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New Zirconium Hydrocarbyl Bis(phosphoranimino) "Pincer" Carbene Complexes

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Summary: Reaction of the bis(iminodi(phenyl)phosphorano)methanes $CH_2(Ph_2P{=}NR)_2$ (R = Ad ***1****, $SiMe_3$* ***2****) with $Zr(CH_2Ph)_4$ in toluene under mild conditions gave novel electronically unsaturated bis(hydrocarbyl) carbene complexes of the formula $[Zr\{C(Ph_2P{=}NR)_2\text{-}\kappa^3C,N,N'\}(CH_2Ph)_2]$ (R = Ad* ***3****, $SiMe_3$* ***4****) in high yields. The ^{13}C NMR resonances for the metal-bound carbon (82.8 (****3****), 84.7 (****4****) ppm) are shifted upfield relative to the previously known group 4 carbene complexes. The crystal structure of* ***3*** *shows a short metal carbon link which is common to two fused four-membered rings which are almost coplanar. The rings are formed by chelation of the two pendant imine centers of the ligand. These complexes represent the first examples of hydrocarbyl-metal carbene complexes of a group 4 metal.*

Introduction

Since the first synthesis of a transition metal carbene complex by Fischer and Maasböl in 1964,[1] interest in and applications of these species have expanded enormously.[2−14] In general, carbene complexes $L_nM{=}CXY$ are classified either as heteroatom stabilized (or Fischer type) when X or Y are O, N, or S, etc., or as alkylidene (or Schrock type) when X or Y are H or carbon substituents.[3,7,10] Here we report a new class of zirconium hydrocarbyl derivatives in which a strong metal carbene interaction in a supported (or encapsulated) "pincer" ligand structure is formed. The carbon center is substituted by two iminophosphorane units which supply the nitrogen bases that coordinate to the metal to form two four-membered rings, thus creating a fused bicyclic "pincer" chelate ring system. These new complexes, which have been synthesized from the metal tetraalkyl by means of an alkane elimination reaction that removes the two protons from the methylene unit in the $CH_2(Ph_2P{=}NR)_2$ ligands, represent the first examples of stable, electronically unsaturated (12 valence electron systems), hydrocarbyl complexes of group 4 metal carbenes. We have recently reported[15] related carbene complexes of Ti and Zr chlorides obtained by a very different route, namely, the metathetical elimination of LiCl from the dilithio salt of the ligand.[16,17] A few previous examples of group 4 metal carbene complexes of titanium[18] and zirconium[19] that contain cyclopentadienyl substituents are known. In contrast there are many examples of group 5 and 6 metal carbenes,[2,4,5,8,9] some of which are Cp and CO free.

Results and Discussion

The reaction of the tetrabenzyl zirconium(IV) complex $[Zr(CH_2Ph)_4]$[20] with bis(iminodi(phenyl)phosphorano)methane, $CH_2(Ph_2P{=}NR)_2$ {R = Ad **1**,[21] $SiMe_3$ **2**[22]}, in toluene (eq 1) yielded $[Zr\{C(Ph_2P{=}NR)_2\text{-}\kappa^3C,N,N'\}(CH_2\text{-}$

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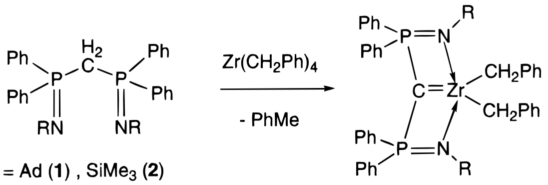

R = Ad (**1**) , SiMe$_3$ (**2**)

R = Ad (**3**), SiMe$_3$ (**4**)

(1)

Ph)$_2$] (R = Ad **3**, SiMe$_3$ **4**) as a result of elimination of 2 mol of toluene to achieve complete deprotonation of the methylene carbon. The reaction was monitored by ^{31}P NMR spectroscopy, which showed that the more acidic trimethylsilyl-substituted ligand **2** reacted more rapidly at room temperature than the adamantyl-substituted ligand **1**. The latter required mild heating to complete the reaction. In both cases, conversion to the carbene complexes was nearly quantitative according to the ^{31}P NMR spectra of the reaction mixtures. Pale yellow crystals of **3** (yield: 78%) or pale brown crystals of **4** (yield: 74%) were obtained. These new complexes were highly soluble in relatively polar and aromatic solvents such as diethyl ether, benzene, and toluene and also showed high thermal stability (for example, toluene solutions of **3** and **4** do not decompose upon heating at 120 °C for 2 days under Ar).

