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Cationic *Ansa*-Zirconocene and Hafnocene Derivatives of a Monoanionic Phosphonium-Bridged Bis(permethylcyclopentadienyl) Ligand: Synthesis and Structural Characterization of $\{[Me_2P(C_5Me_4)_2]MCl_2\}^+$ (M = Zr, Hf) and $\{[Me_2P(C_5Me_4)_2]ZrMe_2\}^+$

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The phosphonium-bridged *ansa*-metallocene complexes $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ and $\{[Me_2P(C_5Me_4)_2]HfCl_2\}^+$ have been prepared by the reactions of $\{[Me_2P(C_5Me_4)_2]Li_2\}I$ with $ZrCl_4$ and $HfCl_4$, respectively; the isolation and structural characterization of $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ complete a series of isostructural zirconocene derivatives, namely, $[R_2P(Cp^R)_2ZrCl_2]^+$, $[R_2E(Cp^R)_2ZrCl_2]$ (E = C, Si, Ge), and $[R_2B(Cp^R)_2ZrCl_2]^-$, which differ according to the charge on the complex.

Introduction

Ansa-metallocene complexes, $[ACp^R{}_2]MX_n$, and in particular zirconocene derivatives, presently feature prominently in organometallic chemistry due to their use in organic syntheses[1] and as catalyst precursors for olefin polymerization.[2] Although a principal motivation for the application of *ansa*-metallocenes may be attributed to the configurational stability imparted by the *ansa* bridge, the electronic and geometric perturbation introduced by the *ansa* bridge can also be profound.[3] For example, we have recently demonstrated how incorporation of a $[Me_2Si]$ bridge (i) promotes C−H, C−C, and C−S cleavage reactions in permethylmolybdenocene chemistry,[4] (ii) enhances reductive elimination and olefin insertion in permethyltantalocene chemistry,[5] and (iii) increases the electrophilicity of zirconocene complexes.[6] In this paper, we report the synthesis of a permethylated *ansa* ligand which incorporates a $[Me_2P]$ phosphonium bridge, namely, $[Me_2P(C_5Me_4)_2]^-$, which is a monoanionic counterpart to the isoelectronic $[MeP(C_5Me_4)_2]^{2-}$ and $[Me_2Si(C_5Me_4)_2]^{2-}$ ligands.

Results and Discussion

To date, the majority of studies on *ansa*-metallocene complexes that incorporate single atom linkers has focused on derivatives in which the *ansa* bridges are formally dianionic in their closed shell configurations,[7,8] e.g., $[RB]^{2-}$, $[R(L)B]^{2-}$ ($L = Me_3P$, Me_2S), $[R_2X]^{2-}$ (X = C, Si, Ge, Sn), $[RX^{III}]^{2-}$ (X = P, As), and $[S]^{2-}$, with only two reports of *ansa* bridges that do not fall into this category, namely, $[R_2P^V]^+$ [9,10] and $[R_2B]^-$.[11] The ability to incorporate *ansa* bridges of different formal charges is, nevertheless, of significance since such substitution would be expected to exert an electronic influence that would modulate the reactivity of the metal center. Furthermore, incorporation of *ansa* bridges with different formal charges provides potential for the synthesis of isostructural complexes for metals of different periodic groups, e.g., $[R_2P(Cp^R)_2]ZrH_3$, $[R_2Si(Cp^R)_2]TaH_3$, and $[R_2B(Cp^R)_2]MoH_3$, in a manner analogous to that achieved by exchange between cyclopentadienyl and benzene, e.g., $(\eta\text{-}C_5H_5)_2Fe$ and $(\eta\text{-}C_6H_6)_2Cr$.

We have recently reported the synthesis of permethylated *ansa* ligands that incorporate [RP] bridges, namely, $[RP(C_5Me_4)_2]^{2-}$ (R = Me, Ph), together with several titanium, zirconium, and hafnium derivatives, $[RP(C_5Me_4)_2]MX_2$ (R = Me, Ph; M = Ti, Zr, Hf).[7,12] Extending this study, we now report that the monoanionic counterpart $[Me_2P(C_5Me_4)_2]^-$, as its $\{[Me_2P(C_5Me_4)_2]Li_2\}I$ derivative, may be obtained by the procedure illustrated in Scheme 1, a method that is analogous to that used by Brintzinger to generate $[R_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]^-$.[9]

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(1) See, for example: Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262−1284, and references therein.

