Synthesis, Structure, and Reactivity of η^2-Phosphabenzyne−Zirconocene Dimers

Patrick Rosa, Pascal Le Floch, Louis Ricard, and François Mathey*

Contribution from the Laboratoire "Hétéroéléments et Coordination", URA CNRS 1499, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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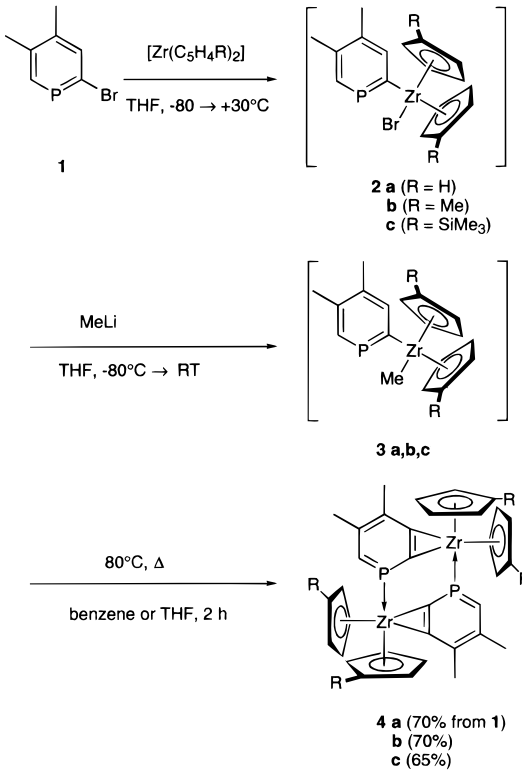
Abstract: The extrusion of methane from (2-phosphininyl)(methyl) zirconocenes **3a**−**c** at 80 °C in benzene affords the corresponding η^2-phosphabenzyne−zirconocene dimers **4a**−**c**, one of which has been characterized by X-ray crystal structure analysis. The parameters of the C−C−Zr three-membered ring are exactly similar to those found in the η^2-benzyne−zirconocene complex: C−C, 1.361(2); C−Zr, 2.238 and 2.250(2) Å. The P−Zr distances are normal at 2.6857(5) and 2.6922(5) Å. The reaction of these η^2-phosphabenzyne complexes with acetonitrile, $Ph_3P{=}S$, (diphenylphosphino)- and (trimethylsilyl)alkynes, aldehydes, and (+)-camphor have been investigated. In all cases, an insertion into the C_2−Zr bond is observed. Hydrolysis of the intermediate zirconacycles thus obtained yielded several new 2-functional phosphinines, including a thiol **(6)**, a vinylphosphine **(8)**, two secondary alcohols **(14** and **15),** and an homochiral phosphinine-substituted alcohol **(17)**. The regiospecificity of the insertion is ascribed to the huge concentration of negative charge at the α-position of the phosphinine ring.

Introduction

Heteroarynes are unstable intermediates which have found numerous uses in organic synthesis,[1] but whose characterization has remained difficult.[2] Their stabilization as metal complexes is thus an attractive goal. For some time now, Erker, Buchwald, and others have developed the chemistry of η^2-benzyne−zirconium complexes.[3] These reactive species are stable enough for structural characterization by X-ray analysis.[4] It was thus tempting to transpose this approach to heteroarynes. Unfortunately, an insertion of zirconocene into the carbon−heteroatom bond was observed with furan and thiophene instead of C≡C bond complexation.[5] In contrast, more recently, we have been able to synthesize a η^2-phosphabenzyne−zirconocene which is stable enough for in situ characterization by NMR spectroscopy.[6] Hereafter, we build on this preliminary result and describe the successful characterization of more stable η^2-phosphabenzyne−zirconocene dimers and several features of their reactivity.

Results and Discussion

Bromozirconium(IV) complexes **2** resulting from the insertion of zirconocene into the C−Br bond of 2-bromophosphinines are suitable precursors for the preparation of η^2-phosphabenzyne−zirconocene complexes.[7] By following a similar methodology as that developed for benzyne complexes, methylation at zirconium followed by a thermolysis of the resulting Zr−Me complexes turns out to be the best approach to the corresponding η^2-(2,3-didehydrophosphinine) complexes (eq 1).



(1)

All of this sequence can be carried out using a one-pot procedure since complexes **2** and **3**, which are very sensitive toward moisture, need not be isolated. Whereas monomeric species are formed when the extrusion of methane is carried out in the presence of trimethylphosphine,[6] dimeric species are obtained

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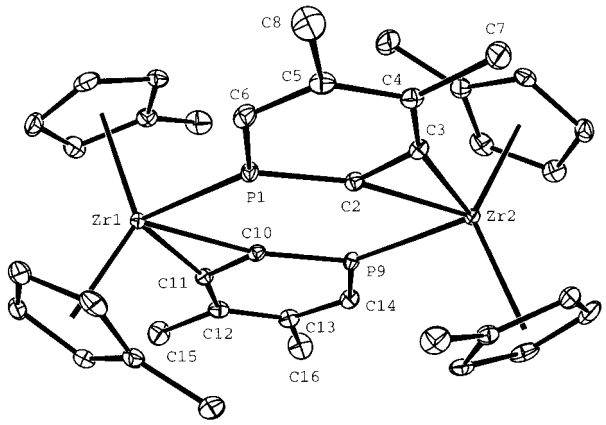


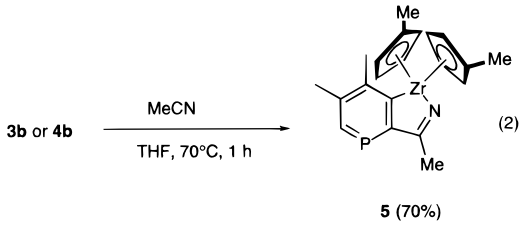
Figure 1. ORTEP drawing of one molecule of **4b**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Zr(1)−P(1), 2.6922(5); Zr(2)−P(9), 2.6857(5); Zr(2)−C(2), 2.238(2); Zr(2)−C(3), 2.250(2); P(1)−C(2), 1.696(2); P(1)−C(6), 1.729(2); C(2)−C(3), 1.361(2); C(3)−C(4), 1.404(2); C(4)−C(5), 1.414(3); C(5)−C(6), 1.405(3). Selected bond angles (deg): P(1)−Zr(1)−C(10), 70.95(4); Zr(1)−P(1)−C(2), 125.31(6); Zr(1)−P(1)−C(6), 133.07(7); Zr(2)−C(2)−C(3), 72.8(1); Zr(2)−C(3)−C(2), 71.9(1); Zr(2)−C(2)−P(1), 163.1(1); Zr(2)−C(3)−C(4), 160.0(1); C(2)−P(1)−C(6), 101.59(9); P(1)−C(2)−C(3), 124.0(1); C(2)−C(3)−C(4), 127.1(2); C(3)−C(4)−C(5), 119.5(2); C(4)−C(5)−C(6), 122.4(2); P(1)−C(6)−(C5), 125.2(1).

in the absence of phosphine. The dimer **4a** derived from [Zr(C_5H_5)$_2$] and 2-bromo-4,5-dimethylphosphinine (**1**) proved to be stable but only poorly soluble in inert organic solvents. To get satisfactory crystals for X-ray analysis, we duplicated the same synthesis with 1,1′-dimethyl- and 1,1′-bis(trimethylsilyl)-zirconocenes (eq 1).