The ^{31}P NMR spectra of **3** (12.6 ppm) or **4** (12.4 ppm) consist of only one sharp singlet; thus the two phosphorus centers are equivalent. These resonances are shifted downfield by 28.0 ppm in the case of **3** and 17.6 ppm in the case of **4** versus the free ligand signals. The ^{13}C-{^{1}H} NMR APT spectra gave positive triplet signals {$^1J_{PC}$ = 171 (**3**), 164 (**4**) Hz} for the carbene, which collapsed to positive singlets upon phosphorus decoupling. The chemical shift values for these carbenes (82.8 ppm for **3** and 84.7 ppm for **4**) show that these centers are shielded relative to the shifts of previously reported Zr carbenes,[19,23] a difference that may arise from the presence of the phosphorus substituents or the effects of the unusual constrained geometry about the carbon center.[24] The values approach those that are typical for ylide complexes of the group IV metals,[25] the carbodi(phosphorane) cationic complexes $[O_3Re{=}C(PPh_3)_2]^+$-$[ReO_4]^-$ [26] and $[Tp'(OC)_2W{=}C(PMe_3)_2]^+[PF_6]^-$ [27] (Tp′ = $[HB(N_2C_3Me_2H)_3]^-$).

The molecular structure of the carbene complex [Zr{C(Ph$_2$P=NAd)$_2$-κ^3*C,N,N′*}(CH$_2$Ph)$_2$] (**3**) was confirmed by X-ray crystallography.[28] An ORTEP[29] plot of the carbene core is shown in Figure 1. Selected distances and angles are listed in Table 1. The core structure consists of a nearly planar pair of fused four-membered rings sharing a common Zr=C edge (the maximum deviating atom lies 0.029 Å out of the least-squares plane). The Zr is both coordinated and bound to the tridentate “pincer” ligand and to two benzyl groups to produce a distorted trigonal bipyramid environment about the Zr. The sum of the angles around the carbene center C(1) is 360°; thus the C(1) geometry is planar. The P(1)−C(1)−P(2) angle is 168.0(2)°, with the carbon center projected toward the metal. The Zr−C(1) bond distance (2.208(3) Å) is about 0.1 Å larger than that observed previously for a Fischer-type carbene complex of Zr, Cp$_2$(Me$_3$P)Zr=C(H)O−Zr(I)Cp*$_2$ (2.117(7) Å),[19c] and is about 8% shorter than the typical Zr−C single-bond distances in secondary alkyl (HCR$_2^-$) complexes.[30]

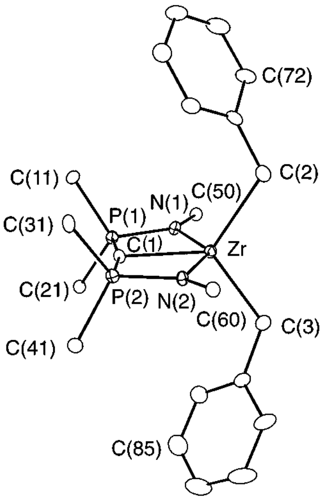

Figure 1. An ORTEP[29] view of [Zr{C(Ph$_2$P=NAd)$_2$-κ^3*C,N,N′*}(CH$_2$Ph)$_2$] (**3**) showing the atom-labeling scheme. The hydrogen atoms as well as all carbon atoms except the *ipso* carbon atoms of the phenyl and adamantyl substituents have been removed for clarity. The phenyl rings of the benzyl substituents on Zr are shown. The illustrated atoms are represented by Gaussian ellipsoids at the 20% probability level.

Table 1. Selected Bond Lengths and Angles for [Zr{C(Ph$_2$P=NAd)$_2$-κ^3*C,N,N′* }(CH$_2$Ph)$_2$], 3

Bond Lengths (Å)			
Zr−C(1)	2.208(3)	P(1)−C(1)	1.655(4)
Zr−N(1)	2.190(3)	P(2)−C(1)	1.651(4)
Zr−N(2)	2.198(3)	P(1)−C(11)	1.818(4)
Zr−C(2)	2.293(4)	P(1)−C(21)	1.822(4)
Zr−C(3)	2.287(4)	P(2)−C(31)	1.820(4)
P(1)−N(1)	1.650(3)	P(2)−C(41)	1.818(4)
P(2)−N(2)	1.649(3)		
Bond Angles (deg)			
P(1)−C(1)−P(2)	168.0(2)	Zr−C(1)−P(2)	96.0(2)
N(1)−Zr−N(2)	138.2(1)	N(1)−P(1)−C(1)	98.0(2)
Zr−C(1)−P(1)	96.0(2)	N(2)−P(2)−C(1)	98.5(2)

