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Reactivity of a diphosphazirconocene dichloride, $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2$. Crystal and molecular structure of a metal-bridged bis(π-heterocyclopentadienyl)zirconium complex, $(CO)_3Fe(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)_2ZrCl_2$

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Abstract

Reaction at the Zr centre in $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2$ (**1**) is exemplified by the reaction with MeLi or PhLi to give $(\eta^5\text{-}C_4Me_4P)_2ZrR_2$, with R = Me or Ph. Complex **1** can also react through the lone pair on the P atom with $L_2M(CO)_n$ to give chelates $(CO)_nM(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)_2ZrCl_2$ where $M(CO)_n = Fe(CO)_3$ or $W(CO)_4$, in which a new type of bridging η^5-ligand is present. The crystal structure of $(CO)_3Fe(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)_2ZrCl_2$ is described.

Introduction

We recently prepared the first structurally characterized diphosphazirconocene dichloride **1** [1]. We have now proceeded to a study of some chemical properties of this compound, namely the reactivity at the zirconium atom, and also an examination of the reactivity of the phosphorus lone pair in **1** which is not engaged in bonding and should be available for reaction with an unsaturated organometallic residue.

Results and discussion

Reactivity at zirconium

Alkyl and aryl cyclopentadienylzirconium compounds are precursors of a wide range of interesting compounds, such as olefin polymerization catalysts [2] and "zirconocene" [3,4] derivatives. Thus we examined the reaction of **1** with methyl- and phenyl-lithium and obtained the expected dimethyl- and diphenyl-diphosphazirconocenes (respectively **2** and **3**) in fair yield as thermally stable air-sensitive yellowish crystals (Scheme 1).

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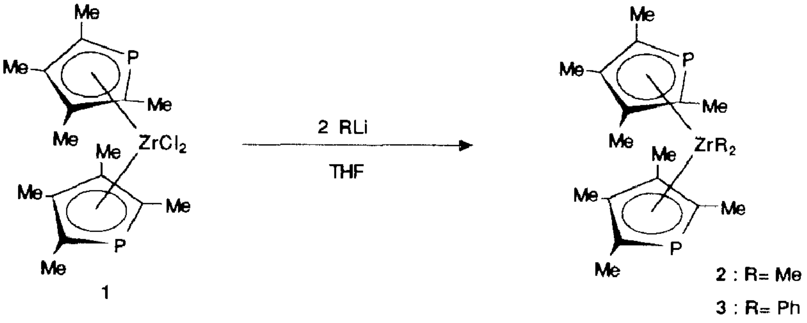