Due to its poor solubility, dimer **4a** was only characterized by ^{1}H and ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis. The characterization of the dimethyl- and bis(trimethylsilyl) derivatives **4b,c** also included their ^{13}C NMR spectra as a result of their higher solubility. The most interesting features of these ^{13}C spectra concern the strongly deshielded C_2 and C_3 resonances of the phosphinine ring. For **4b** (in $CDCl_3$) as an example, the C_2 resonance appears as a pseudo-triplet at 184.75, $\sum J$(C−P) = 86.0 Hz, whereas C_3 is found at 186.20, $\sum J$(C−P) = 47.20 Hz. These values can be compared with that of C_6, δ 155.40, $\sum J$(C−P) = 39.85 Hz, which appears in the normal range for any phosphinine derivative. Another interesting comparison can be drawn with the resonances of the benzyne carbons in [Zr(η^2-C_6H_4)(η^5-C_5H_5)$_2$(PMe_3)] which appear at δ 174.30.[4]

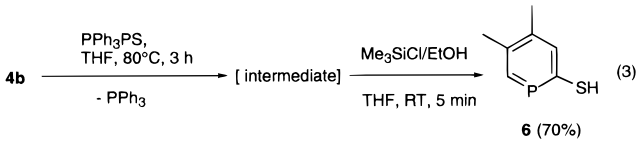
An ORTEP view of **4b** is presented in Figure 1. The geometry of the ZrC(2)C(3) metallacycle in **4b** is remarkably similar to that of the η^2-benzyne−zirconocene complex. The opening of the C−Zr−C angles are quite similar at 35.29(6) and 35.33(6)°, respectively. The Zr−C bonds are found at 2.238(2) and 2.250(2) Å in **4b** vs 2.228(5) and 2.267(5) Å in the benzyne complex. Obviously, the inclusion of phosphorus in the six-membered ring does not disturb the coordination sphere of zirconium. Even the Zr−P distances fall in the same range: Zr−phosphinine 2.6857(5) and 2.6922(5) Å vs 2.687(3) Å for Zr−PMe_3, although phosphinine is known to be a much weaker donor than trimethylphosphine. More severe distortions are seen when comparing the structure of **4b** with that of a σ-precursor such as **2a** (Br replaced by Cl).[7] The C_2−C_3 bond is shortened from 1.395(6) Å in **2a** to 1.361(2) Å in **4b**. Whereas the P−C(6) bond remains unchanged at 1.729(2) Å, the P−C(2) distance decreases in **4b** at 1.696(2) Å. Otherwise, the structure of the phosphinine ring is not significantly perturbed.

The chemistry of these η^2-phosphabenzyne complexes was studied either with dimer **4b** or with freshly prepared THF solutions of precursors **3a,b** (see Experimental Section). A first interesting remark concerns the reaction of dimers with PMe_3. Even under forcing conditions (excess of PMe_3 in boiling THF or benzene), the dimeric structure of **4b** is not destroyed and formation of the PMe_3-complexed monomer is never observed, thus confirming that the phosphinine P−Zr bonds are strong. More useful results were obtained with polar molecules. Two new reactions were first investigated. Both **3b** and **4b** easily react with acetonitrile to give selectively an insertion product into the C_2−Zr bond (eq 2).



Complex **5** has been identified by a combination of NMR experiments, mass spectrometry, and elemental analysis. The regiospecificity of the insertion was easily demonstrated upon inspection of the ^{13}C NMR spectrum of **5** which displays a characteristic C═N resonance at 191.45 with a huge ^2J(C−P) coupling constant at 40.55 Hz. Unfortunately, attempted hydrolysis of **5** to obtain the 2-acetyl derivative has failed so far.

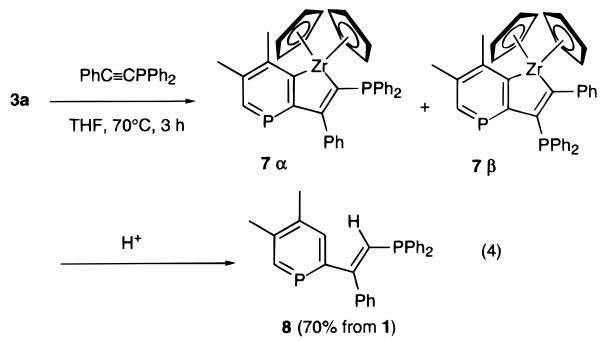
A selective cleavage of the C_2−Zr bond was also observed when using triphenylphosphine sulfide as a sulfur donor. Dimer **4b** readily reacts with Ph_3P═S in THF at 80 °C to give a poorly soluble intermediate which was only characterized by ^{31}P NMR (δ = 185.35 (THF) with ^2J(P−H) = 39.45 Hz) and free triphenylphosphine. Upon hydrolysis with HCl, the original and interesting thiol **6** is formed (eq 3).



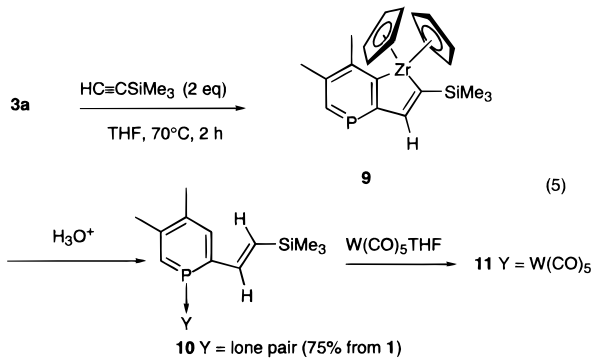
The ^{1}H NMR spectrum of **6** shows one α− and one β-H resonances, thus establishing the insertion of sulfur into the C_2−Zr bond of **4b**. In $CDCl_3$, the SH group appears as a doublet at 4.04 with a ^3J(H−P) coupling of 8.90 Hz, implying that the proton exchange is slow on the NMR time scale.

In our previous report,[6] we presented several examples of reactions of our η^2- phosphabenzyne−PMe_3 complex with alkynes and ketones. Insertion into the C_2−Zr bond was always observed with formation of five-membered zirconacycles. Hereafter, we describe several additional examples of such reactions. In very recent reports, Majoral et al. showed that the insertion of phosphinoalkyne[8a] and vinylphosphine[8b] into the reactive C−Zr bonds of η^2-benzyne−zirconocene exclusively gives the regioisomer where the phosphino substituent is located on the α-position of the five-membered zirconacycle, probably as a result of an initial interaction between phosphorus and zirconium. The reaction of phenethynyldiphenylphosphine with **3a** affords two insertion complexes **7**α and **7**β in a 95:5 ratio (eq 4).

(8) (a) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P.; Dupuis, L.; Pirio, N.; Meunier, P. *J. Chem. Soc., Chem. Commun.* **1997**, 279. (b) Zablocka, M.; Cénac, N.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Skowronska, A.; Meunier, P. *Organometallics* **1996**, *15*, 5436.

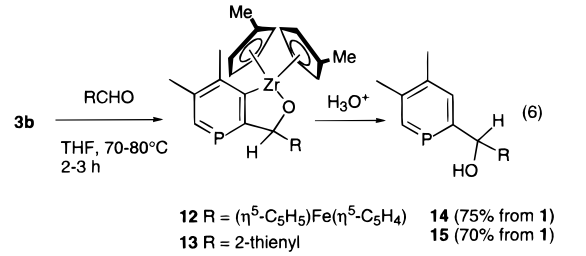


Both the major and minor isomers **7**α and **7**β were characterized by their ^{31}P NMR spectrum. **7α**: δ ^{31}P + 200.45 and −19.95 (THF), ^4J(P−P) = 12.70 Hz. **7**β: δ ^{31}P + 202.10 and −8.25 (THF), ^3J(P−P) = 96.50 Hz. The magnitude of the J(P−P) constant strongly suggests that the regiochemistry of the insertion is identical in **7**α to that observed with η^2-benzyne−zirconocene complex. Upon hydrolysis, only the phosphinine **8** derived from **7**α could be detected. Two significant NMR data confirm the structure of **8**. First, only one α-H (H_6) resonance is observed in the ^{1}H NMR spectrum, thus showing the initial insertion of the alkyne into the C_2−Zr bond. Second, in the ^{31}P NMR spectrum, the absence of J(P−P) coupling confirms that the carbon bearing the diphenylphosphino group was initially bound to the metal. A clear-cut result was also observed with another polar alkyne such as (trimethylsilyl)-acetylene (eq 5).