(2) See, for example: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85−93. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413−1418.

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(12) For other recent examples of zirconocene derivatives with [RP] bridges, see: (a) Alt, H. G.; Jung, M. *J. Organomet. Chem.* **1998**, *568*, 127−131. (b) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A−Chem.* **1998**, *128*, 245−256. (c) Anderson, G. K.; Lin, M. *Organometallics* **1988**, *7*, 2285−2288.

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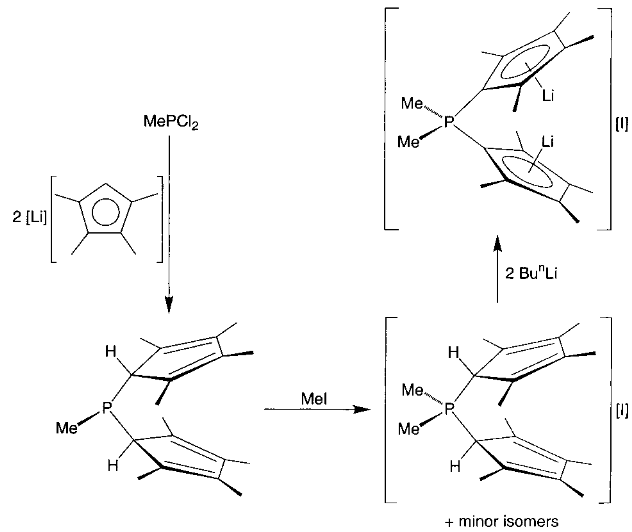
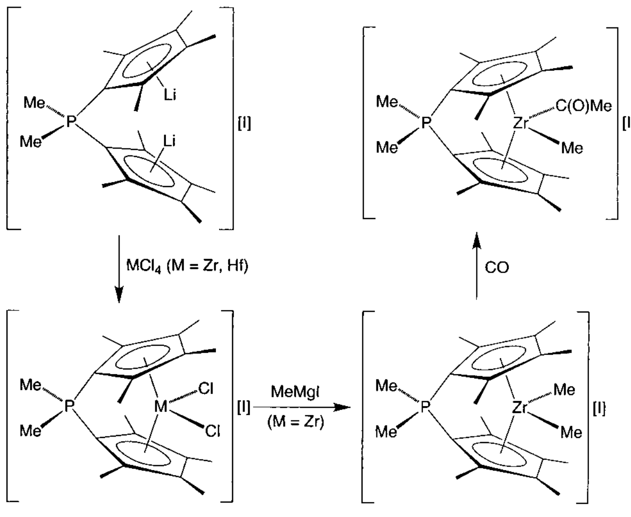
Scheme 1



Scheme 2



Thus, $\{[Me_2P(C_5Me_4)_2]Li_2\}I$ may be generated by alkylation of $MeP(C_5Me_4H)_2$ with MeI followed by deprotonation with Bu^nLi (2 equiv). Subsequent treatment of $\{[Me_2P(C_5Me_4)_2]Li_2\}I$ with either $ZrCl_4$ or $HfCl_4$ yields the corresponding metallocene derivative, $\{[Me_2P(C_5Me_4)_2]MCl_2\}I$ (Scheme 2).[13] The molecular structures of $\{[Me_2P(C_5Me_4)_2]MCl_2\}I$ (M = Zr, Hf) have been determined by X-ray diffraction, as illustrated in Figure 1 for the zirconium derivative.

