34). Anal. Calcd for $C_{20}H_{38}Fe_2NO_6PSSi_3$: C, 37.10; H, 5.92; N, 2.16. Found: C, 36.98; H, 6.11; N, 2.24.

Reaction of $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ with $(Me_3Si)_2NP{=}C(H)SiMe_3$ (3). A solution of $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$[19] was prepared by mixing $Fe_3(CO)_{12}$ (1.50 g, 3.0 mmol), *t*-BuSH (0.34 mL, 3.0 mmol), and Et_3N (0.42 mL, 3.0 mmol) in ca. 20 mL of THF at room temperature. After the mixture was stirred for ca. 2.5 h, the (methylene)phosphine (0.83 g, 3.0 mmol) was added to the red-brown solution of the anion at room temperature. Monitoring by ^{31}P NMR spectroscopy after ca. 15 min indicated that the reaction was still incomplete since a signal at δ 308 for the methylene phosphine was observed along with a very small signal at δ 195 and large signals at δ 176 and 188. The solution was stirred overnight, at which time the signal for the starting material was gone. By frit chromatography two fractions (1.1 g) were isolated with the ^{31}P NMR spectrum of the first showing signals predominantly at δ 176 and 188 with a small resonance at δ 195, while the second band showed only a signal at δ 195. The first band was further purified by column chromatography which yielded an analytically pure sample of isomers of **5**. The red oil resisted attempts at crystallization from a variety of organic solvents: ^{31}P NMR δ 188.1, 176.3; ^1H NMR δ 0.18, 0.23 (s, 9 H, Me_3SiC), 0.41, 0.44 [s, 18 H, $(Me_3Si)_2N$], 1.44, 1.48 (s, 9 H, *t*-Bu), 1.58, 1.97 (d, J_{PCH} = 12.8, 8.8 Hz, 2 H, $SiCH_2$); $^{13}C[^1H]$ NMR δ 0.4, 0.9 (s, Me_3SiC), 6.0, 6.2 (s, Me_3SiN), 22.6 (s, CH_2), 33.7, 33.8 (d, $C\mathit{Me}_3$), 36.0 (d, J_{PC} = 6.3 Hz, CH_2), 49.34 (d, J_{PC} = 20.2 Hz, $\mathit{C}Me_3$), 48.8 (s, $\mathit{C}Me_3$), 212.2, 212.8 (s, CO); IR ($CHCl_3$); 2050 (s), 1980 (vs, br) cm^{-1}. Anal. Calcd for $C_{20}H_{38}Fe_2NO_6PSSi_3$: C, 37.10; H, 5.92; N, 2.16. Found: C, 36.68; H, 6.04; N, 2.06.

A sample of **5** was dissolved in THF, and an excess of H_2O was added to the solution. After 20 h the ^{31}P NMR spectrum of the solution showed a signal at δ 195 as well as several signals clustered between δ 185 and δ 188 and a small signal at δ 176. The signal at δ 195 continued to increase over a 2-week period until all the other signals were gone. Purification of the product by frit chromatography and characterization by ^1H and ^{31}P NMR analysis indicated that the material was **4**.

Reaction of $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (1) with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$. A THF solution of the anion (3.0 mmol), prepared as described above, was treated with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ (0.94 g, 3.0 mmol) at 0 °C. After the solution was stirred for 2 days, ^{31}P NMR analysis showed that the predominant species present was **5** (^{31}P NMR δ 188.4, 176.6, 152.6, 75.4, 63.3, 59.8). Solvent removal under vacuum, followed by frit chromatography yielded 1.0 g of a red oil; ^{31}P NMR δ 187.9, 176.0 (ca. equal intensity), 63.8 (ca. 10% of the intensity of the other two signals).

Acknowledgment. The generous financial support of the National Science Foundation Visiting Professorships for Women in Science and Engineering Program is gratefully acknowledged. P.W.-N. also thanks the Department of Chemistry at Massachusetts Institute of Technology for providing the facilities, technical support, and collaborative arrangements which made this work possible while she was a visiting professor in that department.

Registry No. 1, 107099-49-0; 2, 112925-78-7; 3, 76173-65-4; 4, 112925-79-8; 5, 112925-80-1; $[(\mu\text{-}t\text{-}BuS)(\mu\text{-}P(OMe)CH(SiMe_3)_2)Fe_2(CO)_6]$, 112925-81-2; $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$, 105040-77-5; $(Me_3Si)_2C{=}PCl$, 79454-85-6; $(Me_3Si)_2NP(Cl)CH_2SiMe_3$, 76946-89-9.

Supplementary Material Available: Listings of thermal parameters and idealized of thermal parameters (4 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of the New 2,3,4,5-Tetramethylphospholyl (C_4Me_4P) π-Ligand. Crystal and Molecular Structure of $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2\cdot{}^1/_2C_{10}H_8$

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Received August 26, 1987

The new 1-phenyl-2,3,4,5-tetramethylphosphole (**6c**) has been prepared from 2-butyne, $AlCl_3$, $PhPCl_2$, and $(n\text{-}Bu)_3P$. Reaction of this phosphole with $Mn_2(CO)_{10}$ and $[CpFe(CO)_2]_2$ yields $(\eta^5\text{-}C_4Me_4P)Mn(CO)_3$ and $(\eta^5\text{-}C_4Me_4P)(\eta^5\text{-}C_5H_5)Fe$, respectively. Cleavage of the P–Ph bond of **6c** can be easily achieved with lithium, as with other phospholes. Reaction of the resulting phospholyl anion **14** with iron(II) chloride affords $(\eta^5\text{-}C_4Me_4P)_2Fe$ and with $ZrCl_4$, $(\eta^5\text{-}C_4Me_4P)ZrCl_2$, which is the first heterocyclopentadienylzirconium compound that has been completely characterized. Its X-ray crystal structure shows the normal expected features of a η^5-phospholyl complex and of a $(\eta^5\text{-}L)_2ZrCl_2$ complex.

