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2-Indenylidene Pincer Complexes of Zirconium and Palladium

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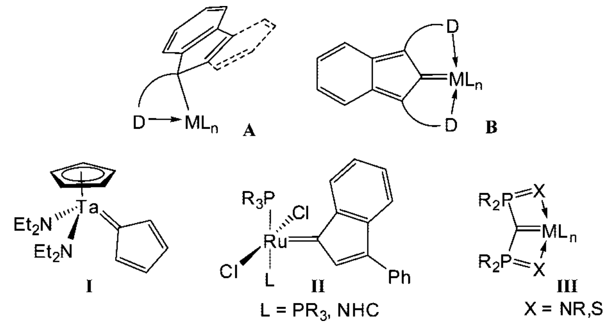
Abstract: [IndH$_2$(Ph$_2$P=X)$_2$] derivatives (**1**, X = NMes; **4**, X = S) react with [Zr(NMe$_2$)$_4$] and [PdCl$_2$(cod)] to afford the complexes {[Ind(Ph$_2$PNMes)$_2$]Zr(NMe$_2$)$_2$} (**3**), {[Ind(Ph$_2$PS)$_2$]Zr(NMe$_2$)$_2$} (**5**), and {[Ind(Ph$_2$PS)$_2$]Pd(HN*c*-Hex$_2$)} (**7**). The ability of the phosphazene and thiophosphinoyl side arms to support the coordination of the indenyl ring as 2-indenylidene was evidenced by NMR spectroscopy and X-ray diffraction studies. Analysis of the bonding situation by density functional theory calculations revealed a strong σ interaction but a negligible (if any) π interaction between C2 and the metal.

Introduction

Intrigued by the ability of cyclopentadienyl (Cp)-type rings to adopt unusual coordination modes, we recently showed that the introduction of a short and strongly donating phosphazene moiety may enforce η^1 coordination of fluorenyl and indenyl (Ind) rings to transition metals (Zr and Rh complexes of type **A** in Chart 1).[1] Such a low hapticity is rare for Cp-type rings[2] but opens interesting perspectives because of the increased accessibility of the metal center.[3] Ylidene coordination of Cp-type rings is even less common. Although related cyclopropenylidene complexes have been known for 40 years,[4,5] it was not until 1997 that the related and to date unique Ta cyclopentadienylidene complex **I** was structurally authenticated.[6] In addition, a few 1-indenylidene Ru complexes of type **II** have been prepared by intramolecular cyclization of allenylidene precursors and have proved to be very efficient catalysts for olefin metathesis and atom-transfer radical polymerization.[7]

Chart 1



The spectacular achievements reported over the past two decades in the synthesis and application of pincer complexes[8] prompted us to investigate the preparation of complexes of type **B** (Chart 1), in which two donor buttresses would support the coordination of the 2-indenylidene fragment. In view of the versatile coordination chemistry reported by Cavell, Le Floch, and others for pincer methanediide complexes **III**,[9] phosphazene and thiophosphinoyl moieties were chosen as strongly donating and easily introduceable side arms for complexes **B**. Here we report the synthesis and complete characterization of the

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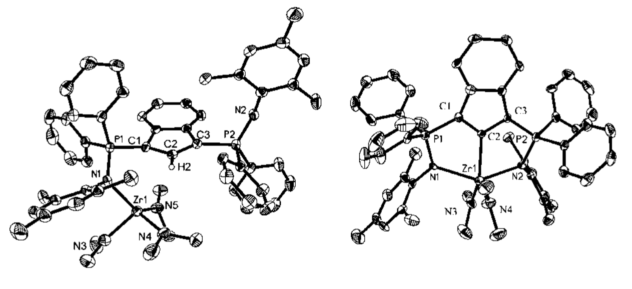
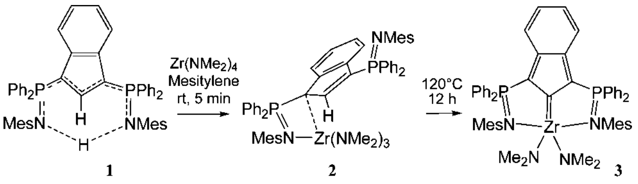


Figure 1. Molecular structures of complexes **2** (left) and **3** (right). Thermal ellipsoids are projected at the 50% probability level. Selected bond distances (Å) and angles (deg) for **2**: Zr1−N1, 2.224(3); N1−P1−C1, 103.41(15); N2−P2−C3, 118.17(16). For **3**: Zr1−C2, 2.22(5); Zr1−N1, 2.286(4); Zr1−N2, 2.262(3); N1−Zr1−N2, 142.87(14).

Scheme 1



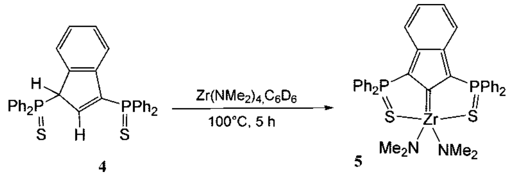
first representatives of such pincer 2-indenylidene complexes with Zr and Pd and discuss their bonding situation on the basis of experimental as well as theoretical data.

