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Phosphorus-Bridged *ansa*-Metallocene Complexes of Titanium, Zirconium, and Hafnium: The Syntheses and Structures of $[PhP(C_5Me_4)_2]MX_2$ and $[Ph(E)P(C_5Me_4)_2]MX_2$ (E = O, S, Se) Derivatives

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Summary: A series of phosphorus-bridged ansa-metallocene complexes of titanium, zirconium, and hafnium, $[PhP(C_5Me_4)_2]MX_2$ *and* $[Ph(E)P(C_5Me_4)_2]MX_2$ *(X* = *Cl, Me, CO,* $(Se_3)_{0.5}$*,* $(Te_3)_{0.5}$*; E* = *O, S, Se), has been synthesized. Structural characterization by X-ray diffraction indicates that, in comparison to their non-ansa counterparts* $(C_5Me_5)_2MX_2$*, the cyclopentadienyl groups in phosphorus-bridged complexes are displaced from symmetric* η^5*-coordination toward* η^3*-coordination. Such* η^3,η^3*-coordination creates more electrophilic metal centers than those in their permethylcyclopentadienyl counterparts, as judged by the ν(CO) stretching frequencies of the zirconium dicarbonyl complexes* $Cp^*{}_2Zr(CO)_2$ *(1946 and 1853* cm^{-1}*) and* $[PhP(C_5Me_4)_2]Zr(CO)_2$ *(1959 and 1874* cm^{-1}*).*

ansa-Metallocenes $[ACp^R{}_2]MX_n$,[1] and in particular zirconocene derivatives, have recently attracted considerable attention. In large part, this interest derives from the use of such complexes as catalyst precursors for olefin polymerization.[2] We are presently interested in delineating the factors that are responsible for the *ansa* bridge modifying the chemistry of a particular metal center, i.e., the "*ansa*-effect".[3] For example, we have recently reported that the $[Me_2Si]$ *ansa* bridge in $[Me_2Si(C_5Me_4)_2]ZrX_2$ derivatives creates more electrophilic metal centers than those in $Cp^*{}_2ZrX_2$ counterparts.[4] In this paper, we report the syntheses and structural characterization of related phosphorus-bridged metallocene complexes of titanium, zirconium, and hafnium.

Our present approach to investigating the *ansa*-effect is concerned specifically with heavily substituted, permethylated, *ansa*-metallocene derivatives of the type $[A(C_5Me_4)_2]MX_n$. The principal reason for such a choice is that permethylation typically stabilizes metal centers with reactive functionalities, as judged by the isolation of complexes that have no counterparts in the corresponding unsubstituted cyclopentadienyl system.[5] A detailed comparison of closely related complexes $[A(C_5Me_4)_2]MX_n$ which differ in the nature of the *ansa* bridge should, therefore, allow the features responsible for the various *ansa*-effects to be ascertained. In this regard, a variety of single-element bridges, including B,[6] Ge,[7−10] Sn,[9,11] P,[12−15] As,[14g,16] and S,[17] have been incorporated into *ansa* ligands, although they have found much less application than their more ubiquitous carbon and silicon analogues.[2] Since phosphorus has a

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[1] The term *ansa* (meaning bent handle, attached at both ends) was first introduced with respect to metallocene chemistry by Brintzinger. See: Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175−185.

[2] (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) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (d) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143−187. (e) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413−1418. (f) Olabisi, O.; Atiqullah, M.; Kaminsky, W. *J. M. S.−Rev. Macromol. Chem. Phys.* **1997**, *C37*, 519−554. (g) Green, J. C. *Chem. Soc. Rev.* **1998**, *27*, 263−271. (h) Ivchenko P. V., Nifantev I. E. *Z. Org. Khim.* **1998**, *34*, 9−38.

[3] Despite numerous studies on *ansa*-metallocene complexes, relatively little attention has been given to delineating the *ansa*-effect in well-defined systems. See for example: (a) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65−75. (b) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159−167. (c) Dorer, B.; Diebold, J.; Weyand, O.; Brintzinger, H. H. *J. Organomet. Chem.* **1992**, *427*, 245−255. (d) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243, and references therein. (e) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838, and references therein.