The synthesis and structural characterization of $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}I$ and $\{[Me_2P(C_5Me_4)_2]HfCl_2\}I$ are particularly noteworthy because such species have so far eluded isolation. For example, although $\{[Me_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2\}I$ and $\{[Bu^n{}_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2\}I$ have recently been mentioned in the literature,[9] the complexes could not be isolated in pure form. Specifically, NMR spectroscopy demonstrated that both $\{[Me_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2\}I$ and $\{[Bu^n{}_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2\}I$ consisted of a mixture of species, which were proposed to be either (i) a combination of C_s- and C_2-symmetric species or (ii) an isomeric mixture in which one of the chloride ligands was replaced by the iodide counterion.[14] The title compounds, $\{[Me_2P(C_5Me_4)_2]MCl_2\}I$ (M = Zr, Hf), however, may be isolated in pure form, with both NMR spectroscopy and X-ray diffraction indicating that halide interchange did not occur.

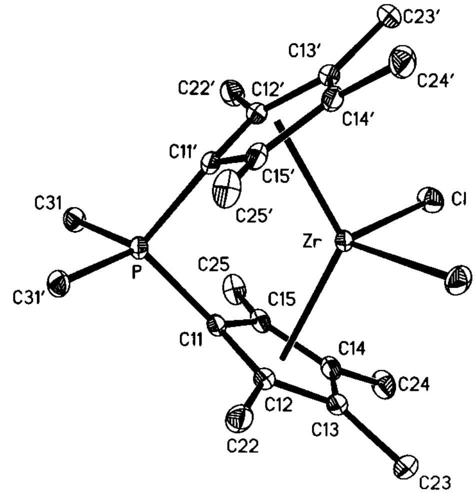


Figure 1. Molecular structure of $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}I$ (only cation is shown). Selected bond lengths (Å) and angles (deg), with values for the hafnium derivative in brackets: Zr−Cl 2.4159(6) [2.449(2)], Zr−C(11) 2.465(2) [2.461(7)], Zr−C(12) 2.509(2) [2.499(7)], Zr−C(13) 2.600(2) [2.585(7)], Zr−C(14) 2.623(2) [2.604(8)], Zr−C(15) 2.535(2) [2.526(8)]; Cl−Zr−Cl 99.31(4) [96.4(1)].

Selected bond length and angle data for $\{[Me_2P(C_5Me_4)_2]MCl_2\}^+$ are compared with the related neutral counterparts, $[RP(C_5Me_4)_2]MCl_2$ and $[Me_2Si(C_5Me_4)_2]MCl_2$, in Table 1. The data indicate that the zirconium and hafnium coordination environments are relatively insensitive to the nature of the *ansa* bridge, with each complex exhibiting a similar distortion from the ideal metallocene geometry as judged by (i) the spread of M−C bond lengths and (ii) the cyclopentadienyl tilt angle (γ). Furthermore, the Zr−Cl and Cl−Zr−Cl bond lengths and angles in these neutral and cationic complexes are comparable with those recently reported by Shapiro for the anionic $\{Me(Ph)B(C_5H_4)_2ZrCl_2\}^-$ species (2.46 Å and 99.3°, respectively).[11] The synthesis and structural characterization of $\{[Me_2P(C_5Me_4)_2]MCl_2\}^+$ thus complete a series of *ansa*-metallocene derivatives, namely, $[R_2P(Cp^R)_2ZrCl_2]^+$, $[R_2E(Cp^R)_2ZrCl_2]$ (E = C, Si, Ge), and $[R_2B(Cp^R)_2ZrCl_2]^-$, which differ according to the charge on the complex.

The most notable spectroscopic feature of $\{[Me_2P(C_5Me_4)_2]MCl_2\}^+$ (M = Zr, Hf) is associated with their ^{31}P NMR spectroscopic signals, which are at substantially lower field than those of their neutral $[PhP(C_5Me_4)_2]MCl_2$ analogues (Table 2); for example, the resonance for $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ is observed at 16.0 ppm, whereas that for $[PhP(C_5Me_4)_2]ZrCl_2$ is observed at −37.7 ppm. The ^{31}P NMR signal for $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ is, however, comparable to the value of 17.9 ppm for the counterpart with a [PhP(O)] *ansa* bridge, [PhP-

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[13] Brintzinger has noted that materials of composition $[R_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]Li$ are unreactive toward $ZrCl_4$ and $HfCl_4$, whereas LiI adducts $\{[R_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2Li_2\}I$ are reactive (ref 9). Likewise, we observe that the use of 1 equiv of Bu^nLi generates a material, presumably $[Me_2P(C_5Me_4)_2]Li$, that is unreactive toward $ZrCl_4$.

