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Synthesis of Phospha- and Diphosphatitanocene Dichlorides. Crystal and Molecular Structures of Bis(η^5-3,4-dimethylphospholyl)dichlorotitanium(IV) and of (η^5-3,4-Dimethylphospholyl)trichlorotitanium(IV)

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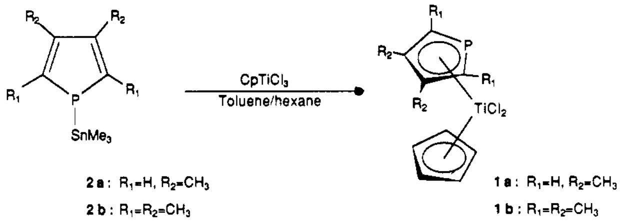
Depending on the conditions used, the reaction of 1-(trimethylstannyl)phospholes with $TiCl_4$ yields (η^5-phospholyl)trichlorotitanium or bis(η^5-phospholyl)dichlorotitanium complexes. 1-(Trimethylstannyl)phospholes also react with $CpTiCl_3$ to yield (η^5-cyclopentadienyl)(η^5-phospholyl)titanium dichloride complexes. The crystal structures of the title compounds, which are the only structurally described (η^5-heterocyclopentadienyl) titanium complexes, appear similar to that of the other known (η^5-phospholyl)transition-metal complexes as well as that of Cp_2TiCl_2 and $CpTiCl_3$, respectively.

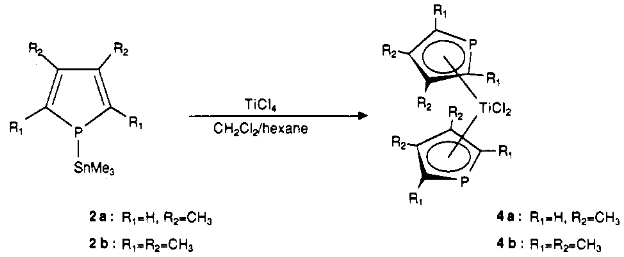
Introduction

Titanocene dichloride derivatives are useful compounds that have found applications as reagents in organic chemistry,[1] as soluble Ziegler–Natta catalysts,[2] and as cancerostatic compounds.[3] Accordingly, the influence of modification of the cyclopentadienyl (Cp) ring on the chemical behavior of these compounds has been widely studied.[4-26] The phospholyl ligand, or phosphacyclopentadienyl ligand, is bidentate because it has the same number of π-electrons than the cyclopentadienyl ligand has and can also act as a σ-donor through its lone pair. In this way, heterobimetallic compounds could be obtained from diphosphaferrocenes.[27] Bis(η^5-phospholyl)- or mixed (η^5-cyclopentadienyl)(η^5-phospholyl)metal complexes have only been described for iron[28] and, in two cases, with zirconium.[29,30] We now wish to report on the successful preparation of mono- and diphosphatitanocene dichlorides

Scheme I



Scheme II



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and on the crystal structures of one diphosphatitanocene dichloride together with that of a closely related complex, (η^5-phospholyl)trichlorotitanium, that we described recently.[31]

Results and Discussion

Synthesis of Phosphatitanocene Dichlorides (1). In a recent paper,[31] we have shown that 1-(trimethylstannyl)phospholes (2) react with $TiCl_4$ in toluene/*n*-hexane with elimination of Me_3SnCl to give (η^5-phospholyl)trichlorotitanium(IV) complexes (3). Since we wanted to obtain a bis-η^5-bonded species and we did not observe at first a bis(η^5-phospholyl)titanium dichloride in this reaction, we tried to obtain a η^5-phospholyl-η^5-cyclopentadienyl compound by reacting 1-(trimethylstannyl)phospholes with $CpTiCl_3$: when a solution of 2 in toluene was added to a solution of $CpTiCl_3$ in toluene, compounds 1 could be isolated in moderate yield after extractive workup as red crystalline powders (Scheme I). These compounds were fully characterized by elemental analysis, mass spectra, and ^1H, ^{13}C, and ^{31}P NMR spectra. These data and particularly the value of the $^1J_{PC}$ coupling constant support an η^5 structure for the phospholyl ligand in 1: this value falls in the 45–60 Hz range that is typical for all known η^5-bonded phospholyl complexes, including the recently prepared diphosphazirconocene dichloride 8[30] and compounds 3.[31] The ^{31}P signals of compounds **1a** and **1b** resonate at much higher field than those of 3 ($\simeq$200 ppm), and this may be due to increased election density at phosphorus in 1, due to the replacement of a chlorine by a Cp ligand. The other data deserve no particular comment.