Results and Discussion

Synthesis and Characterization of the 2-Indenylidene Complexes. The Staudinger reaction of 1,3-bis(diphenylphosphino)indene[10] with 2 equiv of mesityl azide readily afforded [$IndH_2(Ph_2P{=}NMes)_2$] (**1**) in 70% yield. The broad signal centered at ~5 ppm in the ^{31}P NMR spectrum of **1** most likely results from the coexistence of several tautomeric forms, as previously observed with monophosphazene Cp and Ind ligands.[1a,11] Coordination to zirconium was then studied by reacting **1** with [$Zr(NMe_2)_4$] (Scheme 1). Elimination of the first molecule of Me_2NH readily proceeded at room temperature to afford complex **2** having a single phosphazene arm coordinated to the Zr atom, as indicated by the two ^{31}P NMR signals observed at 40.2 and −14.8 ppm attributed to the coordinated and noncoordinated phosphazene moieties, respectively. The presence of a C_q doublet signal ($J_{CP} = 67.3$ Hz) at 74.3 ppm in the ^{13}C NMR spectrum suggested a low hapticity for the indenyl fragment. This was unambiguously confirmed by X-ray diffraction analysis (Figure 1). The zirconium atom is tetracoordinate (three NMe_2 groups and one of the phosphazene side arms) and adopts a distorted tetrahedral geometry. The distance between Zr and C1 (2.94 Å) is significantly longer than those observed in complexes **A** (2.51−2.60 Å),[1a] suggesting a very weak (if any) interaction.

The removal of a second Me_2NH molecule from complex **2** required forcing conditions (heating for 12 h at 120 °C), consistent with the weak acidity of the hydrogen atom at C2. The unique sharp ^{31}P NMR signal observed at 30.1 ppm for the resulting complex **3** was consistent with symmetric coordination of the two phosphazene moieties. In addition, the diagnostic triplet signal observed at 209 ppm ($J_{CP} = 32.7$ Hz) in the ^{13}C NMR spectrum for C2 strongly suggested the formation of a 2-indenylidene zirconium complex.[12] Crystals of **3** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated mesitylene solution at 0 °C, and the obtained structure is shown in Figure 1. The Zr atom is pentacoordinate and deviates slightly (0.495 Å) from the (N1, C2, N2) coordination plane defined by the pincer ligand. The C2−Zr bond deviates by 16° from the mean plane of the indenyl ring, while C1 and C3 are in perfectly planar environments. The C2−Zr bond distance [2.221(5) Å] is significantly longer than those observed in the few structurally characterized Zr alkylidene complexes (2.01−2.02 Å)[12a,b] but lies in the same range as those reported by Cavell and Le Floch for Zr complexes of type **III**.[13]

Scheme 2



The phosphazene groups were then replaced by thiophosphinoyl moieties in order to further demonstrate the propensity of donor side arms to support 2-indenylidene coordination to zirconium. Thus, [$IndH_2(Ph_2P{=}S)_2$] (**4**)[14] was reacted with [$Zr(NMe_2)_4$] in deuterated benzene at 100 °C (Scheme 2). After 5 h of reaction, ^{31}P NMR spectroscopy showed complete consumption of derivative **4** and the clean formation of a new compound **5** exhibiting a single signal at 40.1 ppm, indicating symmetrical coordination of the thiophosphinoyl side arms. The poor stability of **5** prevented the formation of single crystals suitable for X-ray diffraction analysis, but its structure was unambiguously assessed by NMR spectroscopy: (*i*) the ^{1}H NMR spectrum indicated the retention of only two NMe_2 groups at Zr, and (*ii*) a triplet signal at 206.3 ppm ($J_{CP} = 44.5$ Hz) was observed for C2 in the ^{13}C NMR spectrum.

The formation of complexes **3** and **5** substantiates the ability of donor buttresses to support the coordination of the indenyl ring to zirconium as a 2-indenylidene. To demonstrate the generality of this strategy, we then investigated the preparation of 2-indenylidene complexes with a late transition metal. Only complex mixtures were obtained from bisphosphazene **1** and [$PdCl_2(cod)$] (cod = η^4-cycloocta-1,5-diene), whereas a clean reaction was observed with the related 1,3-bis(thiophosphinoyl)-indene **4**[14] (Scheme 3). After 10 days at room temperature, **4** was quantitatively converted into complex **6**. According to the two doublet signals observed at 55.9 and 52.2 ppm ($J_{PP} = 3.1$ Hz) in the ^{31}P NMR spectrum, both thiophosphinoyl groups are coordinated to the Pd atom [the ^{31}P NMR spectrum of compound

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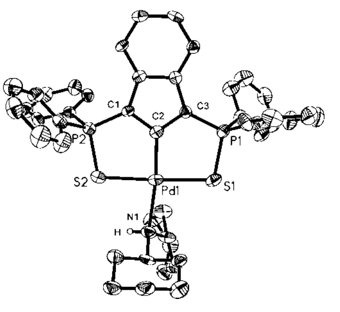
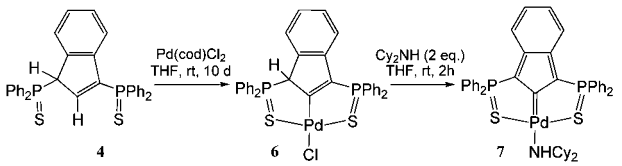


Figure 2. Molecular structure of complex **7**. Thermal ellipsoids are projected at the 50% probability level. Only one of two disordered positions of the Cy_2NH ligand is shown. Selected bonds distances (Å) and angles (deg): Pd1−C2, 1.984(5); Pd1−S1, 2.340(2); Pd1−S2, 2.336(2); Pd1−N1, 2.279(14); C2−Pd1−N1, 172.7(4); S1−Pd1−S2, 176.3(1).

Scheme 3



4 exhibits two doublets at 30.4 and 45.2 ppm (J_{PP} = 5.6 Hz)]. The C_q ^{13}C NMR multiplet signal at 182.0 ppm and the CH doublet of doublets signal at 72.8 ppm (J_{CP} = 53.9 and 18.1 Hz), which is associated with a doublet of doublets ^1H NMR signal at 5.46 ppm (J_{HP} = 24.9 and 2.7 Hz), indicate a Pd atom bonded to the indenyl C2 atom. This fact denotes the preferential activation of the C_{sp^2}−H bond of **4** rather than the C_{sp^3}−H bond.