[14] Furthermore, in the case of $\{[Bu^n{}_2P(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]ZrCl_2\}I$, the product obtained was also contaminated with the protonated ligand, $[Bu^n{}_2P(C_5H_3\text{-}2\text{-}Me\text{-}4\text{-}Bu^t)_2]I$ (ref 9).

Table 1. Geometrical Data for $\{[Me_2P(C_5Me_4)_2]MCl_2\}^+$, $[Me_2Si(C_5Me_4)_2]MCl_2$, and $[RP(C_5Me_4)_2]MX_2$ Derivatives

	d(M−Cl)/Å	Cl−M−Cl/deg	d(M−Cp_{cent})/Å	d(M−C) range /Å	α/deg	β/deg	γ/deg
$\{[Me_2P(C_5Me_4)_2]ZrCl_2\}I$	2.416	99.3	2.240	0.158	126.0	116.9	4.6
$[Me_2Si(C_5Me_4)_2]ZrCl_2$[a]	2.437	99.2	2.243	0.151	128.5	119.0	4.8
$[MeP(C_5Me_4)_2]ZrCl_2$[a]	2.432	99.8	2.226	0.158	125.8	116.0	4.9
$\{[Me_2P(C_5Me_4)_2]HfCl_2\}I$	2.449	96.4	2.225	0.143	126.2	117.6	4.3
$[Me_2Si(C_5Me_4)_2]HfCl_2$[a]	2.407	98.0	2.222	0.143	128.9	119.5	4.7
$[PhP(C_5Me_4)_2]HfCl_2$[a]	2.410	98.5	2.212	0.159	126.3	117.0	4.7

[a] Data taken from ref 7.

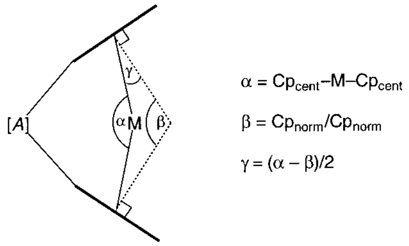

Table 2. ^{31}P NMR Data for Phosphorus Bridged *Ansa*-Metallocene Derivatives[a]

	δ ^{31}P/ppm	
	M = Zr	M = Hf
$\{[Me_2P(C_5Me_4)_2]MCl_2\}I$	16.0	15.3
$\{[Me_2P(C_5Me_4)_2]MMe_2\}I$	12.7	
$[PhP(O)(C_5Me_4)_2]MCl_2$	17.9	
$[PhP(C_5Me_4)_2]MCl_2$	−37.7	−37.2
$[PhP(C_5Me_4)_2]MMe_2$	−38.8	−38.8
$[PhP(C_5Me_4)_2]M(CO)_2$	−33.9	
$[PhP(C_5Me_4)_2]M(Te_3)$	−42.3	

[a] Data taken from this paper and ref 7.

$(O)(C_5Me_4)_2]ZrCl_2$; thus, it is evident that the ^{31}P NMR spectroscopic shift is not so much dependent upon whether the complex is charged or not, but is rather dependent upon whether the phosphorus of the bridge is in the P^{III} or P^{V} oxidation state.