Phospholyl or phosphacyclopentadienyl ligands **1**[1] have been successfully used as substitutes for the isoelectronic cyclopentadienyl ligand in a number of compounds. Many derivatives of mono-[2] and diphosphaferrocenes[3] (**2** and **3**, respectively) and phosphacymantrenes[2c,4] **4** have thus been prepared. However, the phospholyl ligands have thus far proven much less versatile than the ubiquitous Cp ligand: apart from the iron and manganese families, only four

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[1] For a general review of phospholyl complexes, see: Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* (*Berlin*) **1983**, *55*, 153.

[2] (a) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 3537. (b) Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1984**, *263*, 55. Abel, E. W.; Clark, N.; Towers, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1552.

[3] (a) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994. (b) Mathey, F.; de Lauzon, G. *Organomet. Synth.* **1986**, *3*, 259.

[4] (a) Mathey, F. *Tetrahedron Lett.* **1976**, 4155. (b) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

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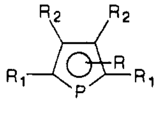
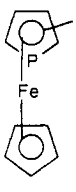
complexes with η^5-phospholyl ligands have been reported for Co,[5] Re,[2c] W,[6] and Zr.[7] In the latter case, the product bis(η^5-3,4-dimethylphospholyl)zirconium dichloride (5) has been prepared in modest yield and only partially characterized. However, a diphosphazirconocene dichloride appeared to us as particularly interesting because of the relevance of cyclopentadienylzirconium compounds in areas such as hydrozirconation[8] and small molecule (N_2 and CO) activation.[9] It has been shown that peralkylation of the cyclopentadienyl ligand can stabilize π-complexes (particularly low-valent ones) of this ligand with zirconium.[10] In order to try to obtain this stabilizing effect with a phosphorus analogue of the peralkyl Cp ligand, we sought to prepare the previously unknown 2,3,4,5-tetramethylphospholyl ligand (**1c**).



1a, $R_1 = H$, $R_2 = H$
b, $R_1 = H$, $R_2 = Me$
c, $R_1 = Me$, $R_2 = Me$



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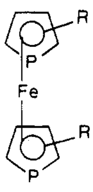

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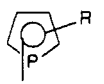

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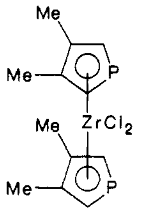

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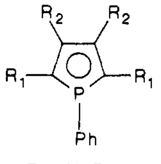
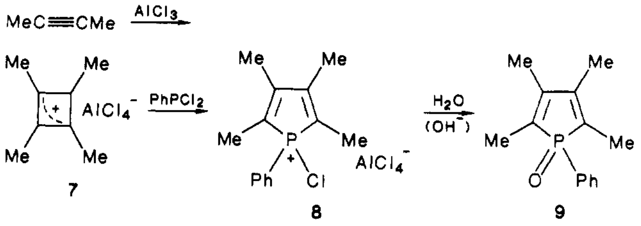


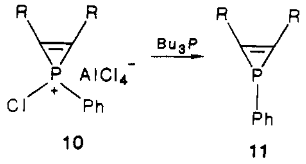
6a, $R_1 = H$, $R_2 = H$
b, $R_1 = H$, $R_2 = Me$
c, $R_1 = Me$, $R_2 = Me$

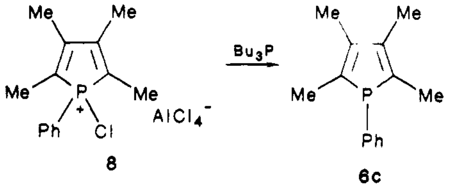
Since phospholyl ligands can be obtained from phenylphospholes **6** by cleavage of the P–Ph bond, we first studied the synthesis of 1-phenyl-2,3,4,5-tetramethylphosphole (**6c**).

Results and Discussion

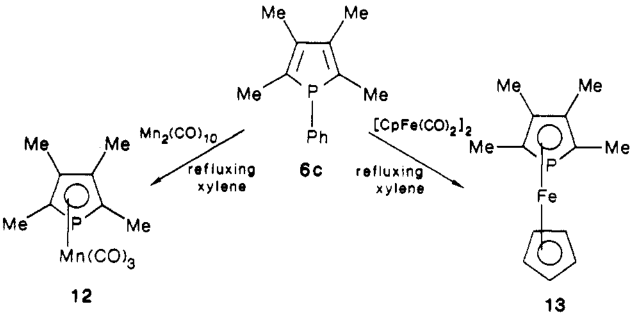
Synthesis of 1-Phenyl-2,3,4,5-tetramethylphosphole (6c). The phosphole **6c** has never been previously prepared. However, the tetramethylphosphole ring structure had already been synthesized by Fongers et al.[11] Reaction of phenylphosphonous dichloride with the cyclobutadiene complex **7** obtained by dimerization of 2-butyne with aluminium chloride led to a chlorophospholium tetrachloroaluminate **8** which was subsequently hydrolyzed to give the phosphole oxide **9**. On the other hand, a mild method for reducing chlorophosphonium tetrachloroaluminates to phosphines has recently been successfully applied to the synthesis of phosphirenes[12] in our laboratory: treatment of chlorophosphirenium salt **10** with a basic phosphine such as tributylphosphine smoothly affords the tervalent phosphirene **11**. Likewise, treatment of salt **8** with Bu_3P efficiently liberates the phosphole **6c** which can be easily extracted from the reaction mixture with hexane. Thus, **6c** can be conveniently prepared from 2-butyne, $AlCl_3$, $PhPCl_2$, and Bu_3P in a one-pot reaction and in fair yield. The crude product was spectroscopically pure and was used thereafter without further purification.