Synthesis of Diphosphatitanocene Dichlorides (4). We could not at first isolate diphosphatitanocene dichlorides compounds 4 from reactions of (trimethylstannyl)phospholes with $TiCl_4$ because of the extreme air and water sensitivity of compounds 4 in solution. By using vacuum line techniques, however, we were eventually able to isolate these products. Thus, when a hexane solution of stannylphospholes was added to a dichloromethane solution of $TiCl_4$, we could obtain bis(η^5-phospholyl)dichlorotitanium(IV) complexes 4 in moderate to fair yield as dark greenish black crystalline powders (Scheme II). Evidence for their structure was inferred from their spectroscopic data and confirmed by an X-ray crystal study of **4a** (see below). The NMR spectra are complicated by second-order effects due to strong coupling between the chemically equivalent phosphorus atoms. Thus, the protons of the methyl group α to phosphorus in **4a** resonate as the X part of a $X_6AA'X'_6$ spectrum, whereas the protons α to phosphorus in **4b** give an $X_2AA'X'_2$ spectrum, which was analyzed by a standard simulation program: a value of 37.5 Hz for $J_{PP'}$ was found, slightly less than that for the zirconium complex 8.[30] These second-order effects are also apparent in the ^{13}C spectra of **4a** and **4b**, where the signal of the carbon α to phosphorus appears as the X part of an ABX system, A and B being phosphorus: chemical inequivalence between the two ligand phosphorus atoms is due to a $^{13}C-^{12}C$ isotope effect. The $^1J_{PC}$ coupling constant ($\simeq$45 Hz) falls in the usual range of a η^5-bonded phospholyl ligand.

Reactivity at Phosphorus: Preliminary Results. In order to try to prepare a heterobimetallic complex, we reacted equimolecular amounts of **1a** and $W(CO)_5$ (CH_3CN) in THF. ^{31}P monitoring of this reaction mixture revealed slow transformation of **1a** into a mixture of products, in which we could not detect any heterobimetallic compound such as **10** but instead we isolated the known biphospholyl complex **11** in low yield[32] (Scheme III). A possible explanation for the formation of **11** could be that **10** is formed in the first place but is unstable and decomposes into a titanium(III) residue and a (phospholyl)$W(CO)_5$ radical which thereafter undergoes coupling. The behavior of **1a** is in sharp contrast with that of covalent diphosphaferrocenes as well as ionic lithium phospholides,[32] who both form stable complexes with $W(CO)_5$.[27] ^{31}P monitoring of a THF solution of **4a** containing 2 equiv of water shows complete disappearance of **4a** and the appearance of two resonances, at −65 ppm (J_{PH} = 200 Hz) and at +56 ppm (J_{PH} = 560 Hz) that could correspond to a secondary phosphine and a secondary phosphine oxide, respectively. Thus the hydrolysis reaction has a very different outcome for **4a** than for other phospholyl compounds: lithium phospholide is protonated by water but gives a P–H phosphole that dimerizes,[33] and this dimer was not observed during hydrolysis of **4a**; diphosphaferrocene is not hydrolyzed.

Crystal Structures. Suitable crystals were obtained by slow cooling of a warm (60 °C) saturated hexane solu-