Methylation of the zirconium complex $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}I$ with MeMgI yields the methyl derivative $\{[Me_2P(C_5Me_4)_2]ZrMe_2\}I$ (Scheme 2). The latter complex is characterized by signals at −0.56 and 40.1 ($^1J_{C-H}$ = 117) in the ^1H and ^{13}C NMR spectra, respectively, attributable to the $Zr-CH_3$ ligands. $\{[Me_2P(C_5Me_4)_2]ZrMe_2\}I$ is extremely sensitive to air and water and reacts instantaneously with HCl to regenerate $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$. $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ is also obtained by hydrogenation of $\{[Me_2P(C_5Me_4)_2]ZrMe_2\}^+$ in $CDCl_3$ solution at 65 °C, presumably due to a secondary reaction of $\{[Me_2P(C_5Me_4)_2]ZrH_2\}^+$ with the solvent.[15] Finally, $\{[Me_2P(C_5Me_4)_2]ZrMe_2\}I$ reacts rapidly with CO at room temperature to give the acyl derivative $\{[Me_2P(C_5Me_4)_2]Zr[C(O)Me]Me\}I$ (Scheme 2),[16] which is characterized by singlet resonances at −0.32 and 2.75 ppm in the ^1H NMR spectrum attributable to the Zr*Me* and ZrC(O)*Me* moieties, respectively. Although $\{[Me_2P(C_5Me_4)_2]Zr[C(O)Me]Me\}I$ has not been isolated due to its facile decomposition in solution, η^2-zirconocene acyl derivatives are well precedented.[17]

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[18] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker Avance 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. ^{31}P NMR spectra are referenced relative to 85% H_3PO_4 (δ = 0) using $P(OMe)_3$ as an external reference (δ = 141.0). All coupling constants are reported in hertz. IR spectra were recorded as KBr pellets on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in cm^{-1}. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer.

Preparation of $[Me_2P(C_5Me_4H)_2]I$. A solution of tetramethylcyclopentadiene (20.0 g, 164 mmol) in THF (150 mL) was slowly treated with Bu^nLi (103 mL of a 1.6 M solution in hexane, 165 mmol) at −78 °C, depositing a white solid. The mixture was allowed to warm to room temperature and was stirred for 2 h. After this period, the mixture was cooled to −78 °C, and $MePCl_2$ (7.34 mL, 81.9 mmol) was slowly added. The mixture was allowed to warm to room temperature and stirred for 4 h. After this period all volatile components were removed from the mixture in vacuo overnight, giving an oily residue. The residue was extracted into pentane (300 mL) and filtered. The pentane filtrate was then slowly treated with MeI (16 mL, 257 mmol) at −78 °C, warmed to room temperature, and stirred overnight, giving a white solid. The white solid was isolated by filtration, washed with pentane (2 × 50 mL), and dried in vacuo to give $[Me_2P(C_5Me_4H)_2]I$ as a white solid (30.1 g, 85% yield based on $MePCl_2$). Anal. Calcd for $[Me_2P(C_5Me_4H)_2]I$: C, 55.8; H, 7.5. Found: C, 54.9; H, 8.1. IR (KBr pellet, cm^{-1}): 2942 (vs), 2818 (vs), 1646 (s), 1542 (s), 1441 (vs), 1388 (vs), 1330 (m), 1298 (vs), 1260 (m), 1217 (s), 1173 (s), 1148 (vs), 1115 (vs), 1031 (s), 1007 (s), 957 (vs), 928 (vs), 873 (s), 760 (s), 722 (m), 704 (w), 688 (m), 572 (w), 502 (m), 468 (w). ^1H NMR ($CDCl_3$): 1.83 [d, $^4J_{P-H}$ = 4, 2 Me of $C_5(CH_3)_4H$], 1.86 [d, $^2J_{P-H}$ = 13, $P(CH_3)_2$], 2.07 [s, 2 Me of $C_5(CH_3)_4H$], 4.05 [d, $^2J_{P-H}$ = 21, $C_5(CH_3)_4H$]. ^{13}C NMR ($CDCl_3$): 11.7 [q,

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(15) In accord with this suggestion, the reaction is accompanied by formation of CH_4 and $CHDCl_2$.

(16) $\{[Me_2P(C_5Me_4)_2]Zr[C(O)Me]Me\}I$ decomposes in $CDCl_3$ to give $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ over a period of hours at room temperature.

(17) For examples of reversible insertion of CO into zirconocene alkyls to give η^2-acyl derivatives $Cp^R{}_2Zr[C(O)R]X$, see: (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522−523. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716−2724. (c) Christou, V.; Wuller, S. P.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 10545−10552. (d) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049−2056.