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[13] For zirconocene derivatives, see: (a) Anderson, G. K.; Lin, M. *Organometallics* **1988**, *7*, 2285−2288. (b) Anderson, G. K.; Lin, M. *Inorg. Chim. Acta* **1988**, *142*, 7−8. (c) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A−Chem.* **1998**, *128*, 245−256. (d) Leyser, N.; Schmidt, K.; Brintzinger, H.-H. *Organometallics* **1998**, *17*, 2155−2161.

[14] For studies on phosphorus-bridged ferrocene derivatives, see: (a) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91−101. (b) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503−5512. (c) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128−135. (d) Mizuta, T.; Yamasaki, T.; Nakazawa, H.; Miyoshi, K. *Organometallics* **1996**, *15*, 1093−1100. (e) Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1987**, *6*, 872−880. (f) Houlton, A.; Roberts, R. M. G.; Silver, J.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1990**, 1543−1547. (g) Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275−1282

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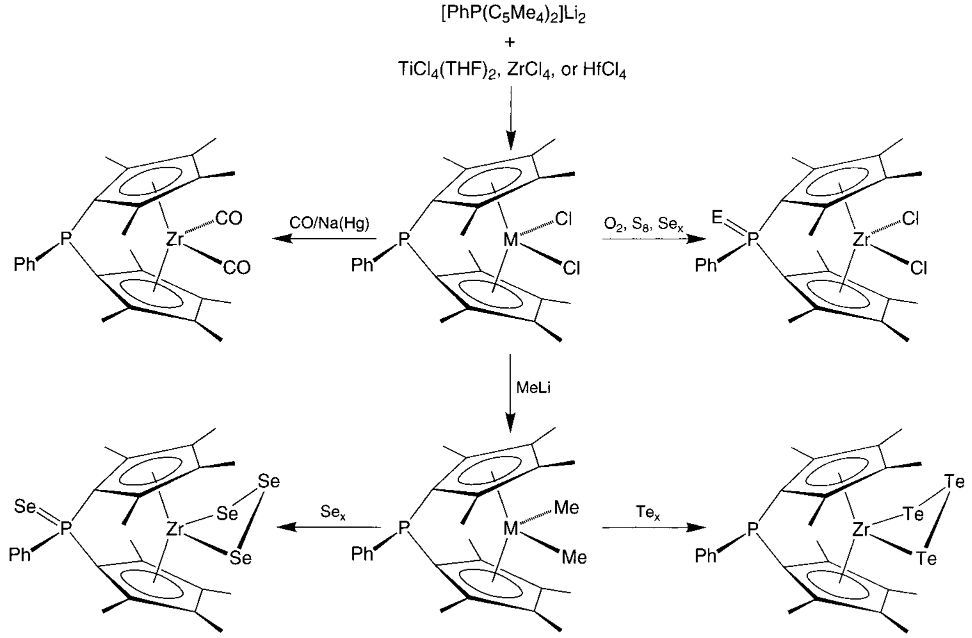
Scheme 1



similar covalent radius to that of silicon (1.10 Å versus 1.17 Å),[18] we are especially interested in developing the chemistry of phosphorus-bridged analogues $[RP(C_5Me_4)_2]MX_2$ for comparison with the $[Me_2Si(C_5Me_4)_2]ZrX_2$ system described above.

In this regard, phosphorus-bridged *ansa*-metallocene complexes of titanium, zirconium, and hafnium, $[PhP(C_5Me_4)_2]MCl_2$ (M = Ti, Zr, Hf), are readily obtained via treatment of $[PhP(C_5Me_4)_2]Li_2$[15] with the appropriate metal chloride (Scheme 1).[19,20] The dichloride complexes $[PhP(C_5Me_4)_2]MCl_2$ are useful precursors to other metallocene derivatives, including the dimethyl $[PhP(C_5Me_4)_2]MMe_2$ (M = Ti, Zr, Hf) and dicarbonyl $[PhP(C_5Me_4)_2]Zr(CO)_2$ complexes, as illustrated in Scheme 1. Most interestingly, the $[PhP(C_5Me_4)_2]$ ligand in $[PhP(C_5Me_4)_2]ZrCl_2$ may be readily elaborated into a new series of *ansa* ligands bearing four-coordinate phosphorus, namely, $[Ph(E)P(C_5Me_4)_2]ZrCl_2$ (E = O, S, Se), by reaction with oxygen, sulfur, and selenium.[21] Tellurium, however, is unreactive toward $[PhP(C_5Me_4)_2]ZrCl_2$, presumably a reflection of the lower P=Te bond energy.[22] Furthermore, whereas elemental selenium reacts with $[PhP(C_5Me_4)_2]ZrMe_2$ to give $[Ph(Se)P(C_5Me_4)_2]Zr(\eta^2\text{-}Se_3)$, the corresponding reaction with elemental tellurium does not functionalize the phosphorus atom but reacts only at the Zr–C bond to give $[PhP(C_5Me_4)_2]Zr(\eta^2\text{-}Te_3)$ (Scheme 1).