Scheme III

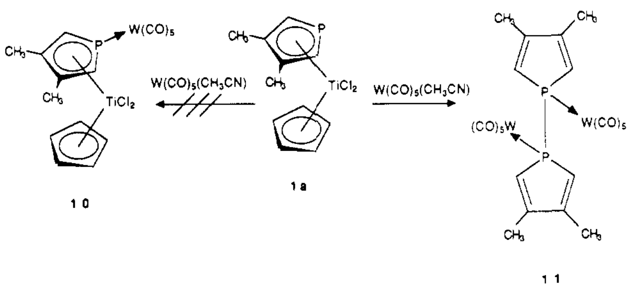

Table I. Crystal Data and Data Collection Parameters

	3a	4a
empirical formula	$C_8H_8Cl_3PTi$	$C_{12}H_{16}Cl_2P_2Ti$
fw	265.34	340.99
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å^2	7.110 (1)	8.939 (1)
b, Å^2	12.840 (1)	13.334 (1)
c, Å^2	11.659 (1)	13.543 (1)
α, deg	90	77.70 (1)
β, deg	99.05 (1)	80.16 (1)
γ, deg	90	72.01 (1)
Z	4	4
cryst size, mm	0.30 × 0.30 × 0.20	0.20 × 0.20 × 0.30
ρ(calcd), g·cm^{-3}	1.677	1.528
radiatn	Mo Kα	Mo Kα
monochromator	graphite	graphite
μ(Mo Kα), cm^{-1}	16.7	11.2
temp, °C	20 ± 1	20 ± 1
$2\theta_{max}$, deg	60	60
scan type	$\Omega/2\theta$	$\Omega/2\theta$
unique reflctns	3410	9919
reflctns with $F_o > 3\sigma(F_o)$	2042	5973
unweighted R	0.035	0.037
weighted R	0.056	0.057
esd of unit weight	1.14	1.16
shift/error max	0.01	0.04

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Table II. Positional Parameters and Their Estimated Standard Deviations for Compound 3a[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ti	0.22496 (7)	0.14640 (4)	0.23268 (4)	2.933 (8)
Cl1	0.3098 (2)	0.05809 (7)	0.08394 (8)	5.89 (2)
Cl2	0.2854 (1)	0.03009 (6)	0.37605 (7)	4.84 (2)
Cl3	0.4592 (1)	0.25998 (7)	0.2790 (1)	5.54 (2)
P	−0.0065 (2)	0.27409 (7)	0.11778 (9)	5.21 (2)
C1	−0.0918 (5)	0.1468 (3)	0.1283 (3)	4.54 (7)
C2	−0.1114 (4)	0.1163 (2)	0.2420 (3)	3.77 (6)
C3	−0.0481 (4)	0.1965 (2)	0.3224 (3)	3.69 (5)
C4	0.0147 (5)	0.2827 (2)	0.2680 (3)	4.31 (6)
C5	−0.1924 (5)	0.0144 (3)	0.2731 (4)	6.4 (1)
C6	−0.0555 (6)	0.1895 (4)	0.4503 (3)	6.8 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Bond Distances (Å) and Angles (deg) for Compound 3a[a]

	Bond Distances		
Ti-Cl1	2.2329 (9)	P-C1	1.754 (4)
Ti-Cl2	2.2323 (9)	P-C4	1.738 (4)
Ti-Cl3	2.2157 (9)	C1-C2	1.410 (5)
Ti-P	2.549 (1)	C2-C3	1.418 (4)
Ti-C1	2.386 (3)	C2-C5	1.497 (5)
Ti-C2	2.442 (3)	C3-C4	1.384 (4)
Ti-C3	2.432 (3)	C3-C6	1.505 (3)
	Bond Angles		
Cl1-Ti-Cl2	101.43 (4)	C1-P-C4	88.0 (2)
Cl1-Ti-Cl3	103.84 (4)	P-C1-C2	114.3 (2)
Cl2-Ti-Cl3	102.06 (4)	P-C4-C3	115.3 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

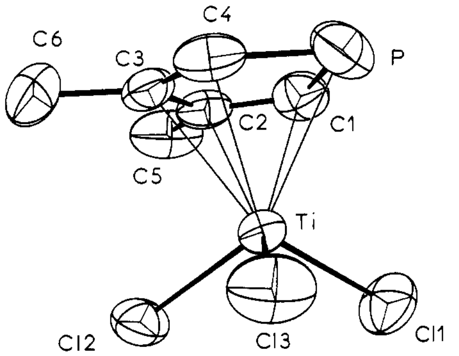

Figure 1. An ORTEP drawing of one molecule of **3a**. Ellipsoid boundaries are scaled to enclose 50% of the overall electronic density.