π-Complexes of 1c with Iron and Manganese. In order to test the complexing ability of **1c**, we first tried some known reactions in which this ligand is created by metal-assisted thermal cleavage of the P–Ph bond in **6c**: reactions of **6c** with $Mn_2(CO)_{10}$ and $[CpFe(CO)_2]_2$ in refluxing xylene respectively afford (η^5-2,3,4,5-tetramethylphospholyl)manganese tricarbonyl (**12**) and (η^5-2,3,4,5-tetramethylphospholyl)(η^5-cyclopentadienyl)iron (**13**), respectively, as air-sensitive, crystalline materials in moderate to fair yield after simple chromatographic workup. In particular, no products in which [1,5] phenyl migration had occurred could be detected in crude reaction mixtures containing **13**, in contrast to the reactions of **6a** or **6b** with $[CpFe(CO)_2]_2$ in refluxing xylene.[2b]



We next tried to obtain π-complexes of **1c** by an anionic route, namely, reaction of the 2,3,4,5-tetramethylphospholyl anion **14** with a metal halide. Indeed, treat-

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(10) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Also see: King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155.

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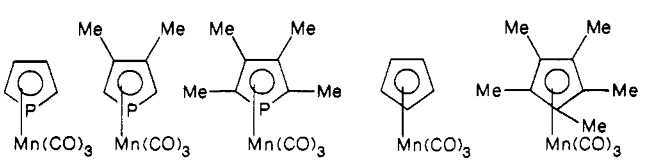
(12) Lochschmidt, S.; Mathey, F.; Schmidpeter, A. *Tetrahedron Lett.* **1986**, *27*, 2635.

(13) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

(14) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773.

Table I. Infrared CO Stretching Frequencies of Phosphacymantrene Complexes 16–19

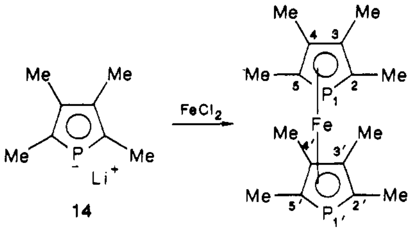


16 17 12 18 19

compd	ν(CO), cm^{-1}	ref
16[a]	2032, 1958, 1954	4a
17[a]	2025, 1953, 1941	4a
12[a]	2009, 1945, 1933	this work
18[b]	2023, 1939	13
19[c]	2017, 1928	14

[a] Decalin. [b] KBr. [c] Hexane.

ment of a THF solution of **6c** by lithium metal leads to cleavage of the P–Ph bond of **6c** to give (tetramethylphospholyl)lithium (**14**), which was not isolated but characterized by its ^{31}P NMR chemical shift at 63 ppm, in the range of other phospholyl anions. THF solutions of **14** in which the phenyllithium also formed by cleavage of the P–Ph bond had been neutralized with $AlCl_3$[3b] were then reacted with iron(II) chloride and gave bis (η^5-2,3,4,5-tetramethylphospholyl)iron (**15**), which was isolated by pentane extraction in fair yield as fairly air-stable, bright red crystals.

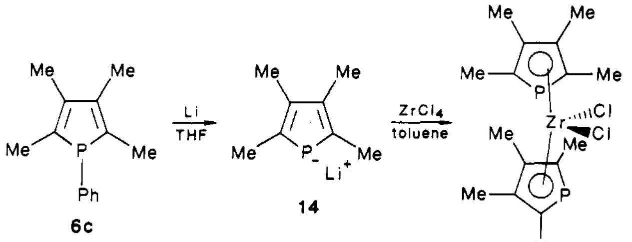


14

15

Spectroscopic Data on the Iron and Manganese Complexes. Compounds **12**, **13**, and **15** display the classical NMR behavior of the phosphametallocenes:[1] the ^{31}P NMR signals of these compounds appear at a typical high-field position and the ^{13}C NMR spectra show that the $^1J_{C_2-P}$ coupling constant falls in the 50–60-Hz range, slightly smaller than in the other known phosphametallocenes, but still very characteristic. The effect of methyl substitution on the properties of the phospholyl ligand can be assessed by comparing the IR carbonyl stretching frequencies of a series of phospholylmanganese tricarbonyl complexes (Table I). The expected low-energy shift of this band from **16** to **17** and **12** is significant and is indicative of the increased electron-donating properties of **1c** with respect to **1a** and **1b**. A similar effect can be found when the ν(C=O)'s in **18** and **19** are compared.

Synthesis and Spectroscopic Properties of Bis(η^5-2,3,4,5-tetramethylphospholyl)dichlorozirconium (20). The synthesis of dichlorozirconocenes classically involves reaction of a cyclopentadienyl anion with zirconium tetrachloride.[15] Compound **5** has already been prepared by allowing (3,4-dimethylphospholyl)magnesium bromide to react with $ZrCl_4$ but was incompletely characterized, as stated above.[7] When a THF solution of phospholyllithium **14** was added to a suspension of $ZrCl_4$ in toluene, an orange solution resulted from which the title compound **20** could be isolated by simple extractive workup in fair yield as fairly air-stable orange crystals which could easily be purified by recrystallization from pentane.



