_6$H$_4$)OH (238.3 mg, 1.0 mmol) were each weighed into a Schlenk flask and suspended in THF (10 mL) and an excess amount of HNEt$_2$ (ca. 0.5 mL). The suspension was left to stir overnight. The red-brown suspension was diluted with hexane (10 mL), then filtered through a frit into a clean Schlenk tube, along with several hexane washings of the filter cake. The solvent was concentrated to approximately 5 mL, which caused a red microcrystalline precipitate to form. The flask was left to stand at –20 °C overnight to induce further precipitation. The pale red supernatant was removed by using a cannula and the solids were washed with hexane before being dried under vacuum. Compound **13** was obtained as a red microcrystalline solid; yield 401.2 mg, 0.89 mmol, 89%. ^{1}H NMR (400 Hz, [D$_6$]benzene): δ = 7.60 (dt, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.9 Hz, 1 H, HC^6) 7.49 (ddd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, HC^4), 7.19 (dt, ddd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, HC^5), 6.79 (overlapping ddd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, HC^3), 6.15 (s, 10 H, C_5H_5), 1.20 [d, $^3J_{H,P}$ = 11.5 Hz, 18 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (100 Hz, [D$_6$]benzene): δ = 176.7 (d, $^3J_{C,P}$ = 22.6 Hz, C^1), 135.4 (d, $^3J_{C,P}$ = 3.4 Hz, C^6), 131.2 (s, C^4), 123.2 (d, $^1J_{C,P}$ = 21.8 Hz, C^2), 120.0 (s, C^5), 119.1 (d, $^2J_{C,P}$ = 3.1 Hz, C^3), 118.07 (s, C_5H_5), 32.9 [d, $^1J_{C,P}$ = 24.1 Hz, *C*(CH_3)$_3$], 31.4 [d, $^2J_{C,P}$ = 15.6 Hz, C(*C*H_3)$_3$] ppm. ^{31}P{^{1}H} NMR (161 Hz, [D$_6$]benzene): δ = 11.7 (s) ppm. ESI-MS: 451.14 [M + H]$^+$. Elemental analysis: calcd. C 63.94, H 7.15; found C 64.05, H 7.46.

Attempted Synthesis of 14 by Halide Abstraction with [Ag(C$_6$H$_6$)$_3$][B(C$_6$F$_5$)$_4$]: A sample of **13** (22.6 mg, 0.05 mmol) was loaded into an NMR spectroscopy tube fitted with a Teflon needle valve and dissolved in PhCl (0.7 mL) to give a bright red solution. Solid [Ag(C$_6$H$_6$)$_3$][B(C$_6$F$_5$)$_4$] was added in one portion, thereby immediately lightening the colour of the solution and producing a

silvery-grey precipitate. The $^{31}P\{^1H\}$ NMR spectra of the solution revealed approximately 90% conversion to a new species. The sample was returned to the glovebox and an aliquot was removed for analysis by ESI-MS. $^{31}P\{^1H\}$ NMR (161 Hz, unlocked, PhCl): δ = 21.0 ppm. ^{31}P NMR (161 Hz, unlocked, PhCl): δ = 21.0 (d, $^1J_{P,H}$ = 469 Hz) ppm. ESI-MS: 433.37 $[M]^+$.

Synthesis of 14: Compound **13** (45.1 mg, 0.1 mmol) and $[Et_3Si][B(C_6F_5)_4]$ (71.5 mg, 0.9 mmol) were each weighed into vials and each compound was dissolved in PhCl (ca. 1 mL). The two solutions were quickly mixed resulting in a dark brown/black solution. The solution stood for 30 min before being precipitated by being added dropwise to rapidly stirred hexanes (ca. 5 mL). It was necessary to repeat this procedure four more times to obtain a solid. The resulting black solid was dissolved in PhCl (ca. 1 mL) and carefully layered with hexanes (ca. 2 mL). This was allowed to stand overnight precipitating some black crystals and a black oil. The crystals were carefully removed from the vial and were washed with hexane and dried under vacuum. Black/purple needles; yield 18.4 mg, 0.041 mmol, 45%. ^1H NMR (500 Hz, PhCl/[D$_6$]benzene, 5:1): HC^3, HC^4 and HC^6 aromatic H signals are obscured by PhCl signals and could not be unambiguously identified. δ = 6.27 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 4.4 Hz, 1 H, HC^5), 5.87 (s, 5 H, C_5H_5), 0.99 [d, $^3J_{H,P}$ = 13.6 Hz, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ (125 Hz, PhCl/[D$_6$]benzene, 5:1): δ = 170.6 (d, $^2J_{C,P}$ = 15.6 Hz, C^1), 133.2 (d, $^4J_{C,P}$ = 2.0 Hz, C^5), 132.6 (d, $^3J_{C,P}$ = 2.5 Hz, C^4), 124.2 (d, $^1J_{C,P}$ = 28.4 Hz, C^2), 123.0 (d, $^3J_{C,P}$ = 4.4 Hz, C^6), 116.6 (s, C_5H_5), 115.6 (d, $^2J_{C,P}$ = 4.9 Hz, C^3), 39.4 [d, $^1J_{C,P}$ = 3.4 Hz, $C(CH_3)_3$], 30.2 [d, $^2J_{C,P}$ = 3.9 Hz, $C(CH_3)_3$] ppm. $^{31}P\{^1H\}$ (161 Hz, PhCl/[D$_6$]benzene): δ = 70.2 (s) ppm. ESI-MS: 415.17 $[M]^+$. Elemental analysis: calcd. C 52.68, H 2.95; found C 52.52, H 3.27.