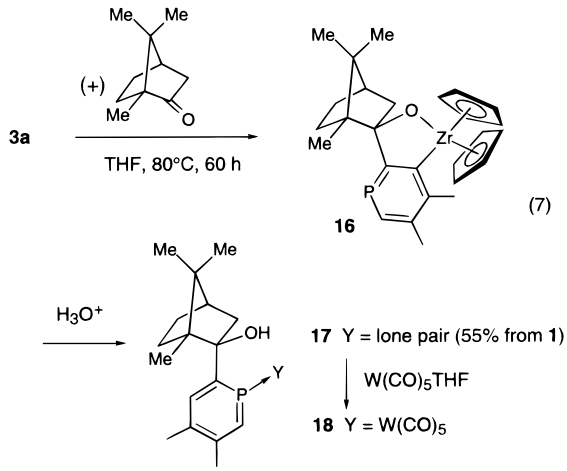
The insertion takes place into the C_2−Zr bond as usual, and the trimethylsilyl group is located on the α-carbon of the resulting five-membered ring as observed for the insertion product of η^2-benzyne−zirconocene complex.[3b] This regiochemistry is unambigously established by the vinyl H resonance in **9** which appears at 7.64, ^3J(H−P) = 8.85 Hz, in the ^{1}H NMR spectrum and by the corresponding ^{13}C resonance at 136.85 which exhibits a strong ^2J(C−P) coupling of 49.10 Hz. Phosphinine **9** which is slightly oxygen-sensitive was also characterized as its P−$W(CO)_5$ complex.

In our previous report, we did not investigate the reactivity of η^2-phosphabenzyne−zirconocene−(PMe_3) complexes toward aldehydes. As expected, the insertion selectively takes place into the C_2−Zr bond (eq 6).



Both hydrolysis products **14** and **15** display characteristic CH−O resonances in their ^{13}C spectra ($CDCl_3$). **14**: δ(CH) 74.55, ^2J(C−P) = 35.55 Hz. **15**: δ(CH) 75.15, ^2J(C−P) = 32.20 Hz. The magnitude of these J(C−P) coupling and the presence of one α-H (H_6) resonance in each ^{1}H spectrum unambiguously demonstrate the α-substitution.

In a very recent report, Breit underlined the potential use of phosphinines as ligands in homogeneous catalysis.[9] In such a context, the synthesis of homochiral phosphinines for enantioselective catalysis becomes a very attractive challenge. As an outcome of the chemistry of η^2-phosphabenzyne−zirconocenes, we can propose a simple access to one type of such molecules. The reaction of (+)-camphor with **3a** which proceeds very slowly, probably as a result of an important steric crowding during the formation of the intermediate metallacycle **16**, gives a single diastereomer in 55% overall yield after hydrolysis (eq 7).



The structure of **17** was ascertained by X-ray crystal structure analysis of its P−$W(CO)_5$ complex **18**. An ORTEP view of **18** is presented in Figure 2. The latter indicates that the phosphinine ring was selectively grafted onto the endo position of the norbornane skeleton giving enantiomerically pure **17**. This result can be easily rationalized in terms of stericity if one acknowledges that the formation of the other possible diastereomer of **16** is strongly disfavored because of important steric hindrance between the phosphinine and the two methyl groups of the bridge.

As a general conclusion of this study, it can be confidently stated that the chemistry of η^2-phosphabenzyne−zirconocene complexes closely mimics that of its η^2-benzyne counterpart. The only question which remains to be addressed concerns the extraordinary regiospecificity of the insertion reactions into the C_2−Zr bond. If we take the insertion of alkynes as a model reaction, we can acknowledge as usual that the first step of the mechanism is the formation of an η^2-alkyne−zirconium complex. The second step can be viewed as an intramolecular nucleophilic attack of C_2 (or C_3) onto the coordinated alkyne.

It can be argued that steric effects may be at the origin of this regiochemical preference if we consider that the presence of the methyl group at the C_4 position will disfavor the insertion of the alkyne into the C_3−Zr bond by hindering its approach to zirconium. Similar effects have been been reported by Büchwald et al. during their studies on substituted benzyne complexes.[13] Although probably non-negligible, we feel that this

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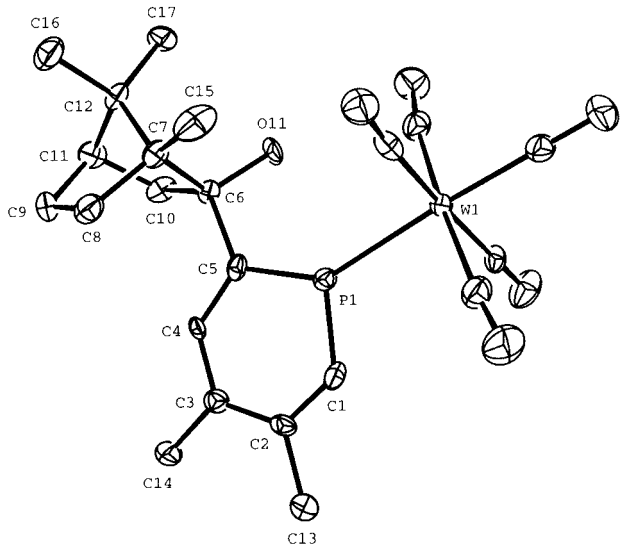

Figure 2. ORTEP drawing of one molecule of **18**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignment of the ^{13}C spectra. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): W(1)−P(1), 2.525(2); P(1)−C(1), 1.740(5); C(1)−C(2), 1.383(7); C(2)−C(3), 1.40(1); C(3)−C(4), 1.387(8); C(4)−C(5), 1.412-(7); C(5)−P(1), 1.743(6); C(5)−C(6), 1.544(8). Bond angles (deg): C(1)−P(1)−C(5), 102.8(3); P(1)−(C1)−C(2), 126.4(5); C(1)−C(2)−C(3), 121.7(5); C(2)−C(3)−C(4), 121.1(5); C(3)−C(4)−C(5), 129.1-(6); C(4)−C(5)−P(1), 118.8(5); C(1)−P(1)−W(1), 115.3(2); C(5)−P(1)−W(1), 141.8(2).

effect is not decisive and it is clear that electronic effects must also be taken into accounts. Indeed, it is well established that the HOMO of phosphinines is mainly localized at P, C_α (C_2) and C_γ (C_4). Besides, it appears that there is a much larger concentration of negative charge at C_α than C_β (C_3): C_α, −0.54; C_β, −0.22.[10] Significantly, as shown in the structure of dimer **4b**, the positively charged zirconium is closer to C_2 than to C_3. Thus we can safely concede that C_2 is more nucleophilic than C_3 in **4** and that the selective insertion into C_2−Zr bond is fully rational.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, ether, benzene, toluene, hexane, and pentane were obtained by distillation from Na/benzophenone, and dry CH_2Cl_2 and MeCN were obtained by distillation from P_2O_5. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pintuplet; m, multiplet; b, broad. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Zr-$(C_5H_4Me)_2Cl_2$ and $Zr(C_5H_4SiMe_3)_2Cl_2$ were prepared by the reaction of the corresponding cyclopentadienyllithium salts with $ZrCl_4$ in THF according to ref 12. Phenethynyldiphenylphosphine was prepared according to a published procedure.[11]