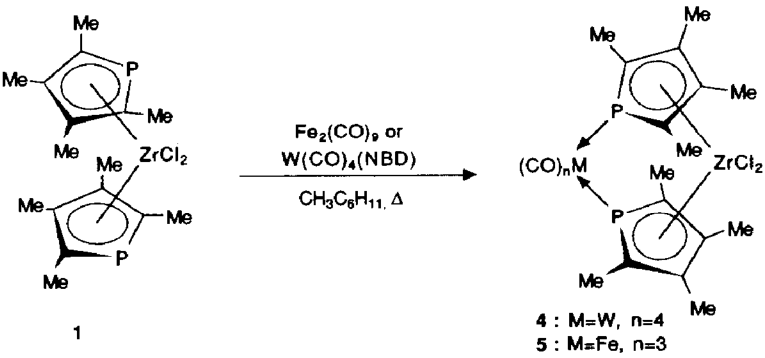
Scheme 1

The products were characterized by mass spectroscopy and by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The NMR data are very similar to those for **1**. In the case of **2**, methyl signals appear at -0.62 ppm in the ^1H spectrum and at 38.1 ppm in the ^{13}C spectrum. This clearly indicates that the methyl groups are bonded to zirconium. In the ^{13}C spectrum of **3**, the resonance of the *ipso* carbon bonded to Zr is located at 191.8 ppm, a position similar to that for $(\eta^5\text{-}C_5Me_5)_2ZrPh_2$ [4]. At 20 °C, the signals of the *meta* and *ortho* carbons are broad, and furthermore the *ortho* carbons are inequivalent, indicating restricted rotation around the C–Zr bond due to steric hindrance by the methyl groups. A similar effect has previously been noted for $(\eta^5\text{-}C_5Me_4H)_2ZrPh_2$ [5]. The ^1H and ^{13}C signals are also complicated by second-order effects due to coupling between the two magnetically inequivalent P atoms, as it is the case for **1** [1]. Treatment of **1** with either $LiAlH_4$ or $LiAlH(O\text{-}t\text{-}Bu)_3$ in the expectation of obtaining diphosphazirconocene hydrides gave only intractable mixtures.

Reactivity at phosphorus

The availability of the P atom lone pair on the phospholyl ligand of phospha- and diphospha-metallocenes has been established previously by preparation of heterobimetallic complexes [6,7]. In diphosphaferrocenes, the two phospholyl rings are planar and parallel, and the P atom lone pairs are located in these planes, and so it would be difficult to chelate another metal through the P atoms without substantial distortion of the diphosphaferrocene geometry. In contrast, the crystal structure of **1** showed that the phospholyl ring planes dihedral angle is 48° and that the lone pairs are pointing towards each other [1], so that chelation could take place, and so we treated **1** with (norbornadiene)$W(CO)_4$ and $Fe_2(CO)_9$. When a solution of equimolecular amounts of **1** and (NBD)$W(CO)_4$ in methylcyclohexane was heated, ^{31}P NMR analysis of the reaction mixture showed progressive disappearance of **1** and the growth of a new singlet at 34 ppm with ^{183}W satellites, and these came from chelate **4** (Scheme 2), which was obtained in fair yield.

The reaction of **1** with $Fe_2(CO)_9$ was more complex. At room temperature, **1** is converted into a compound in which only one P atom is complexed with $Fe(CO)_4$, as indicated by an AX quartet in the ^{31}P spectrum. When the temperature is raised, this signal weakens and a singlet at 71 ppm, corresponding to chelate **5** (Scheme 2) appears, together with signals from many unidentified impurities, and so **5** was obtained only in low yield. Evidence for a chelate structure for **4** and **5** stems mainly from their mass spectra and elemental analysis, which show the molecule to be



Scheme 2

monomeric, from the X-ray crystallographic study of **5** (see below), and from the NMR data. The ^{31}P singlet indicates that the molecule is symmetrical. In the ^{13}C spectra, the ^{1}J(PC) coupling constant falls from ≈ 50 Hz for **2** and **3** to less than 10 Hz for **4** and **5**, this effect has been noted in other μ-η^5,η^1 phospholyl complexes [7]. Although air-sensitive in solution, **4** and **5** seem to be air-stable in the solid state.