Dehydrochlorination of **6** with 2 equiv of Cy_2NH (Cy = cyclohexyl)[15] readily afforded the amine complex **7**, which was isolated in 84% yield as an orange powder. The symmetric structure of **7** was substantiated by the single signal observed at 41.7 ppm in the ^{31}P NMR spectrum, and the 2-indenylidene structure of **7** was supported by the low-field triplet at 164.5 ppm (J_{CP} = 27.5 Hz) observed for C2 in the ^{13}C NMR spectrum. The molecular structure of complex **7** was definitely confirmed by X-ray crystallography (Figure 2). The Pd atom is surrounded by the two sulfur atoms, the nitrogen atom of Cy_2NH, and C2, which are organized in a quasi-ideal square planar arrangement. The C2−Pd bond length [1.984(5) Å] is very similar to those observed in the few reported Pd carbene complexes free of heteroatomic substituents at carbon (1.97−2.00 Å),[16] and the Pd−N bond distance [2.244(15) and 2.279(14) Å for the two disordered positions] is slightly longer than those reported recently in [LPd(Ar)X(H_2NR)] complexes (2.12−2.14 Å).[17] All of the carbon atoms C1, C2, and C3 remain planar. The planar environment around C2 in the 2-indenylidene complex **7** contrasts with the pyramidal geometry observed in the related methanediide complex {(Ph_3P)Pd[C(Ph_2PS)$_2$]}[18] and presumably results from π delocalization between C2 and C1/C3, in agreement with the short bond distances [1.418(7) and 1.425(7) Å].

Theoretical Study of the 2-Indenylidene Complexes. To shed some light on the bonding situation in complexes **3**, **5**, and **7**, density functional theory (DFT) calculations were carried out.[19] The key geometric features determined experimentally for the {[Ind($Ph_2P{=}NMes$)$_2$]Zr(NMe_2)$_2$} complex **3** were very well reproduced (with deviations of only 0.01 Å in the C2−Zr bond distance and 0.05 Å in the N−Zr ones), indicating the ability of the B3PW91/SDD(Zr, P),6-31G**(other atoms) method in describing such systems (Table 1). The geometry of the related {[Ind($Ph_2P{=}S$)$_2$]Zr(NMe_2)$_2$} complex **5** was optimized at the same level of theory (Figure 3). The zirconium center adopts a quasi-ideal trigonal bipyramidal environment, with C2 and the two NMe_2 groups lying in the equatorial plane and the two sulfur atoms occupying the axial positions. The C2−Zr bond does not deviate from the indenyl plane, and the C2−Zr bond distance (2.29 Å) is very similar to that predicted for **3** (2.23 Å). Thus, the phosphazene and thiophosphinoyl donor side arms induce rather similar geometries in the zirconium complexes **3** and **5**, with only minor distortions that presumably result from different steric shielding. The geometry of the corresponding palladium complex **7** was also very well reproduced at the B3PW91/SDD(Pd, P),6-31G**(other atoms) level of theory. In particular, the C2−Pd bond distance predicted theoretically (1.97 Å) is very close to that determined experimentally [1.984(5) Å]. In order to take into account the different sizes of the metals involved, the C2−M bond distances [*d*(C2−M)] were compared with the corresponding sums of covalent radii (R_{cov}).[20] Accordingly, the ratio $r = d(C2{-}M)/\sum R_{cov}$ falls in the range 0.90−0.93 for all of the complexes, suggesting similar bonding situations.

The atomic charges derived from natural bonding orbital (NBO) analyses[21] of complexes **3**, **5**, and **7** (Table 2) provide further insight into the influence of the donor side arm and the metal. The atomic charges on the indenyl backbone are very similar in the two zirconium complexes **3** and **5** (ca. −0.45 at C2 and −0.61 at C1/C3). The atomic charge at zirconium is positive in both complexes and higher with the phosphazene than with the thiophosphinoyl side arms (2.21 in **3** vs 1.65 in **5**), consistent with the higher electronegativity of nitrogen relative to sulfur (3.0 for N vs 2.5 for S). In the corresponding palladium complex, similar negative atomic charges were predicted at C1/C3 (−0.66). A small negative charge at C2 (−0.09) and a positive charge of 0.44 at palladium were found. Accordingly, the C2−Pd bond in **7** appears to be less polarized than the C2−Zr bonds in **3** and **5**, in agreement with the carbon−metal electronegativity differences ($\Delta\chi_{C-Pd} = 0.3$ vs $\Delta\chi_{C-Zr} = 1.1$).

The NBO analyses[21] also provide a more precise description of the nature of the C2−Zr and C2−Pd bonds. For the {[Ind($Ph_2P{=}NMes$)$_2$]Zr(NMe_2)$_2$} complex **3**, a strong σ donation from C2 to Zr (~140 kcal/mol) was found at the second-order donor−acceptor perturbation level. The σ interaction between C2 and Zr was found at the first-order level for the related {[Ind($Ph_2P{=}S$)$_2$]Zr(NMe_2)$_2$} complex **5** but remained highly polarized (80% C2/20% Zr), in agreement with the weaker but still significant atomic charge at Zr. For both complexes, no significant π interaction between C2 and Zr was