Crystallographic Information: X-ray diffraction experiments on all crystals were carried out at 100 K on a Bruker APEX II diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[47] from several series of exposures measuring 0.5° in ω or ϕ. Absorption corrections were based on equivalent reflections using SADABS.[48] The structures were solved by direct methods or Patterson methods in XS[49] and structures were refined against all F_o^2 data with hydrogen atoms on carbon atoms riding in calculated positions using SHELXTL.[50] The crystallographic details for compounds **2**, **3**, **4** and **14** are given in Tables 3 and 4).

Table 3. Crystallographic details for **2** and **3**.

	2	**3**
Colour, habit	colourless block	colourless block
Size [mm]	0.22 × 0.15 × 0.10	0.38 × 0.33 × 0.22
Empirical formula	$C_{23}H_{39}OPZr$	$C_{23}H_{33}F_6OPZr$
M_r	453.73	561.68
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$I\bar{4}$
a [Å]	9.3758(4)	23.7172(2)
b [Å]	13.7878(5)	23.7172(2)
c [Å]	36.7863(14)	8.7436(1)
α [°]	90.00	90.00
β [°]	90.040(2)	90.00
γ [°]	90.00	90.00
V [Å^3]	4755.4(3)	4918.32(8)
Z	8	8
μ [mm^{-1}]	0.539	0.570
T [K]	100	100
$\theta_{min,max}$	1.11, 27.48	1.21, 30.53
Completeness	0.989 to θ = 27.48°	0.999 to θ = 30.53°
Reflections: total/independent	65530/10780	25509/7462
R_{int}	0.1058	0.0187
Final $R1$ and $wR2$	0.0357, 0.0790	0.0193, 0.0507
Largest peak, hole [e Å^{-3}]	1.400, –1.054	0.368, –0.292
$\rho_{calcd.}$ [g cm^{-3}]	1.268	1.517

Table 4. Crystallographic details for **4** and **14**.

	4	**14**
Colour, habit	colourless block	orange needles
Size [mm]	0.42 × 0.18 × 0.16	0.19 × 0.06 × 0.05
Empirical formula	$C_{35}H_{55}OPZr$	$C_{48}H_{32}BF_{20}OPTi$
M_r	613.98	1094.42
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2(1)/c$
a [Å]	12.9016(2)	11.191(2)
b [Å]	15.6429(3)	17.624(4)
c [Å]	16.8153(3)	22.999(5)
α [°]	90.00	90.00
β [°]	106.9070(10)	103.71(3)
γ [°]	90.00	90.00
V [Å^3]	3246.96(10)	4406.8(15)
Z	4	4
μ [mm^{-1}]	0.413	0.355
T [K]	100	100
$\theta_{min,max}$	1.65, 27.52	1.47, 27.54
Completeness	0.997 to θ = 27.52°	0.994 to θ = 27.54°
Reflections: total/independent	31401/7441	38243/10103
R_{int}	0.0230	0.0843
Final $R1$ and $wR2$	0.0249, 0.0643	0.0841, 0.2603
Largest peak, hole [e Å^{-3}]	0.424, –0.318	1.865, –0.894
$\rho_{calcd.}$ [g cm^{-3}]	1.256	1.650

CCDC-843725 (for **2**), -843726 (for **3**), -822763 (for **4**), and -843727 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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