The molecular structures of $[PhP(C_5Me_4)_2]MCl_2$ (M = Ti, Zr, Hf), $[MeP(C_5Me_4)_2]ZrCl_2$, $[PhP(C_5Me_4)_2]MMe_2$ (M = Ti, Hf), $[PhP(C_5Me_4)_2]Zr(CO)_2$, $[Ph(E)P(C_5Me_4)_2]ZrCl_2$ (E = S, Se), $[Ph(Se)P(C_5Me_4)_2]Zr(\eta^2\text{-}Se_3)$, and $[PhP(C_5Me_4)_2]Zr(\eta^2\text{-}Te_3)$ have been determined by X-ray diffraction,[23] as illustrated for $[PhP(C_5Me_4)_2]ZrCl_2$ and $[Ph(S)P(C_5Me_4)_2]ZrCl_2$ in Figures 1 and 2. Of most interest are the geometric and electronic consequences of incorporating different *ansa* bridges.[24] In this regard, the data listed in Table 1 demonstrate that the coordination of the cyclopentadienyl groups in $[RP(C_5Me_4)_2]MCl_2$ is similar to those in the corresponding $[Me_2Si\text{-}$

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[18] Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

[19] Likewise, the methyl–phosphine derivative $[MeP(C_5Me_4)_2]ZrCl_2$ may be prepared by an analogous procedure from $[MeP(C_5Me_4)_2]Li_2$.

[20] Representative examples of the syntheses follow. (a) $[PhP(C_5Me_4)_2]ZrCl_2$: benzene (200 mL) was added to a mixture of $ZrCl_4$ (5.0 g, 21.5 mmol) and $[PhP(C_5Me_4)_2]Li_2$ (8.6 g, 23.7 mmol) at 0 °C, after which the mixture was allowed to warm to room temperature while stirring. The mixture was then heated at 80 °C for 3 days and subsequently filtered. The residue was further extracted into benzene (150 mL) and combined with the reaction filtrate. The volatile components were removed in vacuo, and the residue obtained was washed with pentane (2 × 20 mL) and dried in vacuo to give $[PhP(C_5Me_4)_2]ZrCl_2$ as a pale yellow solid (8.6 g, 79%). (b) $[Ph(O)P(C_5Me_4)_2]ZrCl_2$: a solution of $[PhP(C_5Me_4)_2]ZrCl_2$ (570 mg, 1.12 mmol) in toluene (20 mL) was treated with oxygen at room temperature for 1 day. After this period, the volatile components were removed in vacuo, and the residue was washed with pentane and dried in vacuo to give $[Ph(O)P(C_5Me_4)_2]ZrCl_2$ as a white solid (520 mg, 88%).

[21] For similar functionalization of phosphorus-bridged ferrocene derivatives, see ref 14g.

[22] For example, the P=E bond energies in $Bu^n{}_3PE$ decrease rapidly as the chalcogen becomes heavier: S, 96 kcal mol^{-1}; Se, 75 kcal mol^{-1}; Te, 52 kcal mol^{-1}. See: Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861–2864.