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[15] The corresponding ammonium salt was readily removed after precipitation with pentane, thereby facilitating the isolation of the Pd complex **7**.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3**, **5**, and **7**[a]

complex	method	X−M	C2−M	X−P	P−C	X−P−C	$\Sigma C1_\alpha$	$\Sigma C3_\alpha$	$\Sigma C2_\alpha$	C1−C2	C2−C3
3	X-ray	2.262(3) 2.286(4)	2.221(5)	1.644(4) 1.634(4)	1.740(5) 1.734(5)	103.3(2) 104.7(2)	360	360	356	1.405(6)	1.417(6)
	DFT	2.31 2.31	2.23	1.69 1.68	1.76 1.76	104 104	360	360	357	1.41	1.41
5	DFT	2.68 2.68	2.29	2.06 2.06	1.76 1.76	127 127	360	360	360	1.42	1.42
7	X-ray	2.3398(17) 2.3360(17)	1.984(5)	2.0297(19) 2.030(2)	1.719(6) 1.714(5)	105.13(19) 106.39(19)	359	360	360	1.418(7)	1.425(7)
	DFT	2.36 2.36	1.97	2.07 2.07	1.75 1.75	106 106	360	360	360	1.42	1.42

[a] For **3**, M = Zr and X = N; for **5**, M = Zr and X = S; for **7**, M = Pd and X = S. The DFT calculations were performed at the B3PW91/SDD(Zr, Pd, P),6-31G**(other atoms) level of theory.

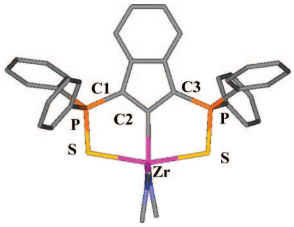


Figure 3. Structure of complex **5** optimized at the B3PW91/SDD(Zr, P),6-31G**(other atoms) level of theory. Hydrogen atoms have been omitted.

Table 2. NBO Atomic Charges for Complexes **3**, **5**, and **7**[a]

complex	M	C2	X	P	C1/C3
3	2.21	−0.47	−1.18	2.03	−0.61
5	1.65	−0.41	−0.54	1.62	−0.61
7	0.44	−0.09	−0.55	1.64	−0.66

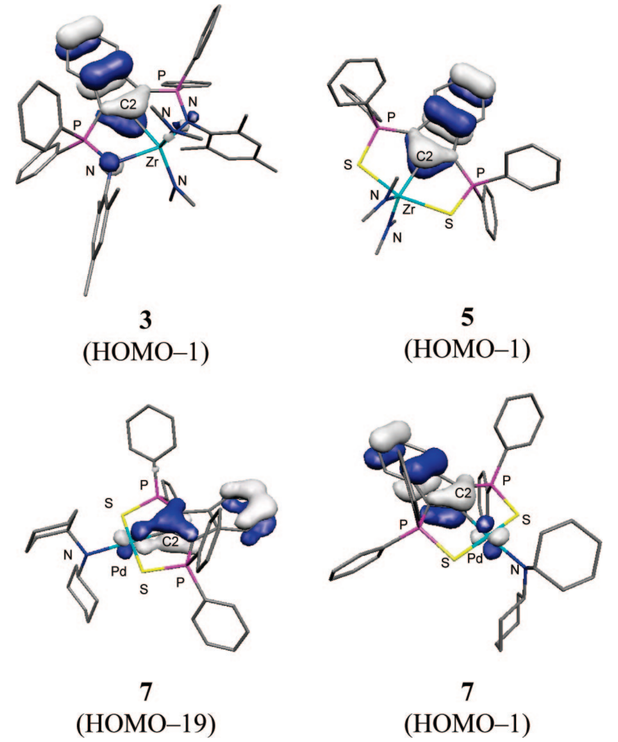
[a] For **3**, M = Zr and X = N; for **5**, M = Zr and X = S; for **7**, M = Pd and X = S.

Table 3. Wiberg Indices for Complexes **3**, **5**, and **7**

complex	M−C2	C2−C1/C3
3	0.57	1.34 1.34
5	0.63	1.34 1.34
7	0.66	1.35 1.35

identified. As expected, a highly covalent σ bond was found between C2 and Pd in the corresponding $\{[Ind(Ph_2P{=}S)_2]Pd(NHCy_2)\}$ complex **7** (53% C2/47% Pd), but in this case as well, no π interaction between C2 and Pd was found. Overall, the three complexes **3**, **5**, and **7** thus exhibit similar bonding situations, with strong σ bonding but weak (if any) π interactions between C2 and M. This is reminiscent of the bonding found in pincer complexes of type **III**.[22]

This bonding situation was further confirmed by computing Wiberg indices[23] (Table 3). The values found for the C2−M bonds in complexes **3**, **5**, and **7** (0.57−0.66) fall in the same range as those computed for the methanediide complexes $\{(Ph_3P)_2Ru[C(Ph_2P{=}S)_2]\}$ (0.67)[22b] and $\{(Me_3SiCH_2)(THF)Y[C(Ph_2P{=}NSiMe_3)_2]\}$ (0.606)[22d] and are consistent with essentially single bonds. In addition, bond orders of 1.34−1.35 were found between C2 and C1/C3, indicating some multiple-bond character.



3 (HOMO−1) **5** (HOMO−1)

7 (HOMO−19) **7** (HOMO−1)

Figure 4. Kohn−Sham representations of selected molecular orbitals for complexes **3**, **5**, and **7**.

The molecular orbitals of the zirconium complexes **3** and **5** confirmed the π interactions of C2 with C1 and C3 and the absence of π interactions between C2 and Zr. Indeed, the HOMO−1 orbitals (Figure 4) display π interactions between C2 and C1/C3, but no bonding molecular orbital displaying a π interaction between C2 and Zr was found. For the palladium complex **7**, the HOMO−19 and HOMO−1 orbitals both display π interactions between C2 and C1/C3, but they differ in the bonding versus antibonding π overlap between C2 and Pd (Figure 4). This is consistent with the essentially single-bond character of the C2−Pd bond.[24]

Lastly, atoms in molecules (AIM)[25] calculations show the presence of a bond critical point between C2 and M in all of

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(22) For theoretical studies of the bonding situation in pincer complexes of type **III**, see: (a) Smurnyy, Y.; Bibal, C.; Pink, M.; Caulton, K. G. *Organometallics* **2005**, *24*, 3849. (b) Cantat, T.; Demange, M.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Organometallics* **2005**, *24*, 4838. (c) Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676. (d) Liddle, S. T.; McMaster, J.; Green, J. C.; Arnold, P. L. *Chem. Commun.* **2008**, 1747, and refs 13c and 18.