6c 14 20

Proof of the structure originated from the mass spectrum, which displays the molecular peak with an isotopic distribution characteristic of an ion containing $ZrCl_2$, and from the C, H elemental analyses; it was confirmed by an X-ray crystallographic study. The ^{31}P NMR spectrum displays a single peak at +80 ppm which is not in the usual range of phosphametallocenes. This may be due to the strong electron-withdrawing effect of the Zr(IV). The other NMR spectra are less straightforward. In the ^1H spectrum, the methyl groups attached to the carbon atoms α to phosphorus give rise to a complex multiplet, which can be represented as the X part of a $X_6AA'X'_6$ spectrum[16] because of strong coupling between the two phosphorus atoms. Simulation of this multiplet by the PANIC program[17] indicates that the coupling constant between the two phosphorus atoms was as high as 52 Hz, which was more than that has been bound in unsymmetrical diphosphaferrocenes[3a] (10 Hz). The ^{13}C spectrum also shows manifestations of this strong P–P′ coupling; pseudotriplets are observed for C_3 and the methyl attached to C_2. A further complication for the signal of C_2 is that of an isotope effect.[18] The molecule that has a ^{13}C at C_2 on one ring and gives rise to the NMR signal for C_2 does not have a ^{13}C at C'_2 on the other phospholyl ring and so the phosphorus atoms on these rings become chemically inequivalent. Therefore, C_2 resonates as a sextet, characteristic of the X part of an ABX spectrum. One can extract from this sextet an approximate value of 49 Hz for $^1J_{P-C_2}$ which is fully consistent with η^5-coordination of the phospholyl ring in **20**. The difference in the physical properties of **20** and those described for **5** is striking. Whereas **5** is an insoluble air-sensitive powder,[7] **20** is a crystalline, fairly air-stable material (in the solid state) which readily dissolves and can be recrystallized from nonpolar solvents.

Crystal Structure of Compound 20. In the very first attempt to synthesize **20**, a small quantity of naphthalene had been used to initiate the cleavage of the phosphole–exocyclic carbon bond by lithium; this later proved unnecessary for synthetic purposes. The product that was obtained from this first preparation was recrystallized by slow evaporation of a pentane solution at 4 °C, and one of the resulting crystals was used for the crystallographic study because it proved to be of better quality than crystals obtained from preparations where no naphthalene has been used. It turned out that this crystal contained naphthalene and that the composition of the molecule is

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(16) Harris, R. K. *Can. J. Chem.* **1962**, *42*, 2275.

(17) Supplied with the Bruker software package. The PANIC program was not able to simulate the 14-spin $X_6AA'X'_6$ system and a simpler 8-spin $X_3AA'X'_3$ was chosen instead, since it has been shown[16] that in these two systems, the positions (but not intensities) of the most intense lines are not changed.

(18) Pregosin, P. S.; Kunz, R. W. *NMR Basic Princ. Prog.* **1979**, *16*, 68.

Table II. Crystal Data and Data Collection Parameters

empirical formula	$C_{16}H_{24}Cl_2P_2Zr\cdot{}^1/_2C_{10}H_8$
fw	504.52
cryst system	triclinic
space group	$P\bar{1}$
a, Å	7.852 (1)
b, Å	8.687 (2)
c, Å	17.123 (2)
α, deg	92.32 (1)
β, deg	102.55 (1)
γ, deg	79.55 (2)
V, Å^3	1121.2 (5)
Z	2
cryst size, mm	0.10 × 0.30 × 0.32
μ(Mo Kα), cm^{-1}	59.25
D_{calcd}, g/cm^3	1.49
temp, °C	20
radiatn	Mo K α (graphite monochromator)
scan range θ, deg	$(1 + 0.345 \tan\theta)°$
2θ range, deg	$2 \leqslant 2\theta \leqslant 25$
scan type	$\omega/1.33\theta$
standard	2, −436, −3, −310
reflcns collected	4099
reflcns merged	3954
reflcns obsd	3296
criteria	$I > 3\sigma(I)$
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0229
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.0244 (unit wt)
final shift/error max (av)	0.13 (0.05)

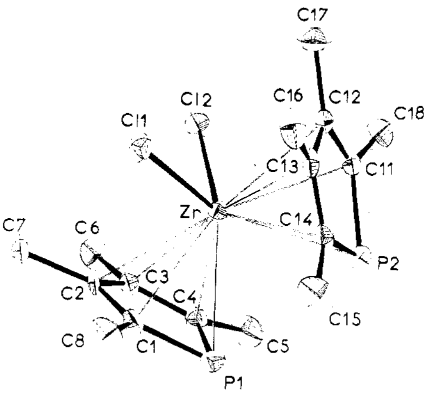

Figure 1. ORTEP plot of one molecule of **20** together with the numbering scheme used. Hydrogen atoms are omitted.