tion of **3a** and keeping a concentrated toluene solution of **4a** at −20 °C for several days. Crystal data and data collection parameters are listed in Table I. Tables II and III give the atomic coordinates for the non-hydrogen atoms of **3a** and **4a**, respectively, and Tables IV and V list selected bond lengths and angles for **3a** and **4a**, respectively. Figures 1 and 2 represent ORTEP plots of one molecule of **3a** and **4a**, respectively. In **4a**, there are two independent molecules in the unit cell, which are not significantly different from each other, although not related by a symmetry operation. The structural data of **3a** and **4a** confirm that the titanium atom is η^5-bonded to the phospholyl ligand which deviates only slightly from planarity: the ring carbons of the ligand are coplanar within experimental error and the distance of the phosphorus atom to this plane is only 0.06 Å for **3a** and 0.04 Å (mean value) for **4a**. The geometry of the ligand is very similar to that of other phospholyl complexes, if one considers the values of intracyclic bond lengths and angles in **3a** and **4a** (Table VI). The metal–P bond is longer than the metal–ring carbon bonds; this effect has already been noted in other phosphametallocenes.

Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound 4a

atom	*x*	*y*	*z*	*B*, Å^2
Ti1	0.30674 (5)	0.42471 (3)	0.23928 (3)	2.397 (7)
Ti2	−0.21762 (5)	1.06557 (3)	−0.27996 (3)	2.449 (7)
Cl1	0.45553 (8)	0.54447 (5)	0.16848 (5)	4.04 (1)
Cl2	0.10600 (8)	0.55446 (5)	0.31927 (4)	3.54 (1)
Cl3	−0.38657 (7)	0.96902 (5)	−0.18323 (5)	3.59 (1)
Cl4	−0.0644 (1)	0.91999 (5)	−0.35983 (5)	4.38 (2)
P1	0.3515 (1)	0.32089 (6)	0.09044 (6)	4.64 (2)
P2	0.5627 (1)	0.27088 (7)	0.28451 (7)	4.81 (2)
P3	−0.00668 (8)	1.15163 (6)	−0.25484 (6)	4.35 (2)
P4	−0.21575 (9)	1.20717 (6)	−0.44370 (6)	4.10 (2)
C1	0.2687 (4)	0.4606 (2)	0.0571 (2)	3.93 (6)
C2	0.1179 (3)	0.5022 (2)	0.1036 (2)	3.40 (5)
C3	0.0632 (3)	0.4202 (2)	0.1709 (2)	3.50 (5)
C4	0.1778 (3)	0.3211 (2)	0.1744 (2)	3.87 (5)
C5	0.0192 (5)	0.6173 (2)	0.0828 (2)	5.61 (8)
C6	−0.1003 (4)	0.4368 (3)	0.2260 (3)	6.18 (9)
C7	0.3832 (4)	0.2436 (2)	0.3396 (2)	3.83 (6)
C8	0.2958 (3)	0.3077 (2)	0.4099 (2)	3.04 (5)
C9	0.3740 (3)	0.3821 (2)	0.4225 (2)	3.23 (5)
C10	0.5145 (3)	0.3729 (2)	0.3587 (2)	4.03 (6)
C11	0.1422 (4)	0.2991 (2)	0.4682 (2)	4.46 (7)
C12	0.3161 (4)	0.4546 (2)	0.5009 (2)	4.32 (6)
C13	−0.1753 (3)	1.1687 (2)	−0.1652 (2)	3.93 (6)
C14	−0.1867 (3)	1.0760 (2)	−0.1011 (2)	3.88 (6)
C15	−0.0643 (3)	0.9845 (2)	−0.1280 (2)	3.75 (5)
C16	0.0399 (3)	1.0139 (2)	−0.2091 (2)	3.99 (6)
C17	−0.3081 (5)	1.0701 (4)	−0.0096 (3)	7.0 (1)
C18	−0.0416 (4)	0.8710 (3)	−0.0736 (3)	6.28 (8)
C19	−0.3190 (3)	1.1173 (2)	−0.4497 (2)	3.77 (6)
C20	−0.4556 (3)	1.1248 (2)	−0.3821 (2)	3.34 (5)
C21	−0.4786 (3)	1.2035 (2)	−0.3189 (2)	3.24 (5)
C22	−0.3587 (3)	1.2532 (2)	−0.3441 (2)	3.48 (5)
C23	−0.5697 (3)	1.0631 (2)	−0.3791 (2)	4.48 (6)
C24	−0.6178 (4)	1.2326 (3)	−0.2413 (3)	4.94 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Like in $CpTiCl_3$[37] and Cp_2TiCl_2,[38] the Ti centers in **3a** and **4a** can be described as distorted tetrahedra, if one considers the centroid L–Ti–Cl angles (mean value = 115.7°) of **3a** and the centroid L_1–Ti–centroid L_2 angles (mean value = 133.7°) of **4a**, that are larger than the tetrahedral angle. These values are similar to those of $CpTiCl_3$ and Cp_2TiCl_2, respectively. In **3a** and **4a**, the Ti–Cl bond lengths (mean values = 2.23 and 2.35 Å, respectively) and Cl–Ti–Cl angles (respectively 102.4° and 92.9°) are similar to those found for $CpTiCl_3$ and Cp_2TiCl_2. On the other hand, the Ti–C bond lengths are slightly longer in **3a** and **4a** (2.41 and 2.50 Å, respectively) than in $CpTiCl_3$ and Cp_2TiCl_2 (2.31 and 2.37 Å, respectively). As for the Ti–P bond lengths in **3a** and **4a**, their value (2.55 and 2.59 Å, respectively) is in the range of those observed for σ-phosphine complexes of Ti(II): they are longer than those in $Cp_2Ti(PMe_3)_2$[39] but shorter than for the longest Ti–P bond distances in $(dmpe)_2Ti(CO)_3$.[40] The dihedral angle between the ligand planes is slightly larger in **4a** (52°)