(23) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(24) Similarly, two occupied molecular orbitals involving π and π* C−Pd interactions were found in the methanediide complex $\{(Ph_3P)Pd[C(Ph_2P{=}S)_2]\}$.[18]

(25) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

the complexes **3**, **5**, and **7**, with bond ellipticities (0.11 for **3**, 0.12 for **5**, and 0.04 for **7**) similar to that found by Caulton and co-workers[22a] in the ruthenium methanediide complex $\{(p\text{-cymene})Ru[C(Ph_2P{=}NPh)_2]\}$ (0.04) and consistent with essentially σ bonding.[26]

Conclusion

The first 2-indenylidene complexes were obtained from pincer-type ligands. Both phosphazene and thiophosphinoyl groups were shown to support 2-indenylidene coordination to zirconium. The two zirconium complexes **3** and **5** exhibit similar structures, indicating only a small, essentially steric influence of the donor side arms. In addition, the 1,3-bis(thiophosphinoyl)indene **4** provided access to the 2-indenylidene palladium complex **7**. DFT calculations, including NBO and AIM analyses, revealed similar bonding situations in these three complexes, with strong σ bonding but weak (if any) π interactions between C2 and M. Accordingly, the 2-indenylidene coordination in the zirconium and palladium complexes **5** and **7** differs only in the polarization of the C2−M σ bond. Current efforts aim at (*i*) further extending the variety of metal fragments and (*ii*) extrapolating the strategy to the preparation of fluorenylidene pincer complexes.[27]

Experimental Section

All of the reactions were performed using standard Schlenk techniques under an argon atmosphere. ^{31}P, ^{1}H, and ^{13}C spectra were recorded on Bruker Avance 300 or 400 and AMX500 spectrometers. ^{31}P, ^{1}H, and ^{13}C chemical shifts are expressed with a positive sign in parts per million relative to external 85% H_3PO_4 and Me_4Si. Unless otherwise stated, NMR was recorded at 293 K. THF, mesitylene, and toluene were dried under sodium and distilled prior to use. All of the organic reagents were obtained from commercial sources and used as received, except for dicyclohexylamine, which was distilled over KOH. [Pd(cod)Cl_2] and [Zr(NMe_2)$_4$] were purchased from Strem Chemicals, stocked in the dark in a glovebox and used without further purification. Mesityl azide,[28] 1,3-bis(diphenylphosphino)indene,[10] and 1,3-bis(diphenylthiophosphinoyl)indene **4**[14] were prepared according to literature procedures. The *N* values corresponding to $^{1}/_{2}(J_{AX} + J_{AX'})$ are provided when second-order AXX′ systems were observed in the ^{13}C NMR spectra.[29]

Synthesis of $IndH_2[Ph_2P{=}NMes]_2$ (1). A degassed solution of $MesN_3$ (1.045 g, 6.48 mmol) in toluene (5 mL) was added dropwise at 0 °C to a degassed suspension of [$IndH_2(PPh_2)_2$] (1.57 g, 3.24 mmol) in toluene (20 mL). After the mixture was stirred for 1 h at room temperature, 20 mL of pentane was added, and the reaction medium was then cooled at −20 °C overnight to favor complete precipitation of the product. The solvent was eliminated by filtration to yield a pale-yellow solid, which was washed with cold pentane (2 × 20 mL). Yield: 1.70 g (70%). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 300 K): δ 5 (very broad s). ^{1}H NMR (300.2 MHz, C_6D_6, 300 K): δ 7.72 (broad dd, $^{3}J_{HH} = 10.7$ Hz, $^{3}J_{HP} = 8.0$ Hz, 9H, H_{ortho}PhP and H_2Ind overlapped), 7.32 (m, 2H, $H_{5,8}$Ind), 7.02−6.95 (m, 14H, H_{para}PhP, H_{meta}PhP, and $H_{6,7}$Ind), 6.73 (s, 4H, H_{meta}Mes), 3.52 (broad s, 1H, N*H*), 2.15 (s, 6H, CH_{3para}Mes), 2.02 (s, 12H, CH_{3ortho}Mes). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 300 K): δ 140.0 (t, $^{2}J_{CP} = 14.4$ Hz, C_2Ind), 138.2 (pseudo-t, $^{2-3}J_{CP} = 14.8$ Hz, $C_{4,9}$Ind), 135.3 (C_{ipso}Mes), 132.9 (d, $^{2}J_{CP} = 10.0$ Hz, C_{ortho}PhP), 131.1 (C_{para}PhP), 129.1 (C_{meta}Mes), 128.0 (d, $^{2}J_{CP} = 12.6$ Hz, C_{meta}PhP), 119.9 ($C_{5,8}$Ind), 119.2 ($C_{6,7}$Ind), 20.6 (CH_{3para}Mes), 20.5 (CH_{3ortho}Mes), $C_{1,3}$ not observed. Mp: 119−220 °C. Anal. Calcd for $C_{51}H_{48}N_2P_2$: C, 81.58; H, 6.44; N, 3.73. Found: C, 81.84; H, 6.69; N, 3.36.