Crystal and molecular structure of 5

A suitable crystal was obtained by crystallization from warm dichloromethane. Crystal data and data collection parameters are listed in Table 1. Table 2 gives the atomic coordinates for the non-hydrogen atoms, and Table 3 lists selected bond lengths and angles for **5**. Figure 1 presents an ORTEP plot of a molecule of **5**, showing the chelate structure. The geometry around the iron atom is that of a trigonal bipyramid, with the two phosphorus atoms in the *cis* configuration, one in an axial and the other in an equatorial position. This trigonal bipyramid is distorted, however, as indicated by the angles P1–Fe–P2 (80.9° instead of 90°) and C18–Fe–P1 (171.1° instead of 180°). The other angles around Fe are also different from the theoretical values, but not much more than in simple phosphine complexes such as (Ph$_3$P)Fe(CO)$_4$ [8] or (Ph$_2$PH)Fe(CO)$_4$ [9]. The P–Fe and Fe–C bond in **5** are shorter than in these complexes, and are more like those found in (dpe)Fe(CO)$_4$ [10]. Thus the bonding situation in **5** and in this last complex are similar, the iron ligands both having a small "bite" that puts strain on the trigonal bipyramid structure. The strain on the molecule is also evidenced by the increased dihedral angle between the two phospholyl ring planes (52.56°) and the smaller centroid–Zr–centroid angles in **5** compared with that in the free "ligand" **1** [1]. This centroid–Zr–centroid angle can be compared with those in other *ansa*-zirconocene dichlorides, and the nearest value we found is that for η^5-$\{$(C$_5$Me$_4$)$_2$C$_2$H$_4\}$ZrCl$_2$ (127.7°) [11]. Other compounds have either higher (η^5-$\{$(C$_5$H$_4$)$_2$C$_3$H$_6\}$ZrCl$_2$, 129° [12]) or lower values ($\eta^5\{$(C$_5$H$_4$)$_2$SiMe$_2\}$ZrCl$_2$, 125.4° [13], η^5-$\{$Me$_4$C$_2$(1-C$_5$H$_3$-3-CMe$_3$)$_2\}$ZrCl$_2$, 124.8° [14]) for this angle. In the molybdenum-bridged bis(phosphinocyclopentadienyl)zirconium complex (CO)$_4$Mo$\{\mu$-η^1,η^5(C$_5$H$_4$PPh$_2$)$\}$ZrCl$_2$ [15], the centroid–Zr–centroid angle is similar to that in Cp$_2$ZrCl$_2$. There is little difference between the phospholyl rings geometry in **5** and those in other η^5-phospholyl complexes, except for the C–P–C angle: its mean value (92.1°) is somewhat larger than in the other complexes (≈ 89°) [16]. The Fe–Zr distance, although

Table 1

Crystal data and details of data collection

Empirical formula	$C_{19}H_{24}Cl_2FeO_3P_2Zr$
FW	580.29
Cryst. system	triclinic
Space group	$P\bar{1}$
a, Å	9.303(1)
b, Å	10.249(1)
c, Å	12.641(1)
α, deg.	96.78(1)
β, deg.	93.69(1)
γ, deg.	108.79(1)
Z	2
Crystal size, mm.	0.12×0.12×0.20
ρ calcd, g cm^{-3}	1.711
Radiation	Mo-K_α
Monochromator	graphite
μ (Mo-K_α), cm^{-1}	15.0
Temp °C	18 ± 1
2θ max.	60 °
Scan type	$\Omega/2\theta$
Unique refl.	6528
Refl. with $F_o > 3\sigma(F_o)$	4507
Unweighted R	0.033
Weighted R	0.048
esd of unit weight	1.05
Shift/error max.	0.00

shorter than the metal–metal distance in $(CO)_4Mo\{\mu\text{-}\eta^1,\eta^5(C_5H_4PPh_2)\}ZrCl_2$ (4.8524 Å) [15], still rules out any significant bonding interaction between the Fe and Zr metal centers.

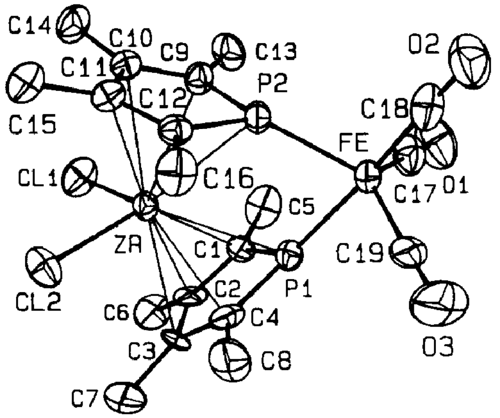


Fig. 1. ORTEP plot of one molecule of **5**, together with the numbering scheme adopted. Ellipsoids are scaled to enclose 30% of the overall electronic density.