Synthesis of Dimer (4a). To a solution of $(C_5H_5)_2ZrCl_2$ (7.30 g, 25 mmol) in THF (200 mL) was added dropwise *n*-butyllithium (31.25 mL, 50 mmol, solution 1.6 M in hexane) at −78 °C. The solution was allowed to stir for 15 min at −78 °C, then some 20 drops of chlorotrimethylsilane were added to neutralize any excess of *n*-butyllithium. The solution was allowed to stir for a few minutes at −78 °C before 2-bromophosphinine **1** (5.05 g, 25 mmol) was added. The reaction mixture was then quickly warmed to room temperature and stirred for 30 min at 40 °C. A ^{31}P NMR control showed the unambiguous formation of complex **2a**. Methyllithium (15.6 mL, 25 mmol, solution 1.6 M in diethyl ether) was then added dropwise at −78 °C. The reaction mixture was warmed slowly to room temperature, and the transformation of complex **2a** into complex **3a** was controlled by ^{31}P NMR. The solvents were evaporated in vacuo, and the resulting brown oil was dissolved in benzene (100 mL), filtrated, and then heated at 80 °C. Formation of insoluble dimeric complex **4a** could not be followed by ^{31}P NMR since it precipitated as soon as it formed. After 2 h of warming, the mixture was cooled to room temperature and dimer **4a** was isolated by filtration under nitrogen. The yellow powder obtained was washed successively with benzene (20 mL) and hexane (40 mL) and then dried under reduced pressure. Yield: 6.00 g (70%). **2a**: ^{31}P NMR (THF) δ 224.40. **3a**: ^{31}P NMR (THF) δ 218.25. **4a**: ^{31}P NMR ($CDCl_3$) δ 194.35; ^1H NMR ($CDCl_3$) δ 2.42 (s, 6H, Me), 2.60 (AXX′, 6H, $\Sigma J(H-P) = 7.90$, Me), 5.50 (s, 20H, 4 × C_5H_5), 8.25 (AXX′, $\Sigma J(H-P) = 22.80$, $H_{6,6'}$); mass spectrum, *m/z* (ion, relative intensity) 687 (M, 15), 343 (M/2, 50). Anal. Calcd for $C_{34}H_{34}P_2Zr_2$: C, 59.44; H, 4.99. Found: C, 59.31; H, 5.18.

Synthesis of Dimer 4b. The experimental procedure is identical with the one yielding dimer **4a**. The insertion complex **2b** was obtained from $(C_5H_4Me)_2ZrCl_2$ (8.00 g, 25 mmol), butyllithium (31.25 mL, 1.6 M in hexane), and 2-bromophosphinine **1** (5.05 g, 25 mmol). After checking the formation of complex **2b** by ^{31}P NMR, the mixture was cooled to −78° and methyllithium (15.6 mL, 25 mmol) was added dropwise. The solution was then warmed to room temperature. ^{31}P NMR showed the formation of complex **3b**. Upon removal of the solvents in vacuo, the brown oil obtained was dissolved in benzene (100 mL), filtrated, and heated at 80 °C for 2 h. The unambiguous formation of complex **4b** could be followed by ^{31}P NMR. The half-part of solvent was removed under reduced pressure (30 mL), and the resulting solution was left to stand for 2 h. After this period, the solid that precipitated was isolated by filtration under nitrogen. The yellow powder thus obtained was washed with hexane (50 mL) and dried in vacuo. Yield: 6.50 g (70%). **2b**: ^{31}P NMR (THF) δ 224.05. **3b**: ^{31}P NMR (THF) δ 218.40 ($^2J(H-P) = 34.05$, $^3J(H-P) = 14.50$). **4b**: ^{31}P NMR ($CDCl_3$) δ 195.15; ^1H NMR ($CDCl_3$) δ 1.23 (s, 12H, Me of C_5H_4Me), 2.53 (s, 6H, Me of C_7H_7P), 2.69 (AXX′, 6H, $\Sigma J(H-P) =$ 6.05, Me of C_7H_7P), 5.47 (m, 8H, CH of C_5H_4Me), 5.62 (m, 4H, CH of C_5H_4Me), 5.70 (m, 4H, CH of C_5H_4Me), 8.25 (AXX′, 2H, $\Sigma J(H-P) = 22.96$, $H_{6,6'}$); ^{13}C NMR ($CDCl_3$): δ 15.40 (s, Me of C_5H_4Me), 23.35 (s, Me of C_7H_7P), 23.70 (s, Me of C_7H_7P), 98.90 (s, CH of C_5H_4-Me), 103.45 (s, CH of C_5H_4Me), 104.90 (s, CH of C_5H_4Me), 108.25 (s, CH of C_5H_4Me), 117.65 (s, Cq of C_5H_4Me), 139.45 (AXX′, $\Sigma J(C-P) = 31.00$, C_4 or C_5 of C_7H_7P), 143.35 (AXX′, $\Sigma J(C-P) = 19.55$, C_5 or C_4 of C_7H_7P), 155.40 (AXX′, $\Sigma J(C-P) = 39.85$, C_6 of C_7H_7P), 184.75 (AXX′, $\Sigma J(C-P) = 86.00$, C_2 of C_7H_7P), 186.20 (AXX′, $\Sigma J(C-P) = 47.20$, C_3 of C_7H_7P); mass spectrum, *m/z* (ion, relative intensity) 743 (M, 8), 371 (M/2, 30), 81 (C_5H_4Me + 2, 100). Anal. Calcd for $C_{38}H_{42}P_2Zr_2$: C, 61.42; H, 5.70. Found: C, 61.77; H, 5.72.

Synthesis of Dimer 4c. The experimental procedure is identical with the one yielding dimers **4a**,**b**. The insertion complex **2c** was obtained from $(C_5H_4SiMe_3)_2ZrCl_2$ (2.18 g, 5 mmol), butyllithium (6.25 mL, 10 mmol), and 2-bromophosphinine **1** (1.01 g, 5 mmol). After checking the formation of complex **2c** by ^{31}P NMR, the mixture was cooled to −78° and methyllithium (3.12 mL, 5 mmol) was added dropwise. The solution was then warmed to room temperature. ^{31}P NMR showed the formation of complex **3c**. Upon removal of the solvents in vacuo, the brown oil obtained was dissolved in benzene (10 mL), filtrated, and heated at 80 °C for 2 h. The solvent was then removed in vacuo, and complex **4c** was purified by extraction with hexane (20 mL) and filtration under nitrogen. The resulting solution was then dried in vacuo to yield an yellow slightly air-sensitive oil. Yield: 1.58 g (65%). **2c**: ^{31}P NMR (THF) δ 224.65. **3c**: ^{31}P (THF) δ 221.65. **4c**: ^{31}P NMR ($CDCl_3$) δ 19.50; ^1H NMR ($CDCl_3$): δ 0.05−0.50 (m, 36H, $SiMe_3$), 2.50 (s, 6H, Me of C_7H_7P), 2.74 (AA′X′, 6H, $\Sigma J(H-P) = 5.75$, Me of C_7H_7P), 5.45 (m, 4H, CH of $C_5H_4SiMe_3$), 5.70 (m, 4H, CH of $C_5H_4SiMe_3$), 5.85 (m, 8H, CH of $C_5H_4SiMe_3$), 8.3

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(AXX′, 2H, Σ*J*(H−P) = 22.75, $H_{6,6'}$); ^{13}C NMR ($CDCl_3$): δ 0.50−0.55 (m, $SiMe_3$), 23.30 (d, *J*(C−P) = 2.65, Me of C_7H_7P), 30.35 (s, Me of C_7H_7P), 104.45 (s, CH of $C_5H_4SiMe_3$), 108.65 (s, CH of $C_5H_4SiMe_3$), 109.90 (s, Cq of $C_5H_4SiMe_3$), 112.00 (s, CH of $C_5H_4SiMe_3$), 113.5 (s, CH of $C_5H_4SiMe_3$), 138.15 (pseudo t, AXX′, Σ *J*(C−P) = 30.50, C_4 or C_5 of C_7H_7P), 142.80 (pseudo t, AXX′, Σ *J*(C−P) = 19.65, C_4 or C_5 of C_7H_7P), 155.85 (pseudo t, AXX′, Σ *J*(C−P) = 39.80, C_6 of C_7H_7P), 180.30 (pseudo t, AXX′, Σ *J*(C−P) = 87.80, C_2 of C_7H_7P), 184.65 (pseudo t, AXX′, Σ *J*(C−P) = 48.55, C_3 of C_7H_7P); mass spectrum, *m*/*z* (relative intensity) 975 (M, 5), 489 (M/2 + 1, 30), 138 ($C_5H_4SiMe_3$ + 1, 100). Complex **4c** turned out to be too oxygen-sensitive to give a satisfactory elemental analysis.