Synthesis of $Zr(NMe_2)_3[IndH(Ph_2P{=}NMes)_2]$ (2). A mixture of **1** (746 mg, 0.99 mmol) and [Zr(NMe_2)$_4$] (267 mg, 1.00 mmol) in toluene (4 mL) was stirred at room temperature for 5 min. ^{31}P NMR spectroscopy revealed quantitative conversion of **1** into complex **2**, which was obtained as a pale-green powder after removal of the volatiles. Compound **2** was characterized by NMR spectroscopy and employed in the next reaction without further purification. $^{31}P\{^{1}H\}$ NMR (202.3 MHz, C_6D_6): δ 40.2 (s, coordinated P=NMes), −14.8 (s, free P=NMes). ^{1}H NMR (500.3 MHz, C_6D_6): δ 8.10 (m, 1H, H_2), 7.95−7.90 (m, 4H, H_{ortho}PhP), 7.89 (d, $^{3}J_{HH} = 7.8$ Hz, 1H, H_8), 7.25−7.20 (m, 4H, H_{ortho}PhP), 7.14−7.00 (m, 6H, H_{meta}PhP), 7.00−6.90 (m, 10H, *H*Mes, H_{meta}PhP, H_{para}PhP, H_7), 6.87 (m, 1H, H_6), 6.68 (s, 2H, *H*Mes), 6.50 (d, $^{3}J_{HH} = 8.1$ Hz, 1H, H_5), 2.67 (s, 18H, NMe_2), 2.27 (d, $^{3}J_{HP} = 2.7$ Hz, 3H, CH_{3para}Mes), 2.19 (d, $^{3}J_{HP} = 1.5$ Hz, 6H, CH_{3ortho}Mes), 2.09 (d, $^{3}J_{HP} = 2.1$ Hz, 3H, CH_{3para}Mes), 1.94 (s br, 6H, CH_{3ortho}Mes). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ 146.0 (C_{ipso}Mes), 140.7 (m, C_3), 139.7 (C_{ipso}Mes), 139.0 (m, C_2), 136.6 (C_qMes), 135.8 (d, $^{1}J_{CP} = 92.6$ Hz, C_{ipso}PhP), 134.0 (C_qMes), 132.6 (d, $^{2}J_{CP} = 10.0$ Hz, C_{ortho}PhP), 132.3 (d, $^{2}J_{CP} = 9.5$ Hz, C_{ortho}PhP), 132.0 (C_{para}PhP), 130.0 (C_{para}PhP), 129.8 (d, $^{3}J_{CP} = 3.0$ Hz, *C*HMes), 128.6 (d, $^{3}J_{CP} = 3.0$ Hz, *C*HMes), 128.4 (d, $^{3}J_{CP} = 9.5$ Hz, C_{meta}PhP), 127.8 (overlapped with C_6D_6, C_{meta}PhP), 122.7 (C_8), 120.7 (br, C_6, C_7), 119.5 (C_5), 74.3 (d, $^{3}J_{CP} = 67.3$ Hz, C_1), 42.3 (NMe_2), 21.1 (br, CH_{3ortho}Mes), 21.0 (br, CH_{3para}Mes), $C_{4,9}$ not observed.

Synthesis of $Zr(NMe_2)_2[Ind(Ph_2P{=}NMes)_2]$ (3). A solution of **2** (880 mg, 0.9 mmol) in mesitylene (4 mL) was heated overnight at 120 °C. ^{31}P NMR spectroscopy revealed quantitative conversion of complex **2** into complex **3**, which was obtained as a pale-green powder after removal of the volatiles. Slow diffusion of pentane in a mesitylene solution of **3** at 0 °C afforded crystals of **3** suitable for X-ray diffraction analysis (151 mg, 18% yield, as a result of the high solubility of **3**). $^{31}P\{^{1}H\}$ NMR (202.3 MHz, C_6D_6): δ 30.1. $^{1}H\{^{31}P\}$ NMR (500.3 MHz, C_6D_6): δ 7.90 (d, $^{3}J_{HH} = 7.5$ Hz, $^{3}J_{HP} = 12.0$ Hz, 8H, H_{ortho}PhP), 7.62 (m, 2H, $H_{5,8}$), 7.26 (m, 2H, $H_{6,7}$), 6.96 (t, $^{3}J_{HH} = 7.5$ Hz, 4H, H_{para}PhP), 6.89 (t, $^{3}J_{HH} = 7.5$ Hz, 8H, H_{meta}PhP), 6.77 (s, 4H, H_{meta}Mes), 2.56 (s, 12H, NMe_2), 2.26 (s, 6H, CH_{3para}Mes), 2.07 (s, 12H, CH_{3ortho}Mes). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ 209.0 (t, $^{2}J_{CP} = 32.7$ Hz, C_2), 142.9 (d, $^{2}J_{CP} = 6.3$ Hz, C_{ipso}Mes), 139.0 (AXX′, $N = 18.9$ Hz, $C_{4,9}$), 136.9 (d, $^{3}J_{CP} = 5.0$ Hz, C_{ortho}Mes), 134.2 (d, $^{1}J_{CP} = 86.8$ Hz, C_{ipso}Ph), 133.2 (d, $^{2}J_{CP} = 10.1$ Hz, C_{ortho}Ph), 131.9 (d, $^{5}J_{CP} = 3.8$ Hz, C_{para}Mes), 129.1 (C_{meta}Mes), 128.2 (C_{para}PhP), 127.9 (C_{meta}PhP), 119.9 ($C_{5,8}$), 119.6 ($C_{6,7}$), 99.7 (AXX′, $N = 86.2$ Hz, $C_{1,3}$), 41.1 (NMe_2), 20.7 (CH_{3para}Mes), 20.1 (CH_{3ortho}Mes). Mp: 138−140 °C.