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${}^1J_{C-H} = 128$, 2 Me of $C_5(CH_3)_4H$], 15.1 [q, ${}^1J_{C-H} = 128$, 2 Me of $C_5(CH_3)_4H$], 51.2 [dd, ${}^1J_{P-C} = 36$, ${}^1J_{C-H} = 137$, 1 C of $C_5(CH_3)_4H$], 127.8 [d, $J_{P-C} = 5$, 2 C of $C_5(CH_3)_4H$], 145.0 [d, $J_{P-C} = 8$, 2 C of $C_5(CH_3)_4H$], 6.4 [dq, ${}^1J_{P-C} = 52$, ${}^1J_{C-H} = 135$, $P(CH_3)_2$]. ${}^{31}P$ NMR ($CDCl_3$): 26.1, s.

Synthesis of $[Me_2P(C_5Me_4)_2ZrCl_2]I$. A suspension of $[Me_2P(C_5Me_4H)_2]I$ (5.0 g, 11.62 mmol) in THF (100 mL) was treated with Bu^nLi (15.0 mL of a 1.6 M solution in hexane, 24.0 mmol) at −78 °C and then allowed to warm to room temperature and stirred overnight. During this period a variety of changes were observed: the white suspension sequentially converted to an orange suspension, a reddish solution, and finally a brown suspension. After this period, all volatile components were removed in vacuo. Toluene (100 mL) was added to the residue, and the suspension obtained was slowly added to a suspension of $ZrCl_4$ (2.5 g, 10.73 mmol) in toluene (50 mL). The mixture was heated at 80 °C for 3 days. After the period the mixture was filtered and the precipitate obtained was washed with toluene (20 mL) and dried. The precipitate was extracted into $CHCl_3$ (300 mL) and filtered. The volatile components were removed from the filtrate in vacuo, and the residue obtained was washed with THF (30 mL) and pentane (2 × 30 mL) and finally dried in vacuo to give $[Me_2P(C_5Me_4)_2ZrCl_2]I$ as a yellow solid (4.0 g, 63% yield based on $ZrCl_4$). Anal. Calcd for $[Me_2P(C_5Me_4)_2ZrCl_2]I$: C, 40.7; H, 5.1. Found: C, 40.9; H, 5.2. IR (KBr pellet, cm^{-1}): 3034 (s), 2955 (vs), 2917 (vs), 1634 (w), 1538 (m), 1447 (s), 1383 (vs), 1310 (s), 1285 (s), 1135 (m), 1020 (s), 930 (vs), 868 (m), 820 (w), 779 (m), 759 (m), 711 (w), 648 (m), 639 (w), 629 (w), 569 (w), 498 (s), 415 (w). ${}^1H$ NMR ($CDCl_3$, saturated): 2.10 [s, 2 Me of $C_5(CH_3)_4$], 2.14 [br s, 2 Me of $C_5(CH_3)_4$], 3.46 [d, ${}^2J_{P-H} = 14$, $P(CH_3)_2$]. ${}^{13}C$ NMR ($CDCl_3$, saturated): 12.6 [q, ${}^1J_{C-H} = 129$, 2 Me of $C_5(CH_3)_4$], 15.0 [dq, ${}^1J_{P-C} = 55$, ${}^1J_{C-H} = 134$, $P(CH_3)_2$], 15.3 [q, ${}^1J_{C-H} = 129$, 2 Me of $C_5(CH_3)_4$], 74.8 [d, ${}^1J_{P-C} = 85$, 1 C of $C_5(CH_3)_4$], 123.7 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$], 137.8 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$].