Table 2

Positional parameters and their estimated standard deviations [a]

Atom	x	y	z	B (Å^2)
Zr	0.21711(3)	0.38491(3)	0.70396(2)	2.203(5)
Fe	0.23951(5)	0.04572(4)	0.82745(3)	2.478(8)
Cl1	0.3654(1)	0.53396(9)	0.58927(7)	3.94(2)
Cl2	0.02983(9)	0.50086(9)	0.73152(8)	3.95(2)
P1	0.14090(8)	0.09918(7)	0.68253(6)	2.39(1)
P2	0.32744(8)	0.27315(7)	0.86658(6)	2.31(1)
O1	0.4380(4)	−0.0804(3)	0.7139(3)	5.85(7)
O2	0.3454(3)	0.0020(3)	1.0387(2)	4.80(6)
O3	−0.0630(4)	−0.1294(4)	0.8657(3)	7.07(9)
C1	0.2239(4)	0.1744(3)	0.5740(3)	2.89(6)
C2	0.1225(4)	0.2257(3)	0.5187(3)	3.25(7)
C3	−0.0098(4)	0.2190(3)	0.5695(3)	3.33(7)
C4	−0.0129(3)	0.1597(3)	0.6666(3)	2.85(6)
C5	0.3678(4)	0.1623(4)	0.5333(3)	4.06(8)
C6	0.1501(6)	0.2729(4)	0.4112(3)	5.0(1)
C7	−0.1421(5)	0.2571(5)	0.5227(4)	5.19(9)
C8	−0.1424(4)	0.1341(4)	0.7352(3)	4.02(8)
C9	0.4673(3)	0.3986(3)	0.8106(2)	2.49(5)
C10	0.4557(3)	0.5329(3)	0.8380(3)	2.60(6)
C11	0.3271(3)	0.5303(3)	0.8918(2)	2.57(5)
C12	0.2384(3)	0.3946(3)	0.9078(2)	2.41(5)
C13	0.5964(4)	0.3716(4)	0.7577(3)	3.80(7)
C14	0.5763(4)	0.6635(3)	0.8190(3)	3.69(8)
C15	0.2956(4)	0.6597(3)	0.9356(3)	3.60(7)
C16	0.0993(4)	0.3617(3)	0.9671(3)	3.53(7)
C17	0.3612(4)	−0.0290(3)	0.7576(3)	3.64(7)
C18	0.3079(4)	0.0213(3)	0.9557(3)	3.23(7)
C19	0.0557(5)	−0.0595(4)	0.8498(3)	4.14(8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Experimental

All reactions were performed under an inert atmosphere with dry, oxygen-free solvents. NMR spectra were recorded at 200 and 50 MHz for ^{1}H and ^{13}C, respectively, with a Bruker AC 200 SY spectrometer and at 32.4 MHz for ^{31}P with a Bruker WP 80 SY instrument. Chemical shifts are expressed in ppm downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Coupling constants are expressed in Hertz. Mass spectra were obtained with a Shimadzu GC-MS 1000 instrument at 70 eV by the direct inlet method. Elemental analyses were carried out at the "Service de Microanalyse du CNRS", Gif-sur-Yvette, France. IR spectra were recorded on a Perkin Elmer model 297 spectrometer.

Bis(η^5-2,3,4,5-tetramethylphospholyl)dimethylzirconium (2)

A diethyl ether solution of methyllithium (1.5 ml of 1.6 *M*, 2.4 mmol) was added to a cold (0 °C) solution of **1** (530 mg, 1.2 mmol) in diethyl ether (10 ml). The mixture was allowed to warm to room temperature, then evaporated to dryness under vacuum, and the residue was taken up in toluene. The solution was filtered

Table 3

Selected distances (in Å) and angles (°) [a]