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Table V. Bond Distances (Å) and angles (deg) for Compound 4a

	Bond Distances		
Ti1-Cl1	2.3519 (7)	Ti2-Cl3	2.3503 (7)
Ti1-Cl2	2.3456 (7)	Ti2-Cl4	2.3393 (7)
Ti1-P1	2.5871 (8)	Ti2-P3	2.6040 (8)
Ti1-P2	2.5900 (8)	Ti2-P4	2.5895 (8)
Ti1-C1	2.472 (3)	Ti2-C13	2.430 (3)
Ti1-C2	2.532 (3)	Ti2-C14	2.523 (3)
Ti1-C3	2.530 (3)	Ti2-C15	2.517 (3)
Ti1-C4	2.430 (3)	Ti2-C16	2.477 (3)
Ti1-C7	2.447 (3)	Ti2-C19	2.492 (3)
Ti1-C8	2.504 (2)	Ti2-C20	2.551 (2)
Ti1-C9	2.555 (2)	Ti2-C21	2.514 (2)
Ti1-C10	2.502 (3)	Ti2-C22	2.450 (3)
P1-C1	1.755 (3)	P3-C13	1.751 (3)
P1-C4	1.761 (3)	P3-C16	1.742 (3)
P2-C7	1.766 (3)	P4-C19	1.755 (3)
P2-C10	1.760 (3)	P4-C22	1.756 (3)
C1-C2	1.376 (4)	C13-C14	1.374 (4)
C2-C3	1.427 (4)	C14-C15	1.415 (4)
C2-C5	1.495 (4)	C14-C17	1.508 (5)
C3-C4	1.380 (4)	C15-C16	1.390 (4)
C3-C6	1.493 (5)	C15-C18	1.500 (4)
C7-C8	1.380 (4)	C19-C20	1.385 (4)
C8-C9	1.438 (3)	C20-C21	1.436 (3)
C8-C11	1.488 (4)	C20-C23	1.495 (4)
C9-C10	1.383 (4)	C21-C22	1.395 (4)
C9-C12	1.500 (4)	C21-C24	1.488 (4)
	Bond Angles		
Cl1-Ti1-Cl2	93.02 (3)	P2-C7-C8	114.2 (2)
Cl3-Ti2-Cl4	92.77 (3)	P3-C13-C14	114.6 (2)
C1-P1-C4	87.6 (1)	P4-C19-C20	114.7 (2)
C7-P2-C10	88.2 (1)	P1-C4-C3	114.5 (2)
C13-P3-C16	87.7 (1)	P2-C10-C9	114.3 (2)
C19-P4-C22	88.2 (1)	P3-C16-C15	114.8 (2)
P1-C1-C2	114.9 (2)	P4-C22-C21	114.5 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