Synthesis of Complex 5. A solution of dimer **4b** (0.74 g, 1 mmol) and acetonitrile (41 mg, 1 mmol) in THF (10 mL) was heated at 70 °C for 1 h. The solvent was removed in vacuo, and the brown oil obtained was partially dissolved in toluene (15 mL) and filtrated under nitrogen. The removal of the solvent yielded complex **5** as a brown water-sensitive powder: yield 0.62 g (75%); ^{31}P NMR ($CDCl_3$) δ 212.85; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 6H, Me of C_5H_4Me), 2.20 (d, 3H, *J*(H−P) = 3.20, Me of C_7H_7P), 2.37 (s, 3H, Me of C_7H_7P), 2.66 (d, 3H, ^{4}*J*(H−P) = 2.43, Me−C═), 5.60−6.40 (m, 8H, CH of C_5H_4Me), 8.36 (d, 1H, ^{2}*J*(H−P) = 37.92, H_6); ^{13}C NMR ($CDCl_3$) δ 14.70 (s, Me of C_5H_4Me), 25.90 (s, *Me*−C═), 26.30 (d, *J* (C−P) = 7.80, Me of C_7H_7P), 26.50 (s, Me of C_7H_7P), 104.25 (s, CH of C_5H_4Me), 105.45 (s, CH of C_5H_4Me), 118.75 (s, CH of C_5H_4Me), 123.35 (s, CH of C_5H_4Me), 128.95 (s, CH of C_5H_4Me), 142.40 (d, *J*(C−P) = 12.35, CH of C_7H_7P), 148.40 (d, *J*(C−P) = 19.90, Me of C_7H_7P), 152.20 (d, ^{1}*J*(C−P) = 39.25, C_6 of C_7H_7P), 167.95 (d, ^{1}*J*(C−P) = 49.40, C_2 of C_7H_7P), 191.45 (d, ^{2}*J*(C−P) = 40.55, C═N), 209.65 (d, ^{2}*J*(C−P) = 18.30, C_3 of C_7H_7P); mass spectrum, *m*/*z* (ion, relative intensity) 413 (M, 15), 166 (M − $(C_5H_4Me)_2Zr$, 80). Anal. Calcd for $C_{21}H_{24}NPZr$: C, 61.13; H, 5.86. Found: C, 61.55; H, 5.90.

Synthesis of Phosphinine 6. A solution of dimer **4b** (0.50 g, 0.81 mmol) and triphenylphosphine sulfide (0.47 g, 1.62 mmol) in THF (5 mL) was heated at 70 °C for 3 h. A yellow solid precipitated during that time. A ^{31}P NMR control showed the disparition of the signal corresponding to the sulfide and the formation of free triphenylphosphine. Upon addition of ether (20 mL) the most part of the intermediary metallacycle precipitated. The mixture was then filtrated under nitrogen. The yellow powder that was collected was washed successively with ether (10 mL) and hexane (10 mL). THF (5 mL) was then added and the mixture was treated with chlorotrimethylsilane (1 mL) and ethanol (1 mL) for 5 min at room temperature. ^{31}P NMR showed the completion of the hydrolysis. After evaporation of the solvent, hexane (30 mL) was added and the mixture was filtrated under nitrogen. Celite (1 g) was added and hexane was removed in vacuo, yielding a yellow powder which was deposited onto the top of a silica gel packed flash column for chromatography. Phosphinine **6** was eluted purified using hexane as eluent. Removal of hexane yielded **6** as a white powder: yield 0.33 g (70%); ^{31}P NMR ($CDCl_3$) δ 183.30; ^{1}H NMR ($CDCl_3$) δ 2.31 (d, 3H, *J*(H−P) = 3.65, Me), 2.35 (s, 3H, Me), 4.04 (d, 1H, ^{3}*J*(H−P) = 8.91, SH), 7.63 (d, 1H, ^{3}*J*(H−P) = 4.77, H_3), 8.26 (d, 1H, ^{2}*J*(H−P) = 43.33, H_6); ^{13}C NMR ($CDCl_3$) δ 22.95 (s, Me), 23.45 (d, *J*(C−P) = 4.35, Me), 136.90 (d, *J*(C−P) = 12.25, C_4 or C_5), 136.90 (d, ^{2}*J*(C−P) = 12.25, C_3), 140.90 (d, *J*(C−P) = 16.80, C_5 or C_4), 156.20 (d, ^{1}*J*(C−P) = 52.05, C_6), 158.20 (d, ^{1}*J*(C−P) = 59.30, C_2); mass spectrum, *m*/*z* (ion, relative intensity) 156 (M, 100). Anal. Calcd for C_7H_9PS: C, 53.83; H, 5.81. Found: C, 54.56 ; H, 5.77.

Synthesis of Phosphinine 8. To a freshly prepared solution of $Zr(C_5H_5)_2(Me)(C_7H_8P)$ complex **3a** (5 mmol) in THF (50 mL) was added phenethynyldiphenylphosphine (1.43 g, 5 mmol). The mixture was then heated at 70 °C for 3 h. ^{31}P NMR showed the transformation of complex **3a** into complexes **7**α and **7**β (95:5). The solvent was removed in vacuo, and the brown oil obtained was dissolved in a mixture of dichloromethane (20 mL) and methanol (20 mL). The solution was then acidified at room temperature with 20 drops of a 12 N HCl solution and stirred for 2 h. A ^{31}P NMR control showed the unambiguous formation of phosphinine **8**. The orange solution thus obtained was washed three times with water (40 mL), dried with $MgSO_4$, and then filtrated under nitrogen. Celite (3 g) was added and the solvent was removed in vacuo. Phosphinine **8** was chromatographed on silica gel. A first fraction, eluted with hexane, yielded some unreacted alkyne. Phosphinine **8** was then eluted with a mixture of hexane/ether (9:1). After removal of the solvent, **8** was isolated as a yellow slightly air-sensitive oil. Yield: 1.43 g (70%). **7**α: ^{31}P NMR (THF) δ 200.45 (d, ^{4}*J*(P−P) = 12.70, ═P−), −19.95 (d, PPh_2). **7**β: ^{31}P NMR (THF) δ 202.10 (d, ^{4}*J*(P−P) = 96.5, ═P−), −8.25 (d, PPh_2). **8**: ^{31}P NMR ($CDCl_3$) δ 185.95 (s, P of C_7H_8P), −2.14 (s, PPh_2); ^{1}H NMR ($CDCl_3$) δ 2.29 (d, 3H, *J*(H−P) = 3.38, Me of C_7H_8P), 2.43 (s, 3H, Me of C_7H_8P), 7.05 (t, 1H, ^{4}*J*(H−P) = ^{2}*J*(H−P) = 3.45, ═CH−P), 7.20−7.80 (m, 15H, 3 × C_6H_5), 8.47 (d, 1H, ^{2}*J*(H−P) = 38.5, H_6); ^{13}C (NMR $CDCl_3$) δ 23.10 (d, *J*(C−P) = 2.50, Me of C_7H_8P), 23.80 (d, *J*(C−P) = 3.3, Me of C_7H_8P), 128.00−130.00 (m, CH of C_6H_5), 132.50−133.0 (m, CH of C_6H_5), 134.55 (d, ^{1}*J*(C−P) = 18.00, ═CH−P), 136.95 (d, ^{3}*J*(C−P) = 6.35, Cq of C_6H_5), 137.40 (d, ^{2}*J*(C−P) = 12.35, C_3), 139.45 (d, *J*(C−P) = 15.6, C_4 or C_5 or Cq of C_6H_5), 140.90 (d, *J*(C−P) = 10.70, C_4 or C_5 or Cq), 143.70 (d, *J*(C−P) = 15.20, C_4 or C_5 or Cq), 155.20 (d, ^{1}*J*(C−P) = 50.30, C_6 of C_7H_8P), 159.60 (dd, ^{2}*J*(C−P) = 25.55, ^{2}*J*(C−P) = 22.10, ═*C*−Ph), 171.30 (dd, ^{1}*J*(C−P) = 53.60, ^{3}*J*(C−P) = 7.10, C_2 of C_7H_8P); mass spectrum, *m*/*z* (ion, relative intensity) 410 (M, 100), 225 (M − PPh_2, 40). Anal. Calcd for $C_{27}H_{24}P_2$: C, 79.01; H, 5.89. Found: C, 79.55; H, 5.92.