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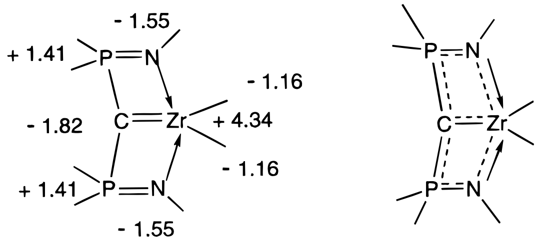
Scheme 1



Moreover, the bond distances in the six-membered bicyclic plane are significantly altered versus similar ligands $Me(H)C(Ph_2P{=}N(4\text{-tolyl}))_2$[31] and $H_2C(Cy_2P{=}NSiMe_3)_2$[21] in that the P−N bond distances are elongated and the endocyclic P−C bond distances are considerably shortened. In addition the Zr−N bonds are slightly shorter than in neutral amine complexes and longer than those characteristic of amide (NR_2^-) ligands.[32] All these factors strongly suggest substantial delocalization of electrons throughout the two fused planar six-membered bicyclic ring structure, which is represented in Scheme 1. This formulation introduces a "ylidic" character to the system, and in some respects the present complexes resemble these systems,[25] although the character of the system does not appear to be as extreme as would be suggested by formulating the ligand as a dianionic carbodi(phosphorane), $\{R'N{-}PR_2{=}C{=}PR_2{-}NR'\}^{-2}$.[33] If however all of the binding to the metal in our system were to occur only through the nitrogen centers in the dianionic limiting case, we might anticipate the neutral carbon center depicted in this limiting formulation to be bent away from the metal to form a less strained six-membered ring system. Instead we see a short metal−carbon bond which can be compared with a formal "carbene" donation to the metal. The bond length and chemical shift properties of **3** and **4** are indeed similar to those of the carbodi(phosphorane) complexes $[O_3Re{=}C(PPh_3)_2]^+[ReO_4]^-$ [26] and $[Tp'(OC)_2W{=}C(PMe_3)_2]^+[PF_6]^-$,[27] wherein substantial M=C bond character is established between the metal and carbon, except that in these cases the phenyl or methyl substituents on the phosphorus do not interact with the metal and the PR_3 units bend away to make shallow (123.1(4)° or 114.5(8)°, respectively) angles at the carbene carbon. A chemical shift argument itself, while useful, may not be a definitive measure of carbene character especially when phosphorus atoms are bound to the carbon in question. Theoretical analysis of our complexes is in progress to ascertain the complete nature of the metal−carbon interaction. Meanwhile, a "single-point energy calculation" carried out at the density functional level[34] gives a charge distribution (Scheme 1) indicating a substantial dianionic character at the central carbon and implies that this carbon may act as a "carbene" donor to the metal center.

The synthesis of these complexes depends on the well-documented knowledge that the protons in the P−C−P backbone in the bisphosphine compounds $\{H_2C(PR_2)_2\}$ are moderately acidic because of the π-acceptor interaction of the phosphorus substituents. However it is unusual to be able to remove *two* protons from the same carbon atom. Typically, strong bases have been used to remove *one* proton from the methylene carbon in the backbone moiety to form a methine carbanion bridge.[35] A few reports describe situations wherein *doubly* deprotonated ligands are formed,[36] but in these cases the dianionic ligand so created bridges two metal centers, not subtended from only one metal, as is the case here. We[16] and others[17] have shown that the dilithium salt of bis(iminodi(phenyl)phosphoranimido)methane is readily accessed.

Conclusion

New dialkyl zirconium complexes were obtained from an alkane elimination reaction, and the resultant complexes belong to the new class of metal carbene complexes derived from bis(iminophosphorano)methane ligands. The strong metal carbon interaction indicated by the structural data suggests possibilities for unusual reactivity. Forthcoming reports will expand on the chemistry of this system as we search for a complete

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(30) See for example: (a) $[Cp_2Zr(CPh_2H)_2]$, Zr−C = 2.379(6), 2.396(6) Å in: Atwood, J. L.; Barker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. *J. Am. Chem. Soc.* **1977**, *99*, 6645−6652. (b) $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH(CH_3)(6\text{-ethylpyrid-2-yl})Cl$, Zr−C = 2.421(4) Å in: Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991−8996. (c) $[Cp_2Zr(\eta^2\text{-}C,O\text{-}CH(Me)CH_2CH_2O)]_2$, Zr−C = 2.382(11) Å in: Takaya, H.; Yamakawa, M.; Mashima, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1283−1284.