Synthesis of $Zr(NMe_2)_2[Ind(Ph_2P{=}S)_2]$ (5). A solution of **4** (110 mg, 0.2 mmol) in toluene (10 mL) was added dropwise to a solution of [Zr(NMe_2)$_4$] (54 mg, 0.2 mmol) in pentane (10 mL) at −10 °C. The solution slowly became yellow, and a white precipitate appeared. After 3 h, the supernatant was removed by filtration. The yellow-white powder was washed three times with 10 mL of pentane and then thermolyzed for 5 h at 100 °C in benzene-d_6 (6 mL). The Schlenk line was continuously evacuated to remove the free amine (Me_2NH). The yellow solution was cooled to room temperature and filtered. NMR analysis was carried out without further purification. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): δ 40.0. ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.98 (dd, $^{3}J_{HH} = 7.0$ Hz, $^{3}J_{HP} = 13.4$ Hz, 8H, H_{ortho}PhP), 7.45 (m, 2H, $H_{5,8}$), 7.08 (m, 2H, $H_{6,7}$), 6.94−6.90 (m, 12H, H_{meta}PhP, H_{para}PhP), 3.02 (s, 12H, NMe_2). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6): δ 206.3 (t, $^{2}J_{CP} = 44.5$ Hz, C_2),

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(26) The cylindrical symmetry of σ bonds typically leads to ellipticities near zero.

(27) An unsupported fluorenylidene ruthenium complex has recently been prepared from the corresponding diazofluorene complex. See: Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2008**, *27*, 3526.

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139.3 (AXX′, $N = 18.3$ Hz, $C_{4,9}$), 134.3 (d, $^1J_{CP} = 82.5$ Hz, C_{ipso}Ph), 132.5 (d, $^3J_{CP} = 11.6$ Hz, C_{meta}Ph), 131.4 (br s, C_{para}Ph), 128.6 (d, $^2J_{CP} = 12.7$ Hz, C_{ortho}PhP), 119.6 (s, $C_{5,8}$), 119.3 (s, $C_{6,7}$), 99.7 (AXX′, $N = 72.8$ Hz, $C_{1,3}$), 39.6 (s, NMe_2).

Synthesis of PdCl[IndH($Ph_2P{=}S$)$_2$] (6). A suspension of [$PdCl_2$(cod)] (210 mg, 0.73 mmol) and **4** (400 mg, 0.73 mg) in 40 mL of THF was stirred for 10 days at room temperature. Addition of 40 mL of pentane induced the precipitation of a yellow solid. After filtration, the solid was washed with 3 × 20 mL of pentane and dried under vacuum to yield a pale-yellow solid. Yield: 480 mg (95%). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2): δ 55.9 (d, $^3J_{PP} = 3.1$ Hz), 52.2 (d, $^3J_{PP} = 3.1$ Hz). ^1H NMR (500.3 MHz, CD_2Cl_2): δ 7.95 (m, 2H, H_{ortho}PhP), 7.85−7.75 (m, 3H, H_{ortho}PhP, H_{para}PhP), 7.70 (m, 2H, H_{meta}PhP), 7.65 (m, 2H, H_{para}PhP), 7.60−7.50 (m, 6H, *H*PhP), 7.40 (m, 2H, H_{meta}PhP), 7.30 (m, 2H, H_{ortho}PhP), 7.23 (m, 2H, H_{para}PhP, H_5), 7.14 (m, 1H, H_7), 7.09 (m, 1H, H_6), 6.57 (d, $^3J_{HH} = 7.5$ Hz, 1H, H_8), 5.46 (dd, $^2J_{PH} = 24.9$ Hz, $^3J_{PH} = 2.7$ Hz, 1H, H_1). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 182.0 (m, C_2), 145.6 (dd, $^2J_{CP} = 18.2$ Hz, $^3J_{CP} = 3.9$ Hz, C_9), 139.8 (dd, $^2J_{CP} = 9.1$ Hz, $^3J_{CP} = 2.9$ Hz, C_4), 134.0 (d, $^4J_{CP} = 3.1$ Hz, C_{para}PhP), 133.3 (d, $^4J_{CP} = 3.1$ Hz, C_{para}PhP), 133.2 (d, $^4J_{CP} = 3.1$ Hz, C_{para}PhP), 133.2 (d, $^3J_{CP} = 9.6$ Hz, C_{meta}PhP), 132.7 (d, $^4J_{CP} = 3.1$ Hz, C_{para}PhP), 132.4 (d, $^3J_{CP} = 11.5$ Hz, C_{meta}PhP), 132.1 (d, $^3J_{CP} = 10.8$ Hz, C_{meta}PhP), 131.6 (d, $^3J_{CP} = 11.5$ Hz, C_{meta}PhP), 129.8 (d, $^2J_{CP} = 12.5$ Hz, C_{ortho}PhP), 129.2 (d, $^2J_{CP} = 13.0$ Hz, C_{ortho}PhP), 129.2 (d, $^2J_{CP} = 12.6$ Hz, C_{ortho}PhP), 128.6 (d, $^3J_{CP} = 1.6$ Hz, C_7), 128.2 (d, $^2J_{CP} = 12.8$ Hz, C_{ortho}PhP), 127.4 (d, $^1J_{CP} = 80.5$ Hz, C_{ipso}PhP), 126.4 (d, $^1J_{CP} = 76.1$ Hz, C_{ipso}PhP), 124.3 (s, C_6), 123.3 (s, C_5), 121.7 (d, $^1J_{CP} = 81.4$ Hz, C_3), 118.6 (s, C_8), 72.8 (dd, $^1J_{CP} = 53.9$ Hz, $^3J_{CP} = 18.1$ Hz, C_1). MS (EI 78 eV) *m*/*z*: 483 $[M]^+$, 318 $[M - Flu]^+$, 240 $[M - Flu - Ph]^+$, 165 $[Flu]^+$. Mp: 182 °C (dec). Anal. Calcd for $C_{33}H_{25}ClP_2PdS_2$: C, 57.48; H, 3.65. Found: C, 56.99; H, 3.52.