	Distance		Distance
Zr–Cl1	2.4001(8)	Zr–Cl2	2.4256(9)
Fe–P1	2.206(9)	Fe–P2	2.1896(8)
Fe–C17	1.782(4)	Fe–C18	1.778(4)
Fe–C19	1.764(4)	O1–C17	1.149(5)
O2–C18	1.144(4)	O3–C19	1.152(5)
P1–C1	1.753(3)	C1–C2	1.406(5)
C2–C3	1.410(5)	C3–C4	1.430(5)
P1–C4	1.742(3)	P2–C9	1.761(3)
C9–C10	1.419(4)	C10–C11	1.408(4)
C11–C12	1.417(4)	P2–C12	1.753(3)
Cnt1–Zr	2.280	Cnt2–Zr	2.268
Fe–Zr	4.0337(5)		
	Angle		**Angle**
Cl1–Zr–Cl2	98.06(4)	P1–Fe–C17	94.3(1)
C1–P1–C4	92.8(2)	P1–Fe–C18	171.1(1)
P1–C1–C2	109.9(2)	P1–Fe–C19	89.9(1)
C1–C2–C3	113.9(3)	P2–Fe–C17	114.9(1)
C2–C3–C4	112.7(3)	P2–Fe–C18	93.1(1)
P1–C4–C3	109.9(2)	P2–Fe–C19	124.4(1)
C9–P2–C12	91.5(1)	C17–Fe–C18	94.2(2)
P2–C9–C10	110.6(2)	C17–Fe–C19	120.4(2)
C9–C10–C11	112.9(3)	C18–Fe–C19	88.1(2)
C10–C11–C12	113.1(3)	Fe–C17–O1	178.1(4)
P2–C12–C11	110.9(2)	Fe–C18–O2	177.0(3)
P1–Fe–P2	80.89(3)	Fe–C19–O3	178.7(4)
		Cnt1–Zr–Cnt2	127

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Cnt1 and Cnt2 indicate the centroids of the phospholyl rings.

and evaporated to dryness, leaving **2** as an air-sensitive lemon-yellow solid (310 mg, 0.78 mmol, 64%). NMR (C_6D_6): ^{1}H: δ − 0.62 (s, CH_3–Zr), 1.94 (s, CH_3–C3), 1.98 (m, ^3J(PH) ≈ 11, CH_3–C2).; ^{13}C: δ 14.55 (s, CH_3–C3), 17.04 (ps.t, ^2J(PC) ≈ 30, CH_3–C2), 38.10 (s, CH_3–Zr), 136.97 (ps.t, ^2J(PC) ≈ 5.5, C3), 140.70 (m, ^1J(PC) ≈ 48.5, C2); ^{31}P: δ 70.47 (s). Mass spec.: m/z 398 (M^+, 1%), 368 ($M - 2CH_3$, 100%).

Bis(η^5-2,3,4,5-tetramethylphospholyl)diphenylzirconium (3)

A diethyl ether solution of phenyllithium (4.9 ml of 0.5 M, 2.45 mmol) was added to a cold (0 °C) solution of **1** (500 mg, 1.14 mmol) in THF (20 ml). The mixture was allowed to warm to room temperature, then solvents were evaporated off under vacuum. The residue was extracted with toluene and the extract evaporated to dryness and thoroughly extracted with hexane. The hexane solution was evaporated to dryness, to leave **3** as an air-sensitive cream-coloured solid, which was rinsed with cold (− 30 °C) hexane (450 mg, 0.86 mmol, 76%). NMR (CD_2Cl_2): ^{1}H: δ 1.50 (s, CH_3–C3), 2.01 (d, ^3J(PH) ≈ 9.5, CH_3–C2), 7.03, 7.12, 7.33 (m, CH arom.); ^{13}C: δ 15.43 (s, CH_3–C3), 18.39 (m, ^2J(PC) ≈ 29, CH_3–C2), 125.07 (s, 4C *para*), 126.5 (br.s, 4C *meta*), 134 (br.s, 2C *ortho*), 141 (br.s, 2C *ortho*), 141.62 (d, ^2J(PC) 4.3, C3), 144.16 (d, ^1J(PC) 51.4, C2), 191.8 (s, C–Zr); ^{31}P: δ 80.17 (s). Mass spec.: m/z 522 (M^+, 17%), 368 ($M - 2C_6H_5$, 100%).