Synthesis of Phosphinine 10 and Complex 11. A solution of freshly prepared $Zr(C_5H_5)_2(Me)(C_7H_8P)$ complex **2a** (5 mmol) in THF (50 mL) was heated with (trimethylsilyl)acetylene (0.49 g, 10 mmol) at 70 °C for 2 h. The mixture was cooled to room temperature, a sample of solution (2 mL) was taken for the NMR characterizations of intermediate **9**, and then the solvent and the excess alkyne were evaporated. The brown oil obtained was dissolved in a mixture of methanol (20 mL) and dichloromethane (20 mL), and the resulting mixture was treated with a 12 N HCl solution (20 drops) for 2 h at room temperature. The transformation of complex metallacycle **9** into phosphinine **10** was controlled by ^{31}P NMR. The orange solution thus obtained was washed three times with water (40 mL), dried with $MgSO_4$, and then filtrated under nitrogen. Celite (3 g) was added, and the solvent was removed in vacuo. Phosphinine **10** was chromatographed on silica gel using hexane as eluent. After removal of the solvent, **11** was isolated as a yellow slightly air-sensitive oil. Yield: 0.83 g (75%). To obtain satisfactory microanalytical data, phosphinine **10** was complexed by $W(CO)_5THF$ using the following procedure. Phosphinine (0.40 g, 1.80 mmol) in solution in THF (5 mL) was added to a freshly prepared solution of $W(CO)_5THF$ (1.85 mmol). The mixture was stirred for 30 min at room temperature. Celite (3 g) was added, and the solvent removed in vacuo. The powder obtained was chromatographed on silica gel. A first fraction, eluted with hexane, yielded some traces of unreacted $W(CO)_6$. Complex **11** was eluted with a mixture of hexane/CH_2Cl_2 (9:1). After removal of the solvent, **11** was obtained as a yellow solid. Yield: 0.88 g (90%). **9**: ^{31}P NMR ($CDCl_3$) δ 199.55; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H, $SiMe_3$), 1.99 (s, 3H, *J*(H−P) = 3.25, Me of C_7H_7P), 2.40 (s, 3H, Me of C_7H_7P), 6.30 (S, 10H, CH of C_5H_5), 7.64 (d, 1H, ^{3}*J*(H−P) = 8.85, ═CH), 8.33 (d, 1H, ^{2}*J*(H−P) = 35.50, H_6); ^{13}C NMR ($CDCl_3$) : δ 1.20 (s, $SiMe_3$), 24.40 (d, *J*(C−P) = 3.95, Me of C_7H_7P), 25.30 (s, Me of C_7H_7P), 111.30 (s, C_5H_5), 136.85 (d, ^{2}*J*(C−P) = 49.10, ═CH), 137.60 (d, *J*(C−P) = 14.05, C_4 or C_5 of C_7H_7P), 144.55 (d, *J*(C−P) = 19.75, C_5 or C_4), 153.45 (d, ^{1}*J*(C−P) = 44.20, C_6), 163.40 (d, ^{1}*J*(C−P) = 50.40, C_2), 189.35 (d, ^{3}*J*(C−P) = 13.55, ═C−Si), 207.50 (d, ^{2}*J*(C−P) = 21.25, C_3). **10**: ^{31}P NMR (THF) δ 202.65; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9H, $SiMe_3$), 2.34 (d, 3H, Me of C_7H_8P), 6.71 (dd, 1H, ^{3}*J*(H−H) = 18.90, ^{4}*J*(H−P) = 4.06, ═CHSi), 7.12 (dd, 1H, ^{3}*J*(H−H) = 18.90, ^{3}*J*(H−P) = 10.35, ═CH), 7.67 (d, 1H, ^{3}*J*(H−P) = 5.94, H_3), 8.41 (d, 1H, ^{2}*J*(H−P) = 8.38, H_6); ^{13}C NMR ($CDCl_3$) δ −0.50 (s, $SiMe_3$), 22.90 (s, Me of C_7H_8P), 23.60 (d, *J*(C−P) = 3.65, Me of C_7H_8P), 129.60 (d, ^{3}*J*(C−P) = 20.65, ═C−Si), 135.70 (d, ^{2}*J*(C−P) = 13.50, C_3), 139.30 (d, *J*(C−P) = 16.90, C_4 or C_5), 142.85 (d, *J*(C−P) = 16.05, C_5 or C_4), 147.00 (d, ^{2}*J*(C−P) = 39.20, ═CH), 155.00 (d, ^{1}*J*(C−P) = 48.80, C_6), 165.65 (d, ^{1}*J*(C−P) = 44.40, C_2); mass spectrum, *m*/*z* (ion, relative intensity) 222 (M, 30), 207 (M − 15, 100). **11**: ^{31}P NMR ($CDCl_3$) δ 155.15 (^{1}*J*(P−W) = 257.20); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H, SiMe3), 2.37 (d, 3H, *J*(H−P) = 6.12, Me of C_7H_8P), 2.41 (d, 3H, *J*(H−P) = 1.84, Me of C_7H_8P), 6.55 (dd, 1H, ^{3}*J*(H−H) = 18.80, ^{4}*J*(H−P) = 3.44, ═CHSi), 7.21 (dd, 1H, ^{3}*J*(H−H) = 18.80, ^{3}*J*(H−P) = 12.80, ═CH),

7.94 (d, 1H, ^3J(H−P) = 19.05, H_3), 8.07 (d, 1H, ^2J(H−P) = 24.90, H_6); ^{13}C NMR ($CDCl_3$) δ −0.80 (s, $SiMe_3$), 23.05 (d, J(C−P) = 4.30, Me of C_7H_8P), 23.90 (d, J(C−P) = 9.60, Me of C_7H_8P), 132.25 (d, J(C−P) = 18.60, ═C−$SiMe_3$ or ═CH), 135.65 (d, J(C−P) = 12.10, ═CH or ═C−$SiMe_3$), 138.25 (d, J(C−P) = 25.90, C_4 or C_5), 142.45 (d, ^2J(C−P) = 20.00, C_3), 147.90 (d, J(C−P) = 16.95, C_4 or C_5), 150.40 (d, ^1J(C−P) = 21.70, C_6), 158.50 (d, ^1J(C−P) = 21.40, C_2), 195.25 (d, ^2J(C−P) = 9.25, CO cis), 199.60 (d, ^2J(C−P) = 29.00, CO trans); mass spectrum, *m*/*z* (ion, relative intensity) 546 (M, 30), 490 (M − 2CO, 85), 390 (M − 4CO − MeH, 100). Anal. Calcd for $C_{17}H_{19}O_5PSiW$: C, 37.38; H, 3.51. Found: C, 37.31; H, 3.68.