Table III. Atomic Coordinates for the Non-Hydrogen Atoms

atom	x/a	y/b	z/c	U(eq),[a] Å^2
Zr	−0.13948 (3)	−0.23740 (3)	−0.27892 (1)	0.0299 (1)
Cl1	−0.3386 (1)	−0.0844 (1)	−0.20227 (4)	0.0526 (3)
Cl2	−0.2739 (1)	−0.47081 (9)	−0.28592 (4)	0.0501 (3)
P1	0.2079 (1)	−0.2064 (1)	−0.24063 (5)	0.0467 (3)
P2	−0.0478 (1)	−0.1947 (1)	−0.42081 (4)	0.0430 (3)
C1	0.1012 (4)	−0.1604 (3)	−0.1607 (2)	0.0412 (9)
C2	0.0502 (3)	−0.2903 (3)	−0.1327 (1)	0.0367 (6)
C3	0.0938 (3)	−0.4276 (3)	−0.1768 (2)	0.0379 (6)
C4	0.1686 (4)	−0.4001 (3)	−0.2404 (2)	0.0411 (9)
C5	0.2299 (5)	−0.5252 (5)	−0.2970 (2)	0.066 (1)
C6	0.0760 (5)	−0.5873 (4)	−0.1528 (2)	0.058 (1)
C7	−0.0250 (5)	−0.2891 (5)	−0.0592 (2)	0.059 (1)
C8	0.0830 (6)	−0.0021 (4)	−0.1220 (3)	0.069 (2)
C11	−0.2466 (4)	−0.2670 (3)	−0.4351 (1)	0.0375 (9)
C12	−0.3822 (3)	−0.1622 (3)	−0.4104 (1)	0.0385 (9)
C13	−0.3261 (4)	−0.0198 (3)	−0.3807 (2)	0.044 (1)
C14	−0.1481 (4)	−0.0213 (3)	−0.3788 (2)	0.045 (1)
C15	−0.0550 (7)	0.1165 (5)	−0.3546 (3)	0.075 (2)
C16	−0.4534 (6)	0.1218 (5)	−0.3620 (2)	0.075 (2)
C17	−0.5685 (4)	−0.1895 (5)	−0.4199 (2)	0.062 (1)
C18	−0.2683 (5)	−0.4223 (4)	−0.4745 (2)	0.056 (1)
C19	0.4933 (5)	0.7127 (4)	−0.0162 (2)	0.062 (1)
C20	0.4441 (5)	0.7746 (5)	0.0513 (2)	0.068 (1)
C21	0.4136 (5)	0.6785 (5)	0.1082 (2)	0.070 (1)
C22	0.4344 (4)	0.5220 (5)	0.0982 (2)	0.061 (1)
C23	0.4848 (4)	0.4521 (4)	0.0293 (2)	0.049 (1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter U(eq) defined as $U(\text{eq}) = (a^2b^2c^2/3V^2)\,[U_{11}(\sin\alpha)^2 + U_{22}(\sin\beta)^2 + U_{33}(\sin\gamma)^2 + 2U_{12}\sin\alpha\sin\beta\cos\gamma + 2U_{13}\sin\alpha\sin\gamma\cos\beta + 2U_{23}\sin\beta\sin\gamma\cos\alpha]$

Table IV. Selected Bond Lengths (Å) and Angles (deg)

Bond Lengths			
Zr–Cl1	2.4351 (7)	P2–C14	1.770 (3)
Zr–Cl2	2.4373 (7)	C1–C2	1.399 (4)
Zr–P1	2.7233 (8)	C1–C8	1.499 (4)
Zr–P2	2.7365 (7)	C2–C3	1.414 (4)
Zr–C1	2.608 (3)	C2–C7	1.502 (4)
Zr–C2	2.631 (2)	C3–C4	1.393 (4)
Zr–C3	2.624 (3)	C3–C6	1.501 (4)
Zr–C4	2.535 (3)	C4–C5	1.509 (4)
Zr–C11	2.641 (2)	C11–C12	1.398 (4)
Zr–C12	2.632 (3)	C11–C18	1.504 (4)
Zr–C13	2.629 (3)	C12–C13	1.425 (4)
Zr–C14	2.572 (3)	C12–C17	1.497 (4)
P1–C1	1.751 (3)	C13–C14	1.389 (4)
P1–C4	1.765 (3)	C13–C16	1.508 (4)
P2–C11	1.751 (3)	C14–C15	1.512 (4)
Bond Angles			
Cl2–Zr–Cl1	94.90 (3)	C14–P2–C11	89.9 (1)
C4–P1–C1	89.8 (1)	C12–C11–P2	113.0 (2)
C2–C1–P1	112.6 (2)	C18–C11–P2	122.4 (2)
C8–C1–P1	123.1 (3)	C13–C12–C11	111.9 (2)
C3–C2–C1	112.3 (2)	C17–C12–C13	123.4 (3)
C7–C2–C3	123.3 (3)	C14–C13–C12	112.8 (2)
C4–C3–C2	112.6 (2)	C16–C13–C12	122.6 (3)
C6–C3–C2	123.3 (3)	C13–C14–P2	112.2 (2)
C3–C4–P1	112.2 (2)	C15–C14–P2	122.9 (3)
C5–C4–P1	123.2 (3)		

in fact $C_{16}H_{24}P_2ZrCl_2\cdot{}^1/_2C_{10}H_8$. Crystal data and data collection parameters are listed in Table II. Table III gives the atomic coordinates for the non-hydrogen atoms. Table IV lists selected bond lengths and angles, and Figure 1 displays on ORTEP plot of one molecule. Each zirconium is sandwiched between two phospholyl ligands (L_1 and L_2) and bonded to two chlorine atoms. The P_1 and C_1–C_4 atoms of L_1 and P_2 and C_{12}–C_{14} of L_2 are planar within experimental error. The P–C bonds of L_1 and L_2 have values similar to those in other phospholyl complexes such as phosphaferrocene (PF) (1.76 Å),[2a] diphosphaferrocene (DPF),[3a] and phosphacymantrene (PC) (1.77 Å).[4b] The intracyclic P–C bonds of L_1 and L_2 also have similar values in DPF (1.41 Å) and PC (1.42 Å), as do the average C–C–C and C–C–P intracyclic angles (DPF and PC, 112.9°). The CPC intracyclic angle is slightly larger than in DPF, PC, and PF (88.2°, 88.5°, and 88.4°, respectively). The methyl carbons C_6, C_7 and C_{16}, and C_{17} do not lie in the L_1 and L_2 planes: they bend slightly away from zirconium. The L_1 and L_2 rings are in staggered configuration, as in Cp_2ZrCl_2.[19] The closest intra-ring atomic distance is that of P_1 to P_2, yet at 3.23 Å this distance indicates no significant interaction between the two phosphorus atoms. The conformation adopted by the molecule in the crystal thus may result from minimization of steric interactions between the L_1, L_2, and $ZrCl_2$ moiety. The Zr–C_1 to C_4 and Zr–C_{11} to C_{14} bonds are longer than in Cp_2ZrCl_2 (2.42 Å). The Zr–P bond is longer than the Zr–C_1 to C_4 and Zr–C_{11} to C_{14} bonds; the same is true for the M–P compared to the M–C(ring) bonds of other phosphametallocenes. The geometry around Zr is that of a distorted tetrahedron, if one considers the values of the Cl–Zr–Cl (94.9°) and centroïd L_1–Zr–centroïd L_2 (131.6°) angle. The Zr–Cl