than in Cp_2TiCl_2 (49°). Within a molecule of **4a**, the phospholyl rings are in slightly staggered conformation, if one considers the dihedral angle between the plane defined by P_1, centroid L_1, centroid L_2 and the one defined by P_2, centroid L_1, centroid L_2, which is equal to 16.2° in molecule 1 and 16.5° in molecule 2. Thus, the conformation of **4a** is different from that of $(C_4Me_4P)_2ZrCl_2$[30] (**8**) where this angle is equal to 42°: in the case of **8**, the phospholyl rings are in a fully staggered conformation. The P_1 to P_2 (and P_3 to P_4) distance that is equal to 3.28 Å (mean value) precludes any bonding interaction. This value is very similar to that found in complex **8**. Finally, all bonds around Ti are longer in **4a** than in **3a**, which is likely due to the better electron-donating properties of the π-phospholyl in comparison with the chloride ligand toward the $(\eta^5\text{-phospholyl})TiCl_2$ moiety.

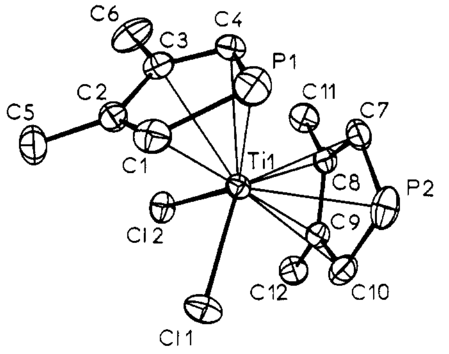


Figure 2. An ORTEP drawing of one molecule of **4a**. Ellipsoid boundaries are scaled to enclose 30% of the overall electronic density.

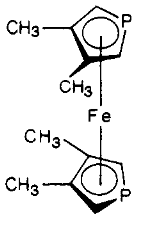
Conclusion

The method that we devised for preparing $(\eta^5\text{-phospholyl})$titanium compounds starting from 1-(trimethylstannyl)phospholes appears quite versatile: depending on the conditions used, we were able to prepare mono$(\eta^5\text{-phospholyl})$-, mixed $(\eta^5\text{-phospholyl})(\eta^5\text{-cyclopentadienyl})$-, or bis$(\eta^5\text{-phospholyl})$titanium compounds in moderate fo fair yield. This method can also accommodate variations of the substitution pattern on the phospholyl ring. Our next plans include the chemical study of these molecules, especially their reactivity at phosphorus.

Experimental Section

All reactions were performed under inert atmosphere by using high vacuum line and drybox techniques and with dry, oxygen-free solvents. NMR experiments were done with a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C and with a Bruker WP 80 SY spectrometer functioning at 32.44 MHz for ^{31}P. Chemical shifts are expressed in parts per million 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 with a Shimadzu GC-MS 1000 instrument by the direct inlet method. Elemental analyses were performed by the "Service d'analyses du CNRS", Gif-sur-Yvette, France. Com-

Table VI. A Comparison between Phospholyl Ring Bond Distances (Å) and Angles (deg) (Mean Values) in Different η^5-Phospholyl Complexes



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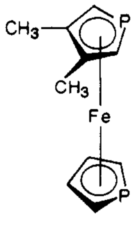

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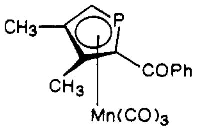

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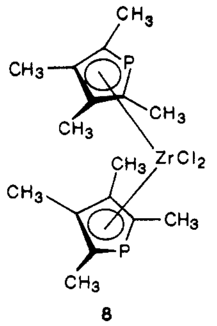
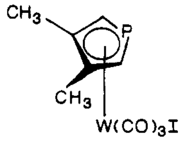


8



9

	5	6	7	8	9	3a	4a
C-C bond	1.41	1.41	1.42	1.40	1.41	1.40	1.40
P-C bond	1.77	1.76	1.77	1.76	1.77	1.75	1.76
C-P-C angle	88.2	88.4	88.5	89.8	88.3	88.0	87.9
P-C-C and C-C-C angles	112.9		112.9	112.4	112.7	113.0	113.0
ref	34	35	36	30	32	this work	

mercial $TiCl_4$ was freeze–pump–thaw–degassed three times before use. (Trimethylstannyl)phospholes were prepared as previously described.[31]