Synthesis of Phosphinine (14). Ferrocenecarboxaldehyde (1.50 g, 10 mmol) was added to a freshly prepared solution of $Zr(C_5H_4Me)_2(Me)(C_7H_8P)$ complex **4b** (5 mmol) in THF (50 mL). The mixture was then heated at 70 °C for 2 h. After this period, a ^{31}P NMR control showed the complete transformation of complex **4b** into metallacycle **12**. A sample of solution was taken for NMR characterizations of **12**. The solvent was then removed in vacuo, and the oil obtained was dissolved in a mixture of dichloromethane (20 mL) and methanol (20 mL). The resulting solution was then acidified with a 12 N HCl solution (20 drops) and stirred for 2 h. Formation of phosphinine **14** was followed by ^{31}P NMR. The organic solution was washed three times with water (40 mL), dried with $MgSO_4$, and then filtrated under nitrogen. Celite (2 g) was added, and the solvent was removed in vacuo. Phosphinine **14** was chromatographed on alumina using a mixture of hexane/ether (5:1) as eluent. Removal of the solvent yielded **14** as a deep red solid. Yield: 1.26 g (75%). **12**: ^{31}P NMR ($CDCl_3$) δ 184.00; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, 3H, J(H−P) = 3.5, Me of C_7H_7P), 1.96 (s, 3H, Me of C_5H_4Me), 2.01 (s, 3H, Me of C_5H_4Me), 2.20 (s, 3H, Me of C_7H_7P), 3.90−4.20 (m, 4H, CH of C_5H_4), 4.08 (s, 5H, CH of C_5H_5), 5.70−6.30 (m, 8H, CH of C_5H_4Me), 8.08 (d, 1H, ^2J(H−P) = 38.00, H_6); ^{13}C NMR ($CDCl_3$) δ 15.15 (s, Me of C_5H_4Me), 15.40 (s, Me of C_5H_4Me), 24.20 (d, J(C−P) = 2.80, Me of C_7H_7P), 26.35 (s, Me of C_7H_7P), 69.10−70.00 (m, $C_{10}H_9Fe$), 89.25 (d, ^2J(C−P) = 39.90, CH−O), 109.05, 109.25, 111.10, 111.90, 112.60, 114.50, 114.90, 115.80 (s, CH of C_5H_4Me), 127.30 (s, Cq of C_5H_4Me), 129.05 (s, Cq of C_5H_4Me), 137.20 (d, J(C−P) = 14.85, C_4 or C_5), 144.20 (d, J(C−P) = 20.85, C_4 or C_5), 152.65 (d, ^1J(C−P) = 44.35, C_6), 188.15 (d, ^2J(C−P) = 13.30, C_3), 194.80 (d, ^1J(C−P) = 56.70, C_2). **14**: ^{31}P NMR ($CDCl_3$) δ 182.00; ^{1}H NMR ($CDCl_3$) δ 2.33 (d, 3H, Me of C_7H_8P), 2.38 (s, 3H, Me of C_7H_8P), 4.13 (m, 9H, CH of $C_{10}H_9Fe$), 5.66 (d, 1H, ^3J(H−P) = 8.94, CH), 7.67 (d, 1H, ^3J(H−P) = 6.00, H_3), 8.40 (d, 1H, ^2J(H−P) = 38.82, H_6); ^{13}C NMR ($CDCl_3$) δ 25.30 (s, Me of C_7H_8P), 25.90 (s, Me of C_7H_8P), 66.30−70.00 (m, $C_{10}H_9Fe$), 74.55 (d, ^2J(C−P) = 35.15, C−O), 135.10 (d, ^2J(C−P) = 12.50, C_3), 139.15 (d, J(C−P) = 17.0, C_4 or C_5), 142.85 (d, J(C−P) = 16.15, C_5 or C_4), 154.20 (d, ^1J(C−P) = 48.60, C_6), 172.05 (d, ^1J(C−P) = 45.95, C_2); mass spectrum, *m*/*z* (ion, relative intensity) 322 (M − 16, 100), 257 (322 − C_5H_5, 100). Anal. Calcd for $C_{18}H_{19}FeOP$: C, 63.93; H, 5.66. Found: C, 63.55; H, 5.86.

Synthesis of Phosphinine (15). A solution of dimer **4b** (2.23 g, 3.00 mmol) and 2-thienecarboxaldehyde (0.70 g, 6.25 mmol) in THF (30 mL) was heated at 80 °C for 3 h. After this period a ^{31}P NMR control indicated the formation of metallacycle **13**. After removal of the solvent, the oil obtained was dissolved in a mixture of dichloromethane (30 mL) and methanol (30 mL). The solution was then acidified with a 12 N HCl solution (20 drops), and stirred for 2 h. The hydrolysis was monitored by ^{31}P NMR. The resulting solution was washed three times with water (40 mL), dried with $MgSO_4$, and then filtrated under nitrogen. Celite (3 g) was added, and the solvent was removed in vacuo. Phosphinine **15** was chromatographed on alumina using a mixture of hexane/ether (5:1) as eluent. Removal of the solvent yielded **15** as an yellow oil. Yield: 1.00 g (70%). **13**: ^{31}P NMR (THF) δ 189.15 (^2J(P−H) = 38.90). **15:** ^{31}P NMR ($CDCl_3$) δ 183.30; ^{1}H NMR ($CDCl_3$) δ 2.59 (d, 3H, J(H−P) = 4.02, Me of C_7H_8P), 2.66 (d, 3H, J(H−P) = 1.45, Me of C_7H_8P), 6.49 (d, 1H, ^3J(H−P) = 8.50, CH), 7.17−7.26 (m, 2H, $H_{3'}$ and $H_{4'}$ of C_4H_3S), 7.50 (m, 1H, $H_{5'}$ of C_4H_3S), 7.98 (d, 1H, ^3J(H−P) = 6.00, H_3), 8.40 (d, 1H, ^2J(H−P) = 54.30, H_6); ^{13}C NMR ($CDCl_3$) δ 23.15 (s, Me of C_7H_8P), 23.85 (d, J(C−P) = 3.50, Me of C_7H_8P), 75.15 (d, ^2J(C−P) = 32.20, CH), 111.85 (s, CH of C_4H_3S), 126.05 (s, CH of C_4H_3S), 127.30 (s, CH of C_4H_3S), 135.80 (d, ^2J(C−P) = 13.70, C_3), 140.10 (d, J(C−P) = 16.90, C_4 or C_5 of C_7H_8P), 143.80 (d, J(C−P) = 15.50,C_4 or C_5 of C_7H_8P), 149.70 (d, ^3J(C−P) = 6.00, Cq of C_4H_3S), 154.5 (d, ^1J(C−P) = 49.00, C_6 of C_7H_8P), 172.45 (d, ^1J(C−P) = 47.15, C_2 of C_7H_8P); mass spectrum, *m*/*z* (ion, relative intensity) 236 (M, 90), 218 (M − H_2O, 30); Anal. Calcd for $C_{12}H_{13}OPS$: C, 61.00; H, 5.55. Found: C, 61.43; H, 5.56.

