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Synthesis of bent titanocene metalloligands with the (diphenylphosphino)tetramethylcyclopentadienyl moiety. X-ray structure of $[(\eta^5\text{-}C_5Me_4PPh_2)_2TiCl_2]Mo(CO)_4$

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Abstract

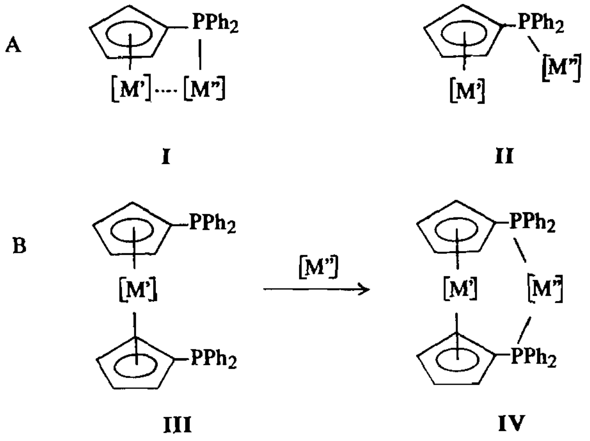
The reactions of lithium(diphenylphosphino)tetramethylcyclopentadienide with $CpTiCl_3$ and secondly with $TiCl_3$ followed by CCl_4 oxidation lead to the formation of two titanocene phosphines: $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5Me_4P(C_6H_5)_2]TiCl_2$ (**2**) and $[\eta^5\text{-}C_5Me_4P(C_6H_5)_2]_2TiCl_2$ (**3**), respectively. The metalloligand **3** reacts readily with $Mo(CO)_4cod$, $Mo(CO)_5THF$ and $Mo(CO)_6$ to give in each case $[(\eta^5\text{-}C_5Me_4PPh_2)_2\text{-}TiCl_2]Mo(CO)_4$ (**6**) as a sole product. The structure of **6** has been determined by X-ray diffraction. Crystal data: $P\bar{1}$, $a=11.716(1)$, $b=11.753(2)$, $c=16.110(2)$ Å, $\alpha=99.06(1)$, $\beta=92.61(1)$, $\gamma=104.20(1)°$, $Z=2$. The molybdenum–titanium distance of 5.194(1) Å rules out any metal–metal interaction. The chlorine substitution reactions by CO in **2** and **3** and by thiolate group ($pH_3C\text{-}C_6H_4\text{-}S$) in **6** are reported.

Introduction

Heterodifunctional ligands, incorporating both a phosphine and a cyclopentadienyl (Cp) coordination unit [1] are suitable to link late and early transition-metal atoms [2]. The derived bimetallic complexes have been shown to possess unusual features comparative to monometallic complexes of simpler ligand systems.

The use of bifunctional ligand $Cp\text{-}PPh_2$ to link two dissimilar transition metals [M′] and [M″] has already been reported [3], and two types of bimetallic complexes may be distinguished (Scheme 1).

For the first type (A), in which one $Cp\text{-}PPh_2$ unit is involved, two metal fragments are held together through a bridging ligand with or without a direct metal–metal bond, **I** [4] or **II** [5], respectively. In the second case (B), two $Cp\text{-}PPh_2$ units gave rise to the formation of the metalloligand **III**, which may further act as a chelating bidentate diphosphine leading to the formation of bimetallic compounds **IV**. The ligand system **III** has been employed mainly in the field of ferrocenyl and cobaltocenyl sandwich structures [1c–h]. It is only recently that a few examples of the canted zirconocene-derived heterobimetallics have been reported [6]. Among them, the Zr–Mo complex synthesized by Tikkanen and co-workers [6a, c] must be especially noted as revealing some interesting structural features.



Scheme 1.

It is known that the introduction of alkyl groups into the Cp ring may modify the electron-donating ability and steric bulk of the resulting ligands [7]. In this matter, we recently reported [8] the synthesis of two new (diphenylphosphino)tetramethylcyclopentadienyl ligands **1a** and **b**, as part of our program to investigate the chemistry and the properties of group 4 late transition-metal binuclear complexes [9].

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$Ph_2P(CH_2)_nCp'H$ where $Cp' = C_5Me_4$
1 (**a**: $n = 0$; **b**: $n = 2$)

In this paper we describe the use of **1a** for the synthesis of the dichloride titanocenes **2** and **3** (see Scheme 2). The chelating abilities of the metalloligand **3** has been revealed by its treatment with the Mo(O) tetra-, penta- and hexacarbonyls. All these reactions have led to the exclusive formation of the canted bimetallic compound **6** (type IV, Scheme 1).