Synthesis of Complex Pd($NHCy_2$)[Ind($Ph_2P{=}S$)$_2$] (7). Distilled Cy_2NH (55 μL, 0.143 mmol, 2 equiv) was added at room temperature to a solution of **6** (52 mg, 0.071 mmol) in 25 mL of THF. After the mixture was stirred for 2 h at room temperature, 40 mL of pentane was added in order to precipitate the ammonium salts. After filtration, the solvent was removed under vacuum to yield an orange solid. Yield: 50 mg (84%). Single crystals of **7** were grown from a THF solution at 20 °C. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ 41.7 (s). ^1H NMR (500.3 MHz, THF-d_6): δ 7.90 (dd, $^3J_{HH} = 13.0$ Hz, $^3J_{PH} = 8.0$ Hz, 8H, H_{ortho}PhP), 7.51 (dt, $^3J_{HH} = 6.0$ Hz, $^5J_{PH} = 1.5$ Hz, 4H, H_{para}PhP), 7.45 (dt, $^3J_{HH} = 7.5$ Hz, $^4J_{PH} = 2.0$ Hz, 8H, H_{meta}PhP), 7.06−7.04 (m, 2H, $H_{6,7}$), 6.62 (dd, $^3J_{HH} = 6.0$ Hz, $^3J_{HH} = 3.0$ Hz, 2H, $H_{5,8}$), 2.95−2.91 (m, 2H, NC*H*), 2.3−2.60 (m, 3H, N*H* and CH_2), 2.00 (d, $^3J_{HH} = 12.0$ Hz, 2H, CH_2), 1.88−1.66 (m, 8H, 4CH_2), 1.39−1.18 (m, 8H, 4CH_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 164.5 (t, $^3J_{CP} = 27.5$ Hz, C_2), 137.5 (AXX′, $N = 16.0$ Hz, $C_{4,9}$), 133.9 (d, $^1J_{CP} = 82.3$ Hz, C_{ipso}PhP), 131.9 (C_{meta}PhP), 128.2 (C_{para}PhP), 128.1 (C_{orto}PhP), 127.9 (C_{para}PhP), 129.2 (d, $^1J_{CP} = 92.1$ Hz, C_{ipso}PhP), 128.7 (d, $^4J_{CP} = 2.3$ Hz, C_{meta}PhP), 127.5 (d, $^3J_{CP} = 10.6$ Hz, C_{ortho}PhP), 127.2 ($C_{5,8}$), 115.7 ($C_{6,7}$), 104.7 (AXX′, $N = 74.2$ Hz, $C_{1,3}$), 52.9 (*C*HN), 33.5 (*C*H_2), 32.9 (*C*H_2), 26.2 (*C*H_2), 26.0 (*C*H_2). Mp: 202 °C (dec). Anal. Calcd for $C_{45}H_{47}NP_2PdS_2$: C, 64.78; H, 5.68. Found: C, 64.23; H, 5.34.

Crystal Structure Determinations for Complexes 2, 3, and 7. Data for each structure (Table 4) were collected at 193(2) K using an oil-coated shock-cooled crystal on a Bruker AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.7103 Å). Semiempirical absorption corrections were employed.[30] The structures were solved by direct methods (SHELXS-97)[31] and refined using the least-squares method on F^2.[32]

Table 4. Crystallographic Data for Complexes **2**, **3**, and **7**

	2	**3**	**7**
empirical formula	$C_{59}H_{69}Cl_4N_5P_2Zr$	$C_{55}H_{58}N_4P_2Zr$	$C_{47}H_{51}NO_{0.5}P_2PdS_2$
formula weight	1143.15	928.21	870.35
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	10.0482(10)	12.8825(14)	11.3074(4)
b (Å)	14.0223(14)	23.109(2)	14.8453(5)
c (Å)	21.011(2)	17.1419(18)	25.2573(7)
α (deg)	94.687(2)	90	90
β (deg)	103.329(2)	110.034(2)	90.580(2)
γ (deg)	91.388(2)	90	90
V (Å^3)	2868.2(5)	4794.3(9)	4239.5(2)
Z	2	4	4
D_{calcd} (Mg/m^3)	1.324	1.286	1.364
abs coeff (mm^{-1})	0.476	0.337	0.647
reflns collected	19734	26697	42235
independent reflns	9549	6171	7158
R1 [$I > 2\sigma(I)$]	0.0465	0.0452	0.0485
wR2	0.1014	0.0710	0.1069
$(\Delta/r)_{max}$ (e/Å^3)	0.590/−0.424	0.463/−0.310	0.508/−0.786

Computational Details. Zirconium, palladium, and phosphorus atoms were treated with Stuttgart−Dresden pseudopotentials in combination with their adapted basis sets.[33,34] In all cases, the basis set was augmented by a set of polarization functions (f for Zr and Pd, d for P).[35] Carbon, sulfur, nitrogen, and hydrogen atoms were described with a 6-31G(d,p) double-ζ basis set.[36] Calculations were carried out using DFT with the hybrid functional B3PW91.[37,38] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the extrema (minima) was verified with analytical frequency calculations. All of these computations were performed with the Gaussian 98 suite of programs.[39] The electronic density was analyzed using the NBO technique.[21]

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Supporting Information Available: Computational data for complexes **3**, **5**, and **7**; complete ref 39; and crystallographic data for complexes **2**, **3**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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