Bis(μ-η^1,η^5-2,3,4,5-tetramethylphospholyl)dichlorozirconium tetracarbonyltungsten (4)

A mixture of **1** (880 mg, 2 mmol) and (norbornadiene) tetracarbonyltungsten (800 mg, 2.06 mmol) in methylcyclohexane (30 ml) was kept at 75 ° C for 5 h, then cooled to room temperature, the solid was taken up in 60 ml of toluene and the solution was evaporated to dryness to leave **4** as a dark red solid (1.2 g, 1.6 mmol, 80%), which was recrystallized from toluene. NMR (CD_2Cl_2): ^1H: δ 2.01 (m, $^3J(PH) \approx 15$, CH_3–C2), 2.17 (s, CH_3–C3). ^{13}C: δ 16.24 (ps.t, $^2J(PC) \approx 15$, CH_3–C2), 16.24 (s, CH_3–C3), 138.96 (ps.t, $J(PC) \approx 3$, C3 or C2), 145.30 (ps.t, $J(PC) \approx 5$, C2 or C3), 191.79 (CO). ^{31}P: δ 34.17 ($^1J(PW)$ 197.5). IR ν(C=O) (cm^{-1}): 2030 (m), 1985 (vs), 1955 (m), 1945 (m), 1925 (s). Mass. spec. m/z 735 (M^+, 20%), 623 ($M-4CO$, 100%). Anal. Found: C, 33.10; H, 3.28. $C_{20}H_{24}Cl_2O_4P_2ZrW$ calcd.: C, 32.62; H, 3.29%.

Bis(μ-η^1,η^5-2,3,4,5-tetramethylphospholyl)dichlorozirconium tricarbonyliron (5)

A mixture of **1** (440 mg, 1 mmol) and $Fe_2(CO)_9$ (460 mg, 1.11 mmol) in methylcyclohexane (15 ml) was stirred for 2 h at room temperature, then heated under reflux for 4 h, and cooled to room temperature. The resulting suspension was filtered and the precipitate (P) was kept aside. The filtrate was treated with 200 mg of $Fe_2(CO)_9$ and heated under reflux for another 4 h. The mixture was then cooled and evaporated to dryness; the residue was washed with hexane, and then was dissolved, along with the original precipitate P, in toluene, the solution was filtered and evaporated to dryness to yield **5** as a dull red solid, which was recrystallized from hexane/toluene (140 mg, 0.24 mmol, 24%). NMR (CD_2Cl_2): ^1H: δ 1.52 (m, $^3J(PH) \approx 15$, CH_3 C2), 1.90 (s, CH_3–C3). ^{13}C: δ 14.78 (ps.t., $^2J(PC) \approx 15.2$, CH_3–C2), 15.39 (s, CH_3–C3), 137.05 (s, C3 or C2), 143.43 (ps.t., $J(PC) \approx 8$, C2 or C3), 212.80 (m, 1CO), 217.78 (t, J 7.2, 2CO). IR ν(C=O) (cm^{-1}): 2010 (s), 1967 (m), 1939 (s). Mass spec. m/z 579 (M^+, 18%), 495 ($M-3CO$, 100%). Anal. Found: C, 39.72; H, 4.07. $C_{19}H_{24}Cl_2O_3P_2ZrFe$ calcd.: C, 39.32; H, 4.17%.

X-ray crystal data collection and processing

Accurate cell dimensions were obtained on an Enraf–Nonius CAD4 diffractometer from the setting of 25 reflexions with $15° < \theta < 16°$. Data were collected in the range $4° \leq 2\theta \leq 60°$ using graphite-monochromated Mo-K_α radiation. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Computations were performed by use of the SDP package running on a microVAX II computer. The structure was solved by the Patterson heavy-atom technique. All atoms were located on successive difference Fourier maps. All non-hydrogen atoms were refined by least-squares, and hydrogen atoms were included as fixed contributions to the structure factor. Tables of hydrogen atomic coordinates, observed and calculated structure factors, and anisotropic thermal displacements are available from the authors.

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