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[19] Prout, K.; Cameron, T. S.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr. Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2290.

distances are equal to 2.44 Å. All these values fall in the normal range for d^0 $(\eta^5\text{-L})_2ZrX_2$ compounds.[15,20] In brief, complex **20** has the normal expected features of a η^5-phospholyl complex and of a $(\eta^5\text{-L})_2ZrX_2$ complex.

Experimental Section

All reactions were performed with dry solvents under dry, oxygen-free nitrogen. NMR experiments were done with a Bruker AC200SY spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C and with a Bruker WP80SY spectrometer functioning at 32.44 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC–MS 1000 by the direct inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif-sur-Yvette, France. Silica gel (70–230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers.

1-Phenyl-2,3,4,5-tetramethylphosphole (6c). The first step of this synthesis (preparation of chlorophospholium tetrachloroaluminate (**8**)) is essentially identical with the procedure of Fongers et al.[11] A solution of 2-butyne (17.44 g, 0.32 mol) in CH_2Cl_2 (250 mL) was added during 20 min to a solution of anhydrous $AlCl_3$ (22.7 g, 0.17 mol) in CH_2Cl_2 (250 mL) cooled at 0 °C. The dark reddish brown reaction mixture was stirred at 0 °C for 30 min, then allowed to warm to room temperature, stirred for a further 30 min, and then cooled to –50 °C. A solution of $C_6H_5PCl_2$ (31.7 g, 0.18 mol) in CH_2Cl_2 (350 mL) was added to the reaction mixture during the course of 20 min. The dark red solution was allowed to warm up to room temperature and stirred for 1 h. The phospholium salt **8** can now be reduced as follows: the reaction mixture was added over 20 min to a cold (–30 °C) solution of tri-*n*-butylphosphine (39 mL, 48 g, 0.24 mol) in 350 mL of CH_2Cl_2. After being warmed to room temperature, the light yellow reaction mixture was evaporated to dryness and the resulting oil extracted with 4 × 150 mL of hexane. The hexane phase was washed with dilute $NaHCO_3$ solution and then with water, dried with $MgSO_4$, and evaporated to dryness, yielding 23.8 g (0.11 mol, 68%) of crude spectroscopically pure **6c** as a colorless, air-sensitive oil, which was used without further purification in the following syntheses; it can be distilled, however, at 105–110 °C (0.5 mm). An analytical sample was freshly redistilled. NMR: ^1H ($CDCl_3$) δ 1.93 (ps q, CH_3C_2 and CH_3C_3, $^4J_{PH}$ = 3.6 Hz for CH_3C_3 and $^3J_{PH}$ = 10.0 Hz for CH_3C_2), 7.27 (m, C_6H_5); ^{13}C ($CDCl_3$) δ 12.71 (d, $^2J_{PC}$ = 22.2 Hz, CH_3C_2), 13.86 (d, $^3J_{PC}$ = 3 Hz, CH_3C_3), 128.50 (d, $^3J_{PC}$ = 8 Hz, C meta), 128.86 (s, C para), 123.40 (d, $^2J_{PC}$ = 18.6 Hz, C ortho), 135.10 (s, C_3), 142.84 (d, $^1J_{PC}$ = 11 Hz, C_2), C ipso was not detected; ^{31}P ($CDCl_3$) δ 12.71. Mass spectrum: *m/e* (relative intensity) 216 (M^+, 100). Anal. Calcd for $C_{14}H_{17}P$: C, 77.75; H, 7.92. Found: C, 76.91; H, 7.95.

(2,3,4,5-Tetramethylphospholyl)lithium (14). A solution of phosphole **6c** (1 molar equiv) in THF was treated with lithium foil[21] (3–4 molar equiv) for 2–3 h. The excess of lithium was removed, and a ^{31}P spectrum of the dark red solution displayed a signal at 63 ppm, attributed to **14**. Phenyllithium, which was formed together with **14**, can be neutralized as follows: the reaction mixture was cooled to 0 °C and anhydrous $AlCl_3$ ($^1/_3$ equiv) was added.[3b] After 30 min of stirring at 0 °C, the light red solution, which contains 1 equiv of **14** and $^1/_3$ equiv of $(C_6H_5)_3Al$ was used for the following syntheses.

Bis(η^5-2,3,4,5-tetramethylphospholyl)iron (15). To a cold (0 °C) solution of **14** prepared as described above from 2.3 g (10.6 mmol) of **6c** in THF (30 mL) was added $FeCl_2$ (680 mg, 5.36 mmol). After 30 min of stirring at room temperature, the dark brown reaction mixture was evaporated to dryness and the residue extracted with diethyl ether. The ether solution was evaporated to dryness and extracted with pentane and the pentane extract evaporated to dryness, yielding 1.14 g (3.41 mmol, 64%) of crude **14** as fairly air-stable, bright red crystals. An analytical sample was recrystallized from pentane at –20 °C; mp 120 °C dec. NMR: ^1H (C_6D_6) δ 1.65 (d, $^3J_{PH}$ = 9.4 Hz, CH_3C_2), 1.83 (s, CH_3C_3); ^{13}C (C_6D_6) δ 12.67 (s, CH_3C_3), 14.12 (d, $^2J_{PC}$ = 24.4 Hz, CH_3C_2), 94.02 (d, $^1J_{PC}$ = 55.2 Hz, C_2), 95.10 (s, C_3); ^{31}P (C_6D_6) δ –58.52. Mass spectrum: *m/e* (relative intensity) 334 (M^+, 100). Anal. Calcd for $C_{16}H_{24}FeP_2$: C, 57.51; H, 7.24. Found: C, 57.47; H, 7.09.