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(32) For some typical values and references to earlier work see: (a) $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$, $Zr{-}NEt_2$ = 2.029(3), 2.047(3) Å in: Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630−3635. (b) *rac*-$Me_2Si(1\text{-}C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}{}^tBu_2Zr(NC_4H_8)_2$, Zr−N = 2.033(1), 2.084(1) Å in: Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045−4053. (c) $CpZrN({}^iPr)_2Cl_2$, Zr−N = 1.988(4) Å and $[(C_5Me_4)SiMe_2(N^tBu)]ZrCl_2$, Zr−N = 2.052(2) Å in: Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581, and references therein.

(33) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; John Wiley & Sons: New York, 1993; p 65.

(34) The adamantyl and benzyl groups were replaced with methyl groups, keeping the N−C and Zr−C distances fixed at experimental values. Single-point energy calculations were carried out at the density functional theory level. (the B3LYP(a) functional was employed in conjunction with model core potentials (MCP) basis sets (b−d) of double-ζ valence plus polarization quality (an *f* function on Zr)). The SPD-type MCPs were used for Zr. All calculations were performed with the CADPAC(e) suite of programs. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Sakai, Y. *J. Chem. Phys.* **1981**, *75*, 1303−1308. (c) Sakai, Y.; Huzinaga, S. *J. Chem. Phys.* **1982**, *76*, 2537−2551. (d) Sakai, Y.; Miyoshi, E.; Klobukowski, M.; Huzinaga, S. *J. Chem. Phys.* **1997**, *106*, 8084−8092. (e) *CADPAC*: The Cambridge Analytical Derivatives Package, Issue 6; Cambridge, 1995. A suite of quantum chemistry programs developed by Amos, R. D. with contributions from Alberts, I. L.; Andrews, J. S.; Colwell, S. M.; Handy, N. C.; Jayatilaka, D.; Knowles, P. J.; Kobayashi, R.; Laidig, K. E.; Laming, G.; Lee, A. M.; Maslen, P. E.; Murray, C. W.; Rice, J. E.; Simandiras, E. D.; Stone, A. J.; Su, M.-D.; Tozer, D. J.

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understanding of the chemical nature of these carbenes and their reactivity patterns.

Experimental Section

All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox with an efficient recirculator. Solvents were dried and distilled under argon prior to use. Hexane and toluene were distilled from Na−K and Na, respectively. NMR spectra were recorded on Bruker WH-200 and WH-400 instruments. The NMR solvents benzene-d_6 and toluene-d_8 were freshly vacuum transferred from Na−K. Shifts were determined with reference to the deuterium signal of the solvent employed. The ^{1}H NMR chemical shifts are reported in ppm from external Me_4Si, and the ^{31}P NMR spectra are reported in ppm from external 85% H_3PO_4. Positive values reflect downfield shifts. Infrared spectra were recorded on a Nicolet 7199 infrared spectrometer.