(η^5-Cyclopentadienyl)(η^5-3,4-dimethylphospholyl)dichlorotitanium (1a). To a cold (0 °C) mixture of $CpTiCl_3$ (220 mg, 1 mmol) in toluene (5 mL) was rapidly added a solution of 1-(trimethylstannyl)phosphole (275 mg, 1 mmol) in toluene (5 mL). The reaction mixture turned dark red and homogeneous. This solution was then filtered, evaporated to dryness, and pumped on the vacuum line for 3 h at room temperature. The residue was then extracted with toluene, this extract concentrated, and the product crystallized on adding hexane. It was then filtered, rinsed with hexane, and dried on the vacuum line. Yield: 140 mg (0.47 mmol) of red crystals. An analytical sample was recrystallized in toluene–hexane; mp 130 °C dec. NMR (CD_2Cl_2): ^1H, 2.27 (s, CH_3), 6.61 (d, $^3J_{PH} \simeq 1$, Cp), 6.89 (d, $^2J_{PH} = 36$, H_2); $^{13}C\{^1H\}$, 18.06 (s, CH_3), 120.43 (d, $^2J_{PC} = 2$, Cp), 141.83 (d, $^1J_{CP} = 53.5$, C_2), 149.66 (d, $^2J_{CP} = 7.3$, C_3); $^{31}P\{^1H\}$, 107.05. Mass spectrum m/z (^{35}Cl, ^{48}Ti): 294 (M^+, 66%), 183 ($CpTiCl_2^+$, 100%). Anal. Calcd for $C_{11}H_{13}Cl_2PTi$: C, 44.79; H, 4.44. Found: C, 44.90; H, 4.51.

(η^5-Cyclopentadienyl)(η^5-2,3,4,5-tetramethylphospholyl)dichlorotitanium(IV) (1b). This reaction, conducted as above with 1-(trimethylstannyl)-2,3,4,5-tetramethylphosphole (300 mg, 1 mmol) and $CpTiCl_3$ (220 mg, 1 mmol) in toluene (10 mL) at 0 °C yielded after workup 146 mg of red crystals (0.45 mmol, 45%). An analytical sample was recrystallized form toluene–hexane: mp 135 °C dec. NMR (CD_2Cl_2): ^1H, 2.09 (s, CH_3C_3), 2.20 (d, $^3J_{PH} = 9.7$, CH_3C_2), 6.46 (d, $^3J_{PH} \approx 0.5$, Cp); $^{13}C\{^1H\}$, 15.48 (s, CH_3C_3), 17.92 (d, $^2J_{PC} = 22.1$, CH_3C_2), 120.11 (d, $^2J_{PC} = 2.2$, Cp), 148.08 (d, $^2J_{PC} = 5.0$, C_3), 150.98 (d, $^1J_{PC} = 50.0$, C_2); $^{31}P\{^1H\}$, 115.60. Mass spectrum (^{35}Cl, ^{48}Ti): m/z 322 (M^+, 50%), 139 (phospholyl, 100%). Anal. Calcd for $C_{13}H_{17}Cl_2PTi$: C, 48.33; H, 5.30. Found: C, 48.29; H, 5.35.

Bis(η^5-3,4-dimethylphospholyl)dichlorotitanium(IV) (4a). To a solution of $TiCl_4$ (0.2 mL, 350 mg, 1.82 mmol) in CH_2Cl_2 (10 mL) was added a hexane (5 mL) solution of 1.1 g (4.0 mmol) of 1-(trimethylstannyl)-3,4-dimethylphosphole. The reaction mixture turned progressively dark brown. After 30 min of stirring, it was evaporated to dryness and pumped on the vacuum line for 2 h. The residue was extracted in toluene and crystallized in toluene/hexane (1:1). Yield: 400 mg of greenish brown crystals (1.17 mmol, 64%). An analytical sample was crystallized in toluene at −20 °C; mp 160 °C dec. NMR (C_6D_6): ^1H, 2.03 (s, CH_3), 6.52 (m, $X_2AA'X'_2$ spin system, $^2J_{HP} = 35.9$, $^3J_{HP'} = 1.4$, $^2J_{PP'} = 37.7$); $^{13}C\{^1H\}$, 18.01 (s, CH_3), 140.4 (m, $^1J_{PC} \approx 48$, C_2 and C_5), 148.33 (pst, $^2J_{PC} = 7.3$, C_3 and C_4); $^{31}P\{^1H\}$, 100.47. Anal. Calcd for $C_{12}H_{16}Cl_2PTi$: C, 42.27; H, 4.73. Found: C, 42.25; H, 4.77.