Synthesis of $[Me_2P(C_5Me_4)_2ZrMe_2]I$. A suspension of $[Me_2P(C_5Me_4)_2ZrCl_2]I$ (200 mg, 0.34 mmol) in THF (20 mL) was treated with MeMgI (0.23 mL of a 3.0 M solution in diethyl ether, 0.69 mmol) at room temperature. The mixture was stirred for 2 h, after which the mixture was filtered and the precipitate obtained was washed with THF (20 mL) and ether (2 × 20 mL) and then dried in vacuo to give $[Me_2P(C_5Me_4)_2ZrMe_2]I$ as a white solid (150 mg, 81%). Anal. Calcd for $[Me_2P(C_5Me_4)_2ZrMe_2]I \cdot MgI_2 \cdot THF$: C, 34.7; H, 4.9. Found: C, 34.8; H, 4.9. IR (KBr pellet, cm^{-1}): 2978 (s), 2914 (s), 1623 (s), 1542 (w), 1448 (w), 1387 (w), 1298 (m), 1125 (w), 1027 (m), 923 (m), 870 (w), 779 (w), 761 (w), 652 (s), 499 (m), 474 (m). ${}^1H$ NMR ($CDCl_3$, saturated): −0.56 [s, $Zr(CH_3)_2$], 2.02 [d, ${}^4J_{P-H} = 0.4$, 2 Me of $C_5(CH_3)_4$], 2.08 [s, 2 Me of $C_5(CH_3)_4$], 3.07 [d, ${}^2J_{P-H} = 14$, $P(CH_3)_2$]. ${}^{13}C$ NMR ($CDCl_3$, saturated): 11.9 [q, ${}^1J_{C-H} = 128$, 2 Me of $C_5(CH_3)_4$], 14.5 [q, ${}^1J_{C-H} = 128$, 2 Me of $C_5(CH_3)_4$], 15.0 [dq, ${}^1J_{P-C} = 56$, ${}^1J_{C-H} = 135$, $P(CH_3)_2$], 40.1 [q, ${}^1J_{C-H} = 117$, $Zr(CH_3)_2$], 68.7 [d, ${}^1J_{P-C} = 78$, 1 C of $C_5(CH_3)_4$], 121.1 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$], 130.3 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$].

Synthesis of $[Me_2P(C_5Me_4)_2Zr\{C(O)Me\}(Me)]I$. A solution of $[Me_2P(C_5Me_4)_2ZrMe_2]I$ (ca. 10 mg) in $CDCl_3$ (1 mL) was treated with CO (1 atm) at room temperature. The reaction was monitored by ${}^1H$ NMR spectroscopy, which demonstrated the formation of $[Me_2P(C_5Me_4)_2Zr\{C(O)Me\}(Me)]I$ over a period of 20 min. ${}^1H$ NMR ($CDCl_3$): −0.32 [s, $Zr(CH_3)$], 1.31 [s, 1 Me of $C_5(CH_3)_4$], 1.77 [s, 1 Me of $C_5(CH_3)_4$], 2.13 [s, 1 Me of $C_5(CH_3)_4$], 2.48 [s, 1 Me of $C_5(CH_3)_4$], 2.75 [s, $Zr\{C(O)CH_3\}$], 3.01 [d, ${}^2J_{P-H} = 14$, 1 Me of $P(CH_3)_2$], 3.19 [d, ${}^2J_{P-H} = 14$, 1 Me of $P(CH_3)_2$].