Preparation of [Zr{C(Ph$_2$P═NAd}$_2$-κ^3*C,N,N′*}(CH$_2$Ph)$_2$] (3). To a pale brown suspension of zirconium tetrabenzyl complex[20] [Zr($CH_2C_6H_5$)$_4$] (0.1 g, 0.219 mmol) in 5 mL of toluene was added CH_2(Ph_2P═NAd)$_2$ (**1**)[21] (0.150 g, 0.219 mmol) at room temperature. The reaction mixture was heated in the absence of light at 70 °C for 24 h. The solution was concentrated and cooled at −15 °C. Pale yellow crystals deposited in a day and were collected by filtration and dried (yield: 0.180 g, 78.4%). IR (Nujol mull): 1594 m, 1488 m, 1436 m, 1362 s, 1353 s, 1304 m, 1206 m, 1185 w, 1143 s, 1104 s, 1021 m, 1005 w, 981 m, 939 w, 840 m, 814 w, 798 w, 775 m, 760 w, 741 s, 734 s, 716 s, 694 s, 667 w, 652 s, 638 m, 624 m, 614 w, 571 m, 548 w, 524 s, 517 s. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.50 (q, 8H, phenyl-P), 7.43 (d, 4H, phenyl-P), 7.31 (t, 4H, phenyl-Bz), 7.07 (m, 2H, phenyl-toluene), 7.03 (t, 4H, phenyl-Bz), 7.01 (m, 2H, phenyl-toluene), 6.98 (m, 8H, phenyl-P), 6.96 (m, H, phenyl-toluene), 6.95 (m, 2H, phenyl-Bz), 2.83 (s, 4H, methylene-Bz), 2.10 (s, 3 H, methyl-toluene), 1.98 (bs, 12H, methylene-Ad), 1.83 (bs, 6H, methine-Ad), 1.47 (b dd, 12H, methylene-Ad). ^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 149.2 (s, 2 C, *ipso* phenyl-Bz), 137.8 (s, 1C, *ipso*, phenyl-toluene), 136.9 (m, 4 C, *ipso* phenyl-P), 132.3 (t, $^2J_{PC}$ = 5.3 Hz, 8 C, *ortho* phenyl-P), 130.2 (s, 4 C, *ortho* phenyl-Bz), 129.3 (s, 2 C, *ortho* phenyl-toluene), 128.7 (s, 4 C, *meta* phenyl-Bz), 128.3 (s, 2 C, *meta*-phenyl-toluene), 128.1 (t, $^3J_{PC}$ = 5.1 Hz, 8 C, *meta* phenyl-P), 127.0 (s, 4 C, *para* phenyl-P), 125.6 (s, 1 C, *para* phenyl-toluene), 120.9 (s, 2 C, *para* phenyl-Bz), 82.8 (t, $^1J_{PC}$ = 171 Hz, 1 C, quaternary C−PCP), 68.1 (s, 2 C, methylene-Bz), 56.9 (s, 2 C, quaternary C-Ad), 46.9 (s, 6 C, methylene-Ad), 36.4 (s, 6 C, methylene-Ad), 30.6 (s, 6 C, methine-Ad), 21.4 (s, 1 C, methyl-toluene). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K): δ 12.6 (2 P). Anal. Calcd for $C_{66}H_{72}N_2P_2$Zr: C, 75.75; H, 6.93; N, 2.68. Found: C, 75.31; H, 7.06; N, 2.77.

Preparation of [Zr{C(Ph$_2$P═NSiMe$_3$)$_2$-κ^3*C,N,N′*}(CH$_2$Ph)$_2$] (4). To a suspension of [Zr(CH_2Ph)$_4$] (1.0 g, 2.19 mmol) in 15 mL of toluene was added CH_2(Ph_2P═NSiMe$_3$)$_2$ (**2**)[22] (1.226 g, 2.19 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 days, during which time a pale brown microcrystalline solid precipitated. The off-white product was isolated by filtration, washed with few milliliters of hexane, and dried (yield: 1.34 g, 73.5%). IR (Nujol mull): 1591 m, 1488 m, 1481 m, 1466 m, 1436 m, 1378 m, 1334 w, 1283 s, 1260 s, 1249 s, 1216 m, 1204 m, 1173 m, 1151 w, 1110 s, 1016 bs, 971 m, 880 w, 834 bs, 793 w, 776 s, 764 m, 743 s, 734 m, 720 s, 693 s, 656 s, 620 m, 614 m, 562 s. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.34 (q, 8H, phenyl-P), 7.26 (m, 4H, phenyl-Bz), 7.24 (m, 4H, phenyl-P), 7.02 (m, 6H, phenyl-Bz), 6.93 (m, 8H, phenyl-P), 2.62 (s, 4H, methylene-Bz), 0.09 (s, 18 H, methyl-TMS). ^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 147.7 (s, 2 C, *ipso* phenyl-Bz), 135.9 (m, 4 C, *ipso* phenyl-P), 131.6 (t, $^2J_{PC}$ = 6.0 Hz, 8 C, *ortho* phenyl-P), 130.5 (s, 4 C, *ortho* phenyl-Bz), 128.9 (s, 4 C, *meta* phenyl-Bz), 128.2 (t, $^3J_{PC}$ = 6.5 Hz, 8 C, *meta* phenyl-P), 126.8 (s, 4 C, *para* phenyl-P), 121.2 (s, 2 C, *para* phenyl-Bz), 84.7 (t, $^1J_{PC}$ = 164 Hz, 1 C, quaternary C−PCP), 68.8 (s, 2 C, methylene-Bz), 3.6 (s, 6 C, methyl-TMS). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K): δ 12.4 (2 P). Anal. Calcd for $C_{45}H_{52}N_2P_2Si_2$Zr: C, 65.10; H, 6.31; N, 3.37. Found: C, 65.65; H, 6.03; N, 3.31.

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Supporting Information Available: The structure report with complete tables of crystal data, atomic coordinates, and bond lengths and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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