Bis(η^5-2,3,4,5-tetramethylphospholyl)dichlorotitanium(IV) (4b). The reaction was conducted as above with 0.27 mL of $TiCl_4$ (2.5 mmol) and 1.65 g of 1-(trimethylstannyl)-2,3,4,5-tetramethylphosphole (5.44 mmol) in 30 mL of CH_2Cl_2/hexane (2:1). The dark green reaction mixture was evaporated to dryness and extracted with hexane, and the residue was crystallized in hexane: yield 390 mg (0.98 mM, 39%) of a greenish black powder; mp 85 °C dec. NMR (C_6D_6): ^1H, 1.88 (pst, $^3J_{PH} = 9.9$, CH_3C_2 and CH_3C_5), 2.09 (s, CH_3C_3 and CH_3C_4); $^{13}C\{^1H\}$, 16.00 (s, CH_3C_3 and CH_3C_4), 18.01 (pst, $^2J_{CP} = 27$, CH_3C_2 and CH_3C_5), 144.16 (psq, $^1J_{CP} \approx 44$, C_2 and C_5), 150.03 (pst, $^2J_{CP} \approx 5$, C_3 and C_4); $^{31}P\{^1H\}$, 95.68. Mass spectrum (^{35}Cl, ^{48}Ti): m/z 396 (M^+, 20%), 140 (L + 1, 100%), 139 (L, 82%). Anal. Calcd for $C_{16}H_{24}Cl_2P_2Ti$: C, 48.39; H, 6.09. Found: C, 47.57; H, 6.02.

Reaction of (η^5-Cyclopentadienyl)(η^5-3,4-dimethylphospholyl)dichlorotitanium (1a) with $W(CO)_5(CH_3CN)$. THF (15 mL) was condensed at −78 °C onto a mixture of **1a** (1.7 mmol, 500 mg) and $W(CO)_5(CH_3CN)$ (620 mg, 1.7 mmol). The reaction mixture was stirred at room temperature for 5 h and evaporated to dryness. The residue was dissolved in dichloromethane, absorbed onto silica gel, and chromatographed (toluene/hexane, 25:75). The first yellow fraction eluted was evaporated to dryness. A yellow crystalline powder was obtained (160 mg) and was chromatographically and spectrally identified as bis(3,4-dimethylphospholyl)octacarbonylditungsten (11) by comparison with an authentic sample[32] (0.18 mmol, 22%).

X-ray Crystal Data Collection and Processing. Accurate cell dimensions were obtained on an Enraf-Nonius CAD4 diffractometer from the setting angles of 25 reflections with 15° < θ < 16°. The intensities were corrected for Lorentz and polarization effects. For **4a**, absorption corrections were applied via an empirical technique whereas for **3a** no absorption corrections were made. Computations were performed by using the SDP package adpated on a micro VAX II computer. Both structures were solved by direct methods. All atoms, including hydrogen, were located on successive difference Fourier maps. The atomic parameters were refined in least squares, including extinction. Hydrogen atoms were refined with $B_{iso}(H)$ fixed at 1.3 times the value of B_{iso} (adjacent carbon).

Registry No. **1a**, 120311-36-6; **1b**, 120311-37-7; **2a**, 120296-97-1; **2b**, 120296-98-2; **3a**, 120311-40-2; **4a**, 120311-38-8; **4b**, 120311-39-9; 11, 105812-22-4; $CpTiCl_3$, 1270-98-0; $TiCl_4$, 7550-45-0; $W(CO)_5(CH_3CN)$, 15096-68-1.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atomic coordinates (6 pages); listings of observed and calculated structure factors (77 pages). Ordering information is given on any current masthead page.