Synthesis of $[Me_2P(C_5Me_4)_2HfCl_2]I$. A suspension of $[Me_2P(C_5Me_4H)_2]I$ (2.0 g, 4.65 mmol) in THF (30 mL) was treated with Bu^nLi (4.0 mL, 2.5 M solution in hexane, 10.0 mmol) at −78 °C, warmed to room temperature, and stirred overnight. After this period, all volatile components were removed from the mixture in vacuo and dried. Toluene (30 mL) was added to the residue, and the suspension obtained was slowly added to a suspension of $HfCl_4$ (1.50 g, 4.68 mmol) in toluene (30 mL). The mixture was heated at 80 °C for 3 days. After this period the mixture was filtered, and the precipitate obtained was washed with toluene (20 mL) and dried in vacuo. The residue was extracted into $CHCl_3$ (100 mL) and filtered. The volatile components were removed in vacuo, and the residue obtained was washed with THF (30 mL) and pentane (2 × 20 mL) and dried in vacuo to give $[Me_2P(C_5Me_4)_2HfCl_2]I$ as a yellow solid (1.51 g, 48% yield). Anal. Calcd for $[Me_2P(C_5Me_4)_2HfCl_2]I$: C, 35.4; H, 4.5. Found: C, 35.5; H, 4.8. IR (KBr pellet, cm^{-1}): 3034 (s), 2955 (vs), 2916 (vs), 1638 (w), 1542 (w), 1443 (s), 1381 (s), 1310 (s), 1295 (s), 1286 (s), 1137 (m), 1026 (s), 951 (s), 931 (vs), 868 (m), 820 (w), 780 (s), 756 (s), 712 (m), 648 (m), 627 (w), 570 (w), 523 (w), 495 (s), 436 (w), 417 (w). ${}^1H$ NMR ($CDCl_3$, saturated): 2.13 [s, 2 Me of $C_5(CH_3)_4$], 2.22 [s, 2 Me of $C_5(CH_3)_4$], 3.44 [d, ${}^2J_{P-H} = 14$, $P(CH_3)_2$]. ${}^{13}C$ NMR ($CDCl_3$, saturated): 12.4 [q, ${}^1J_{C-H} = 128$, 2 Me of $C_5(CH_3)_4$], 15.0 [dq, ${}^1J_{P-C} = 55$, ${}^1J_{C-H} = 135$, $P(CH_3)_2$], 15.1 [q, ${}^1J_{C-H} = 129$, 2 Me of $C_5(CH_3)_4$], 77.2 [d, ${}^1J_{P-C} = 86$, 1 C of $C_5(CH_3)_4$], 121.1 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$], 136.4 [d, $J_{P-C} = 12$, 2 C of $C_5(CH_3)_4$].

X-ray Structure Determinations. X-ray diffraction data for $[Me_2P(C_5Me_4)_2ZrCl_2]I$ and $[Me_2P(C_5Me_4)_2HfCl_2]I$ were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 3. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 5.03).[19] Hydrogen atoms on carbon were included in calculated positions.

Table 3. Crystal, Intensity Collection, and Refinement Data

	$[Me_2P(C_5Me_4)_2ZrCl_2]I$	$[Me_2P(C_5Me_4)_2HfCl_2]I$
lattice	orthorhombic	orthorhombic
formula	$C_{20}H_{30}Cl_2IPZr$	$C_{20}H_{30}Cl_2IPHf$
fw	590.43	677.70
space group	*Pcca* (No. 54)	*Pcca* (No. 54)
a/Å	11.2444(6)	11.312(1)
b/Å	15.0735(9)	15.128(1)
c/Å	13.5240(8)	13.520(1)
α/deg	90	90
β/deg	90	90
γ/deg	90	90
V/Å^3	2292.2(2)	2313.6(4)
Z	4	4
temp (K)	218	233
radiation (λ, Å)	0.71073	0.71073
ρ(calcd), g cm^{-3}	1.711	1.946
μ(Mo Kα), mm^{-1}	2.132	6.145
θ max, deg	28.3	28.3
no. of data	2695	2698
no. of params	121	121
R1[a]	0.0201	0.0408
wR2[a]	0.0602	0.1193
GOF	1.173	1.135

[a] $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$ for $[I > 2\sigma(I)]$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ for $[I > 2\sigma(I)]$.

Summary

In summary, the phosphonium-bridged bis(tetramethylcyclopentadienyl) ligand, $[Me_2P(C_5Me_4)_2]^-$, has been constructed by the sequential reaction of $MePCl_2$ with 2 equiv of $Li(C_5Me_4H)$, followed by methylation with MeI and final deprotonation with Bu^nLi. Subse-

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[19] Sheldrick, G. M. *SHELXTL*, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen: Göttingen, Federal Republic of Germany, 1981.

quent treatment with $ZrCl_4$ and $HfCl_4$ yields the phosphonium-bridged *ansa*-metallocene complexes $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ and $\{[Me_2P(C_5Me_4)_2]HfCl_2\}^+$, respectively. The structural characterization of $\{[Me_2P(C_5Me_4)_2]ZrCl_2\}^+$ thus completes a series of structurally related zirconocene derivatives, namely, $[R_2P(Cp^R)_2ZrCl_2]^+$, $[R_2E(Cp^R)_2ZrCl_2]$ (E = C, Si, Ge), and $[R_2B(Cp^R)_2ZrCl_2]^-$, which differ according to the charge on the complex.

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

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