(η^5-Cyclopentadienyl)(η^5-2,3,4,5-tetramethylphospholyl)-iron (13). A mixture of phosphole **6c** (5.0 g, 23.12 mmol) and $[CpFe(CO)_2]_2$ (8 g, 22.6 mmol) was heated in refluxing xylene (70 mL) for 8 h. The cooled reaction mixture was filtered on a silica gel column packed in toluene. The first fraction, which contained the product and a small amount of unreacted $[CpFe(CO)_2]_2$, was collected and evaporated to dryness and the residue further chromatographed in hexane. A small amount of ferrocene was first eluted, followed by a major orange band, which was collected and evaporated to dryness, yielding 2.05 g (7.88 mmol, 34%) of **13** as orange-brown, air-sensitive crystals. An analytical sample was recrystallized from pentane at –20 °C; mp 70 °C. NMR: ^1H ($CDCl_3$) δ 1.74 (d, $^3J_{PH}$ = 8.8 Hz, CH_3C_2), 2.13 (s, CH_3C_3), 3.97 (s, Cp); ^{13}C ($CDCl_3$) δ, 13.82 (d, $^2J_{PC}$ = 18.3 Hz, CH_3C_2), 14.01 (s, CH_3C_3), 72.44 (s, Cp), 90.61 (d, $^1J_{PC}$ = 55.2 Hz, C_2), 93.71 (d, $^2J_{PC}$ = 3.7 Hz, C_3), ^{31}P ($CDCl_3$) δ –70.96. Mass spectrum: *m/e* (relative intensity) 260 (M^+, 100). Anal. Calcd for $C_{13}H_{17}FeP$: C, 60.03; H, 6.59. Found: C, 59.91; H, 6.31.

(η^5-2,3,4,5-Tetramethylphospholyl)tricarbonylmanganese (12). A solution of phosphole **6c** (1.45 g, 6.7 mmol) and $Mn_2(CO)_{10}$ (2.6 g, 6.7 mmol) in xylene (25 mL) was refluxed for 3.5 h. It was then filtered on Celite, evaporated to dryness, and chromatographed (hexane). A small amount of unreacted $Mn_2(CO)_{10}$ was first eluted, followed by a yellow band which was collected and evaporated to dryness, yielding 760 mg (2.73 mmol, 41%) of **12** as air-sensitive, yellow crystals. An analytical sample was recrytallized from pentane at –20 °C: mp 57 °C. NMR: ^1H (C_6D_6) δ 1.43 (d, $^3J_{PC}$ = 9.7 Hz, CH_3C_2), 1.56 (s, CH_3C_3); ^{13}C (C_6D_6) δ 12.35 (s, CH_3C_3), 14.16 (d, $^2J_{PC}$ = 22.16 Hz, CH_3C_2), 109.40 (d, $^2J_{PC}$ = 5.6 Hz, C_3), 111.40 (d, $^1J_{PC}$ = 58.3 Hz, C_2), 225.0 (br s, CO). Mass spectrum: *m/e* (relative intensity) 278 (M^+, 40), 196 (M^+ – 3CO, 100). IR (decalin): ν (C=O) 2009 (s), 1945 (s), 1933 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{12}MnO_3P$: C, 47.50; H, 4.35. Found: C, 47.43; H, 4.10.

Bis(η^5-2,3,4,5-tetramethylphospholyl)dichlorozirconium (20). A solution of **14** prepared as described above from 2.27 g (10.5 mmol) of phosphole **6c** in 50 mL of THF was slowly added (cannula) to a stirred suspension of $ZrCl_4$ (1.17 g, 5.02 mmol) in toluene (15 mL) at 0 °C. The orange reaction mixture was evaporated to dryness and then extracted with 100 mL of diethyl ether. The ether extract was evaporated to dryness and the residue taken up in pentane and evaporated to dryness, yielding 1.32 g (3.22mmol, 59%) of **20** as fairly air-stable orange crystals. An analytical sample was recrystallized in pentane at –20 °C; mp 120 °C dec; NMR (see text): ^1H (CD_2Cl_2) δ 2.10 (s, CH_3C_3), 2.15 (m, $^3J_{HP} \approx 10.5$ Hz, CH_3C_2); ^{13}C (CD_2Cl_2) δ 17.27 (s, CH_3C_3), 17.95 (ps t, $^2J_{PC}$ = 28.5 Hz, CH_3C_2), 144.77 (ps t, $^2J_{PC}$ = 5.3 Hz, C_3), 146.30 (sextet, $^1J_{PC} \approx 49$ Hz, C_2); ^{13}P (CD_2Cl_2) δ 87.10. Mass spectrum: *m/e* (relative intensity) 440 (M^+, 97), 301 (M – phospholyl, 100). Anal. Calcd for $C_{16}H_{24}Cl_2P_2Zr$: C, 43.63; H, 5.49. Found: C, 43.72; H, 5.46.

X-ray Crystal Data. Accurate cell dimensions and symmetry information were obtained by using a selected crystal on an Enraf-Nonius CAD4 diffractometer from the setting angles of 25 reflections. No variation of the two standard reflections was observed during data collection. Corrections were made for Lorentz and polarization effects. Absorption corrections were then applied on the basis of scan curves via an empirical technique.[22] Computations were performed by using the CRYSTALS[33] system adapted on a VAX 11/725 computer. The positions of all non-hydrogen atoms were determined by using standard Patterson and Fourier techniques. Hydrogen atoms were located on a difference electron density map. All non-hydrogen atoms were refined anisotropically. The hydrogen atomic coor-

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(23) Carruthers, B.; Watkin, D. W. J. CRYSTALS; Chemical Crystallography Laboratory, University of Oxford: Oxford, England.