[23] $[PhP(C_5Me_4)_2]TiCl_2$ is orthorhombic, $P2_12_12_1$ (No. 19), $a = 11.2280(5)$ Å, $b = 13.6608(6)$ Å, $c = 14.4726(7)$ Å, $V = 2219.9(2)$ Å^3, $Z = 4$. $[PhP(C_5Me_4)_2]ZrCl_2$ is orthorhombic, $P2_12_12_1$ (No. 19), $a = 11.238(2)$ Å, $b = 13.833(2)$ Å, $c = 14.843(2)$ Å, $V = 2307.4(5)$ Å^3, $Z = 4$. $[PhP(C_5Me_4)_2]HfCl_2$ is orthorhombic, $P2_12_12_1$ (No. 19), $a = 11.2717(5)$ Å, $b = 13.7817(6)$ Å, $c = 14.8385(6)$ Å, $V = 2305.1(2)$ Å^3, $Z = 4$. $[MeP(C_5Me_4)_2]ZrCl_2$ is monoclinic, $C2/c$ (No. 15), $a = 15.3396(8)$ Å, $b = 11.8005(6)$ Å, $c = 11.1134(6)$ Å, $\beta = 105.106(1)°$, $V = 1942.2(2)$ Å^3, $Z = 4$. $[PhP(C_5Me_4)_2]TiMe_2$ is monoclinic, $P2_1/c$ (No. 14), $a = 8.6383(5)$ Å, $b = 9.2278(5)$ Å, $c = 29.194(2)$ Å, $\beta = 93.588(1)°$, $V = 2322.6(2)$ Å^3, $Z = 4$. $[PhP(C_5Me_4)_2]HfMe_2$ is monoclinic, $P2_1/c$ (No. 14), $a = 8.6417(4)$ Å, $b = 9.2480(5)$ Å, $c = 29.702(2)$ Å, $\beta = 93.781(1)°$, $V = 2368.6(2)$ Å^3, $Z = 4$. $[PhP(C_5Me_4)_2]Zr(CO)_2$ is monoclinic, $P2_1/n$ (No. 14), $a = 14.0286(7)$ Å, $b = 10.6747(5)$ Å, $c = 16.3021(8)$ Å, $\beta = 110.625(\underline{1})°$, $V = 2284.8(2)$ Å^3, $Z = 4$. $[Ph(S)P(C_5Me_4)_2]ZrCl_2$ is triclinic, $P1$ (No. 2), $a = 10.1388(5)$ Å, $b = 11.1709(5)$ Å, c 22.326(1) Å, $\alpha = 76.203(1)°$, $\beta = 81.759(1)°$, $\gamma = 89.8\underline{8}0(1)°$, $V = 2429.0(2)$ Å^3, $Z = 4$. $[Ph(Se)P(C_5Me_4)_2]ZrCl_2$ is triclinic, $P\bar{1}$ (No. 2), $a = 10.0792(5)$ Å, $b = 11.3485(6)$ Å, $c = 22.345(1)$ Å, $\alpha = 103.990(1)°$, $\beta = 98.018(1)°$, $\gamma = 90.026(1)°$, $V = 2454.3(2)$ Å^3, $Z = 4$. $[Ph(Se)P(C_5Me_4)_2]Zr(\eta^2\text{-}Se_3)$ is triclinic, $P\bar{1}$ (No. 2), $a = 9.4988(5)$ Å, $b = 10.0998(5)$ Å, $c = 13.8780(7)$ Å, $\alpha = 84.413(1)°$, $\beta = 83.125(1)°$, $\gamma = 73.096(1)°$, $V = 1262.0(1)$ Å^3, $Z = 2$. $[PhP(C_5Me_4)_2]Zr(\eta^2\text{-}Te_3)$ is monoclinic, $P2_1/c$ (No. 14), $a = 10.8377(6)$ Å, $b = 14.6807(8)$ Å, $c = 16.6853(9)$ Å, $\beta = 104.009(1)°$, $V = 2575.8(2)$ Å^3, $Z = 4$.

[24] For other discussions concerned with *ansa*-metallocene geometries, see: (a) Hortmann, K.; Brintzinger, H.-H. *New. J. Chem.* **1992**, *16*, 51–55. (b) Shaltout, R. M.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1995**, *503*, 205–212. (c) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539–2546.

Table 1. Geometrical Data for $Cp*_2MX_2$, $[Me_2Si(C_5Me_4)_2]MX_2$, and $[RP(C_5Me_4)_2]MX_2$ Derivatives