Synthesis of Phosphinine 17 and Complex 18. A solution of freshly prepared $Zr(C_5H_5)_2(Me)(C_7H_8P)$ complex **3a** (10 mmol) in THF (10 mL) was heated with freshly dried (+)-camphor (1.21 g, 8 mmol) at 80 °C for 60 h. The resulting mixture was cooled to room temperature, and a sample of solution was taken for NMR characterizations of metallacycle **16** before evaporation of the solvent. The brown oil obtained was dried under reduced pressure for 3 h to sublimate any traces of unreacted camphor. The black solid obtained was then dissolved in a mixture of dichloromethane (20 mL) and methanol (20 mL). The resulting solution was then acidified a 12 N HCl solution (20 drops) and stirred for 1 h. A ^{31}P NMR control indicated the completion of the hydrolysis. The orange solution thus obtained was washed three times with water (40 mL), dried with $MgSO_4$, and then filtrated under nitrogen. Alumina (3 g) was added, and the solvent was removed in vacuo. Phosphinine **17** was chromatographed on alumina using a mixture of hexane/ether (4:1) as eluent. After removal of the solvent, **17** was isolated as an yellow-orange oil. Yield: 1.5 g (55%). The complexation of **17** was conducted with $W(CO)_5THF$ as follows. A solution of phosphinine **17** (0.55 g, 2 mmol) in THF (5 mL) was added to a freshly prepared solution of $W(CO)_5THF$ (2 mmol). The mixture was stirred for 30 min at room temperature. Total complexation was controlled by ^{31}P NMR. Alumina (3 g) was added, and the solvent removed in vacuo. The powder obtained was chromatographed on silica gel. Complex **18** was eluted with a mixture of hexane/ether (3:1) as eluent. After removal of the solvent, **18** was obtained as a yellow powder. Yield: 0.84 g (70%). Crystals were obtained by pentane diffusion into a dichloromethane solution of **18**, in a 5 mm NMR tube at room temperature. **16**: ^{31}P NMR ($CDCl_3$) δ 196.05; ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 9H, Me), 1.87 (d, 3H, J(H−P) = 5.68, Me of C_7H_7P), 2.22 (s, 3H, Me of C_7H_7P), 5.87−6.44 (m, 10H, 2 × C_5H_5), 8.14 (d, 1H, ^2J(H−P) = 39.42, H_6 of C_7H_7P); ^{13}C NMR ($CDCl_3$) δ 14.05 (s, $C_{8'}$), 22.35 (s, $C_{9'}$ or $C_{10'}$), 22.65 (s, $C_{10'}$ or $C_{9'}$), 24.10 (s, Me of C_7H_7P), 24.20 (s, Me of C_7H_7P), 25.50 (s, $C_{5'}$ or $C_{6'}$), 32.25 (d, J(C−P) = 36.45, $C_{5'}$ or $C_{6'}$), 46.60 (s, $C_{4'}$), 52.20 (d, ^3J(C−P) = 4.65, $C_{1'}$), 54.15 (d, ^3J(C−P) = 8.45, $C_{3'}$), 55.60 (s, $C_{7'}$), 102.50 (d, ^2J(C−P) = 25.85, $C_{2'}$), 110.40−114.60 (m, CH of C_5H_5), 136.65 (d, J(C−P) = 14.10, C_4 or C_5 of C_7H_7P), 142.80 (d, J(C−P) = 20.60, C_5 or C_4 of C_7H_7P), 152.10 (d, ^1J(C−P) = 44.85, C_6 of C_7H_7P), 189.10 (d, ^2J(C−P) = 13.75, C_3 of C_7H_7P), 199.60 (d, ^1J(C−P) = 64.10, C_2 of C_7H_7P); mass spectrum, *m*/*z* (ion, relative intensity) 494 (M, 1), 152 (camphor, 30), 66 (C_5H_5 + 1, 85). **17**: ^{31}P NMR ($CDCl_3$) δ 186.62; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3H, Me), 0.99 (s, 3H, Me), 1.28 (s, 3H, Me), 1.30−1.80 (m, 4H, $H_{5'}$ et $H_{6'}$), 1.92 (ABMNX, 1H, ^3J(H−H_{eq}) = 4.40, $H_{4'}$) 2.23 (ABMNX, 1H, $^2J_{gem}$ = 13.88, ^3J(H−H_{eq}) = 4.40, ^4J(H−H_{eq}) = 3.05, ^4J(H−P) = 1.45, $H_{3'eq}$), 2.39 (d, 3H, J(H−P) = 3.65, Me of C_7H_8P), 2.41 (d, 3H, J(H−P) = 0.84, Me of C_7H_8P), 2.76 (ABMNX, 1H, ^4J(H−P) = 4.60, $H_{3'ax}$), 7.94 (d, 1H, ^3J(H−P) = 5.62, H_3 of C_7H_8P), 8.39 (d, 1H, ^2J(H−P) = 39.83, H_6 of C_7H_8P); ^{13}C NMR ($CDCl_3$) δ 10.65 (s, $C_{8'}$), 22.30 (s, $C_{9'}$ or $C_{10'}$), 22.50 (s, $C_{10'}$ or $C_{9'}$), 23.45 (s, Me of C_7H_8P), 23.50 (s, Me of C_7H_8P), 26.80 (s, $C_{5'}$ or $C_{6'}$), 32.20 (s, $C_{5'}$ or $C_{6'}$), 46.30 (s, $C_{4'}$), 47.10 (d, ^3J(C−P) = 16.60, $C_{3'}$), 51.25 (d, ^3J(C−P) = 4.40, $C_{1'}$), 54.15 (s, $C_{7'}$), 86.15 (d, ^2J(C−P) = 18.30, $C_{2'}$), 136.55 (d, ^2J(C−P) = 12.30, C_3 of C_7H_8P), 138.95 (d, J(C−P) = 16.75, C_4 or C_5 of C_7H_8P), 142.20 (d, J(C−P) = 15.25, C_5 or C_4 of C_7H_8P), 152.95 (d, ^1J(C−P) = 50.10, C_6 of C_7H_8P), 176.40 (d, ^1J(C−P) = 50.65, C_2 of C_7H_8P); mass spectrum, *m*/*z* (ion, relative intensity) 276 (M, 20), 258 (M − H_2O, 3); 166 (M − C_8H_{14}, 100). **18**: ^{31}P NMR ($CDCl_3$) δ 148.35 (^1J(P−W) = 128.10); ^{1}H NMR($CDCl_3$) δ 0.84−1.43 (m, 4H, $H_{5'}$ et $H_{6'}$), 0.96 (s, 3H, Me), 1.02 (s, 3H, Me), 1.27 (s, 3H, Me), 1.79−1.92 (m, 1H, $H_{3'eq}$), 1.99 (s, 1H, $H_{3'ax}$), 2.08 (s, 1H, $H_{4'}$), 2.34 (d, 3H, J(H−P) = 8.61, Me of C_7H_8P), 2.39 (s, 3H, Me of C_7H_8P), 7.69 (d, 1H, ^3J(H−P) = 19.05, H_3 of C_7H_8P), 8.23 (d, 1H, ^2J(H−P) = 27.09, H_6 of C_7H_8P); ^{13}C NMR ($CDCl_3$) δ 12.00 (s, $C_{8'}$), 22.25 (s, $C_{9'}$ or $C_{10'}$), 22.45 (s, $C_{10'}$ or $C_{9'}$), 23.40 (s, Me of C_7H_8P), 23.50 (s, Me of C_7H_8P), 27.45 (s, $C_{5'}$ or $C_{6'}$), 31.65 (s, $C_{5'}$ or $C_{6'}$), 46.15 (s, $C_{4'}$), 49.55 (d, ^3J(C−P) = 3.40, $C_{3'}$), 51.70 (s, $C_{1'}$), 55.30 (s, $C_{7'}$), 88.30 (d, ^2J(C−P) = 6.90, $C_{2'}$), 136.20 (d, ^3J(C−P) = 26.65, C_4 or C_5 of C_7H_8P), 139.00 (d,

Table 1. Crystal Data for Complexes **4b** and **18**

	4b	**18**
formula	$C_{38}H_{42}Zr_2P_2$	$C_{22}H_{24}O_6PW$
space group	*P*21/*c* (no. 14)	*P*21 (no. 4)
data collection temperature (K)	123	123
a (Å)	8.217(1)	10.966(2)
b (Å)	18.037(5)	12.340(3)
c (Å)	22.328(5)	16.639(4)
β (deg)	97.79(2)	92.95(2)
V (Å^3)	3278.(2.)	2248.(1.)
Z	4	4
d_{calcd} (g/cm^3)	1.506	1.770
μ (cm^{-1})	7.5	53.5
maximum 2θ	60.0	60.0
no. of reflns measd	10041	7141
no. of reflns included	7266	5988
no. of params refined	547	541
unweighted agreement factor:	0.024	0.023
weighted agreement factor:	0.038	0.030
GOF	1.01	1.04
convergence, largest shift/error	0.01	0.00

^2J(C−P) = 12.50, C_3 of C_7H_8P), 145.95 (d, J(C−P) = 16.90, C_5 or C_4 of C_7H_8P), 155.45 (d, ^1J(C−P) = 16.65, C_6 of C_7H_8P), 168.55 (d, ^1J(C−P) = 13.35, C_2 of C_7H_8P), 197.35 (d, ^2J(C−P) = 9.05, CO cis), 200.70 (d, ^2J(C−P) = 21.35, CO trans); mass spectrum, *m*/*z* (ion, relative intensity) 600 (M, 1), 572 (M − CO, 10), 544 (M − 2CO, 10), 528 (M − 3CO, 10), 460 (M − 5CO, 55). Anal. Calcd for $C_{22}H_{25}O_6PW$: C, 44.02; H,4.20. Found: C, 44.02; H, 4.28.

X-ray Structure Determinations. All data sets were collected on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved by direct methods using SIR92 and refined with the Enraf Nonius MOLEN package using reflections having $F^2 < 3.0\sigma(F^2)$. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement for the tungsten complex. The zirconium compound hydrogen atoms were refined with isotropic temperature factors. Anisotropic temperature factors were used for all other atoms. Crystal data are assembled in Table 1.

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Supporting Information Available: X-ray structure deermination for **4b** and **18**, positional parameters, bond distances, angles and β_{ij} values (22 pages). See any current masthead page for ordering and Internet access instructions.

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