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dinates were refined with a constraint on the isotropic thermal parameter shift until a criteria for a satisfactorily completed analysis were met.

Registry No. **6e**, 112549-07-2; **8**, 87322-31-4; **12**, 112549-04-9; **13**, 112549-03-8; **14**, 112549-01-6; **15**, 112549-02-7; **20**, 112549-05-0; **20**·naphthalene, 112549-06-1; $C_6H_5PCl_2$, 644-97-3; $FeCl_2$, 7758-94-3; $[CpFe(CO)_2]_2$, 12154-95-9; $Mn_2(CO)_{10}$, 10170-69-1; $ZrCl_4$, 10026-11-6; 2-butyne, 503-17-3.

Supplementary Material Available: A listing of anisotropic thermal parameters and hydrogen atomic coordinates (2 pages); tables of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Metal–Hydride and Metal–Alkyl Bond Strengths: The Influence of Electronegativity Differences

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Relative metal–alkyl and metal–hydride bond strengths are analyzed in terms of the electronegativity differences between the metal center and carbon or hydrogen. The greater strength of transition metal–hydride bonds in most complexes reflects a high effective electronegativity of the metal center. Arguments are presented that as the effective electronegativity of the metal center decreases (i.e. as the metal center becomes more electropositive), $D(M-H) - D(M-CH_3)$ also decreases.

There has been considerable recent interest in establishing trends in metal–ligand bond strengths[1,2] with a primary goal of developing predictive power for assessing the viability of catalytic reaction cycles. A question of primary importance is the relative strengths of the L_nM-H and L_nM-C bonds, a crucial factor in the energetics of processes such as hydrogenation and the activation of the C–H and C–C bonds of hydrocarbons. It is generally recognized that the L_nM-H bond is stronger than the L_nM–alkyl bond by an amount estimated to fall within the range of 15–25 kcal·mol^{-1}. The reason for this difference is not clear. Halpern has suggested that steric factors contribute to weakening the metal–alkyl bond[2] and points to the fact that for the binary, ligand-free neutral or cationic species $[M-R]^{0/+}$ (R = H, CH_3, etc.), the metal–alkyl bond is generally as strong as or stronger than M–H.[3]

An observation which at first sight appears to be consistent with the above is the apparent one-to-one correspondence between L_nM-X and H–X bond energies: for a variety of transition-metal compounds (L_nM-X = $(\eta^5-C_5Me_5)(PMe_3)_2Ru-X$, $(Ph_2PCH_2CH_2PPh_2)(CH_3)Pt-X$, $(\eta^5-C_5Me_5)_2Sc-X$, etc.) good linear correlations are obtained for plots of the bond energies for H–X against those for the corresponding L_nM-X (in the absence of M–X multiple bonding), *with the exception of the point for X = H*, which consistently falls off the line in the direction of stronger L_nM-H.[4] In these cases the implied "extra" stability of the L_nM-H bond is 5–10 kcal·mol^{-1}, again suggesting that there is some factor which makes the M–H bond particularly strong in such complexes. On the other hand, plots of the bond energies for H–X versus those for R–X show exactly the same trend (see Figure 1 for R = CH_3); the point for X = H is displaced in the direction of stronger R–H from an otherwise linear correlation for a range of different R's (hydrocarbyl, halogen, etc.). Since it is difficult to justify that the R–H bond is anomalously strong for all such R's, it occurred to us that the correlation may fail at X = H because the H–H bond strength is in fact anomalously weak! H–H is the only homonuclear bond in these plots, so that a possible explanation is that all other bonds enjoy a larger ionic contribution due to electronegativity differences,[5] causing H–H to be weaker relative to R–H than all other H–X relative to R–X. A closer examination of the data reveals that the difference in R–X (R = alkyl) and H–X bond energies increases with increasing electronegativity for X.

We have thus attempted to relate L_nM-H and L_nM-C bond strengths to effective electronegativity differences. The original Pauling equation relating bond strength and electronegativity is given in (1).[6] When this formula is

$$D(A-B) = \tfrac{1}{2}\{D(A-A) + D(B-B)\} + a(\chi_A - \chi_B)^2 \quad (1)$$

applied to the difference between A–H and A–CH_3 bond strengths (Δ), the expression in (2) is obtained. Thus a

$$\Delta \equiv D(A-H) - D(A-CH_3) = 2a(\chi_C - \chi_H)\chi_A + \tfrac{1}{2}\{D(H-H) - D(CH_3-CH_3)\} + a\{(\chi_H)^2 - (\chi_C)^2\} \quad (2)$$

plot of Δ versus χ_A should be linear, with A–H becoming relatively stronger than A–CH_3 as A becomes more electronegative. This conclusion follows from the fact that the

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† Contribution No. 7730.

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[6] The value of the empirical constant (a) is 23 kcal·mol^{-1} in the original Pauling relationship. Revised values of electronegativities utilized a geometric mean of homonuclear bond energies and a constant of 30 kcal·mol^{-1}, but these values do not differ substantially from the original ones (see ref 5). A reviewer has pointed out that Pauling's approach to bond strengths is an approximation which in some cases can fail completely (see, for example: Pearson, R. G. *J. Chem. Soc., Chem. Commun.* **1968**, 65). While this criticism has some validity, the good correlation represented by Figure 2 demonstrates that in the present case this method is applicable at least to some degree.

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