	d(M-Cp_{cent})/Å	d(M-C)/Å	d(M-C) range/Å	α/deg	β/deg	γ/deg
$Cp*_2TiCl_2$[a]	2.128	2.404−2.484	0.080	137.4	135.4	1.0
$[Me_2Si(C_5Me_4)_2]TiCl_2$[b]	2.136	2.365−2.552	0.187	132.2	120.6	5.8
$[PhP(C_5Me_4)_2]TiCl_2$	2.117	2.341−2.528	0.187	129.4	118.4	5.5
$Cp*_2ZrCl_2$[c]	2.250	2.525−2.540	0.015	130.5	134.9	−2.2
$[Me_2Si(C_5Me_4)_2]ZrCl_2$[c]	2.243	2.476−2.627	0.151	128.5	119.0	4.8
$[MeP(C_5Me_4)_2]ZrCl_2$	2.226	2.448−2.606	0.158	125.8	116.0	4.9
$[PhP(C_5Me_4)_2]ZrCl_2$	2.225	2.435−2.608	0.173	125.9	116.5	4.7
$[Ph(S)P(C_5Me_4)_2]ZrCl_2$	2.234	2.449−2.634	0.185	126.3	116.0	5.2
$[Ph(Se)P(C_5Me_4)_2]ZrCl_2$	2.302	2.452−2.637	0.185	126.3	115.5	5.4
$Cp*_2HfCl_2$[c]	2.230	2.498−2.580	0.082	137.5	134.2	1.7
$[Me_2Si(C_5Me_4)_2]HfCl_2$[c]	2.222	2.461−2.604	0.143	128.9	119.5	4.7
$[PhP(C_5Me_4)_2]HfCl_2$	2.212	2.439−2.598	0.159	126.3	117.0	4.7

[a] McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457−466. [b] Varga, V.; Hiller, J.; Gyepes, R.; Polasek, M.; Sedmera, Thewalt, U.; Mach, K. *J. Organomet. Chem.* **1997**, *538*, 63−74. [c] Lee, H.; Bonnano, J.; Shin, J. H.; Hascall, T.; Parkin, G. Unpublished results.

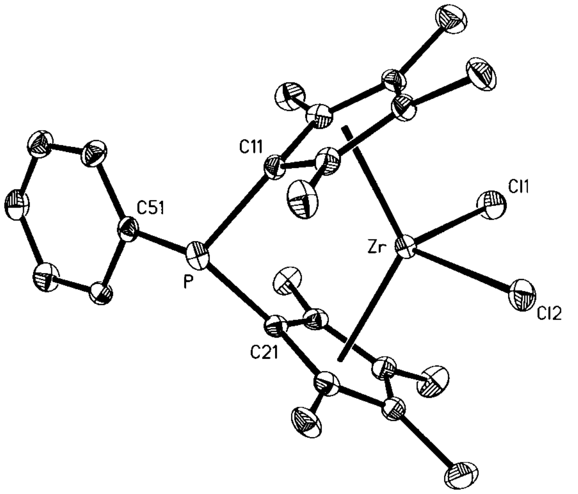

Figure 1. Molecular structure of $[PhP(C_5Me_4)_2]ZrCl_2$.

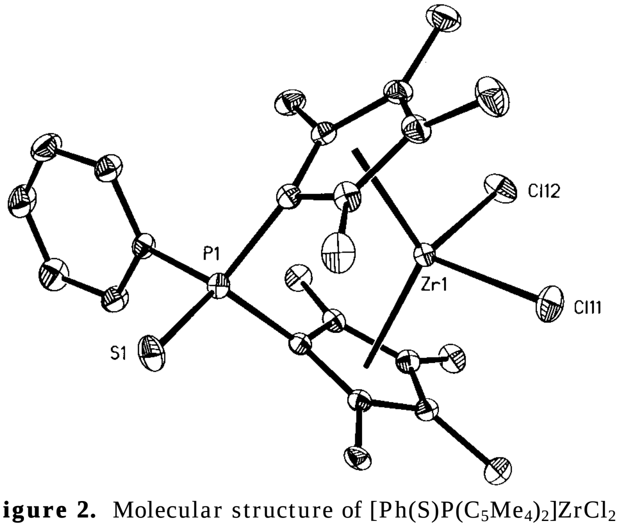

Figure 2. Molecular structure of $[Ph(S)P(C_5Me_4)_2]ZrCl_2$.

$(C_5Me_4)_2]MCl_2$ derivatives. Indeed, the C−P−C bond angles are only slightly smaller (ca. 2°) than the corresponding C−Si−C angles in $[Me_2Si(C_5Me_4)_2]MCl_2$ derivatives.[25] By comparison to the non-*ansa* complexes, however, the cyclopentadienyl groups of the $[Me_2Si]$ and [RP] *ansa*-bridged complexes are displaced from symmetric η^5-coordination toward η^3-coordination. For example, whereas the M−C bond lengths for each $Cp*_2MCl_2$ derivative are equal to within 0.08 Å, the corresponding M−C bond lengths vary by 0.14−0.19 Å for each of the *ansa* complexes (Table 1). Such changes are also accompanied by a small tilting (γ) of the cyclopentadienyl groups from the M−Cp_{cent} vector toward the *ansa* bridge; that is, the Cp_{cent}−M−Cp_{cent} angle (α) is greater than the angle between the Cp ring normals (β).[26] This modified η^3,η^3-coordination geometry creates a more electrophilic metal center, as judged by the ν(CO) stretching frequencies of the dicarbonyl complexes in pentane, $Cp*_2Zr(CO)_2$ (1946 and 1853 cm^{-1}),[27] $[Me_2Si(C_5Me_4)_2]Zr(CO)_2$ (1956 and 1869 cm^{-1}),[28] and $[PhP(C_5Me_4)_2]Zr(CO)_2$ (1959 and 1874 cm^{-1}). On this basis, the phosphorus-bridged *ansa* ligand $[PhP(C_5Me_4)_2]$ may be regarded as engendering a more electrophilic metal center than does the $[Me_2Si(C_5Me_4)_2]$ ligand.[29]

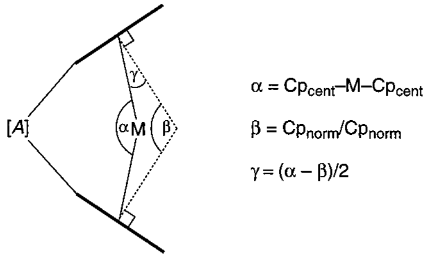

Figure 3. Definition of α, β, and γ for *ansa*-metallocene geometries.

In the presence of methylalumoxane, $[PhP(C_5Me_4)_2]ZrCl_2$ is an active catalyst for ethylene polymerization, with an activity that is comparable to that for $[Me_2Si(C_5Me_4)_2]ZrCl_2$, but less than that for $Cp*_2ZrCl_2$.[30,31]

To summarize, a series of phosphorus-bridged *ansa*-metallocene complexes of titanium, zirconium, and haf-

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[25] It should be noted, however, that a greater disparity in bond angle (ca. 7°) has been predicted for a related system. See ref 13c.

[26] For further comparison, the corresponding values for $[Me_2C(C_5H_4)_2ZrCl_2$ are: α (116.6°), β (108.6°), and γ (4.0°). See ref 24b.

[27] Literature values in Nujol are 1942 and 1850 cm^{-1}. See: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733−6735.

[28] Values in KBr discs are 1947 and 1861 cm^{-1}. See ref 4.

[29] For further discussion of this notion with respect to $[Me_2Si(C_5Me_4)_2]$ ligands see ref 4 and references therein.

[30] For example, the room-temperature activities (g $mmol^{-1}$ atm^{-1} min^{-1}) for C_2H_4 polymerization at 1 atm carried out with ca. 0.015 mmol catalyst and 6.9 mmol methylalumoxane in toluene (30 mL) are: $Cp*_2ZrCl_2$ [5.3(4)], $[Me_2Si(C_5Me_4)_2]ZrCl_2$ [1.9(1)], and $[PhP(C_5Me_4)_2]ZrCl_2$ [1.7(1)]. The chalcogenido derivatives exhibit similar activities: $[Ph(O)P(C_5Me_4)_2]ZrCl_2$ [1.8(1)], $[Ph(S)P(C_5Me_4)_2]ZrCl_2$ [1.7(3)], $[Ph(Se)P(C_5Me_4)_2]ZrCl_2$ [1.9(2)].

[31] It should be noted that Schaverien has also reported that the phosphorus-bridged $[PhP(C_5H_4)(fluorenyl)]ZrCl_2$ and $[PhP(indenyl)_2]ZrCl_2$ derivatives are active catalysts for propylene polymerization. See ref 13c.

nium, namely, $[PhP(C_5Me_4)_2]MX_2$ (R = Me, Ph) and $[Ph(E)P(C_5Me_4)_2]MX_2$ (E = O, S, Se), have been synthesized. By comparison with $Cp^*_2Zr(CO)_2$, the phosphorus-bridged *ansa*-metallocene derivative $[PhP(C_5Me_4)_2]Zr(CO)_2$ possesses a more electrophilic zirconium center.

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Supporting Information Available: Experimental and crystallographic information (107 pages). Ordering information is given on any current masthead page.

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