Some reactions including chlorine substitution in the metalloligands **2** and **3** as well as in the bimetallic compound **6** are also reported.

Experimental

Except where mentioned, all manipulations were carried out under argon atmosphere using vacuum line techniques. Tetrahydrofuran (THF), toluene and pentane were distilled under argon from sodium benzophenone ketyl. $CpTiCl_3$ was obtained from Cp_2TiCl_2 and $TiCl_4$ [10] and recrystallized from benzene saturated with hydrogen chloride. $Mo(CO)_5THF$ and $Cr(CO)_5THF$ were obtained by the irradiation of $Mo(CO)_6$ and $Cr(CO)_6$ in THF. $Mo(CO)_4cod$ was prepared according to the literature method [11]. $(C_5Me_4)PPh_2Li$ was prepared using our procedure described previously [8]. Other reagents were used as purchased. IR spectra were obtained on a Perkin-Elmer 580B spectrometer. ^1H and ^{31}P NMR spectra were recorded at 400 and 162.00 MHz, respectively, on a Brucker WM400 spectrometer. ^{31}P chemical shifts were reported relative to external 85% H_3PO_4, positive shifts representing deshielding. Mass spectra were measured on a Ribermag R 10-10C instrument at 70 eV. Elemental analyses were performed by the CNRS Microanalytical Laboratory of Vernaison (France).

(η^5-Cyclopentadienyl)[η^5-(diphenylphosphino)tetramethylcyclopentadienyl]dichlorotitanium (2)

A solution of 1.11 g (3.55 mmol) of $(C_5Me_4)PPh_2Li$ in THF (25 ml) was added dropwise to a stirred solution of $CpTiCl_3$ (0.78 g, 3.56 mmol) in 15 ml of THF at room temperature. The resulting mixture was stirred overnight. The solvent was evaporated under reduced pressure and 40 ml of toluene was added to the residue. The precipitated lithium chloride was removed by filtration through celite, yielding a deep red solution. The solvent was removed under vacuum at *c*. 30 °C. The resulting oil was then washed with pentane until a homogeneous brick-red powder was obtained. The product was dried under vacuum yielding 1.77 g (85%) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5Me_4P(C_6H_5)_2]TiCl_2$. This material is of sufficient purity for further synthetic purposes. Analytically pure material was obtained by flash chromatography (argon, silica gel, 1:1 toluene: THF). IR (KBr pellet): 3050(w), 2960(m), 2910(m), 1620(w), 1585(w), 1545(w), 1475(m), 1435(s), 1380(m), 1330(w), 1260(m), 1102(vs), 1070(rs), 1020(s), 935(m) cm^{-1}. ^1H NMR (C_6D_6): δ 7.26 (m, 4H, Ph-*o*), 7.06 (m, 6H, Ph-*m*, p), 6.25 (s, 5H, C_5H_5), 1.92 (s, 6H, CH_3), 1.82 (6H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -17.1. MS: *m/e* 488 ($M^+ - {}^{35}Cl$, ^{35}Cl). *Anal.* Calc. for $C_{26}H_{27}Cl_2PTi$:C, 63.82; H, 5.56; Ti, 9.79. Found: C, 63.44; H, 5.79; Ti, 9.67%.

Bis[η^5-(diphenylphosphino)tetramethylcyclopentadienyl]dichlorotitanium (3)

A solution of 1.04 g (3.33 mmol) of $(C_5Me_4)PPh_2Li$ in THF (15 ml) was added to a stirred suspension of 240 mg (1.55 mmol) of $TiCl_3$ in THF (15 ml). The reaction mixture was then refluxed overnight under Ar. The solvent was removed under vacuum and 20 ml of toluene was added to the residue. The white precipitate was filtered by means of a jacketed frit under a vacuum-argon line, and 5 ml of degassed CCl_4 was added to a deep green filtrate. The solution was stirred at room temperature for 1 h, during which time it became brown. The solvent was evaporated under reduced pressure, and the residue washed three times with pentane yielding 1.02 g (90%) of brown powder. IR (KBr pellet): 3050(w), 2955(w), 2905(m), 1620(w), 1585(w), 1540(w), 1475(m), 1430(s), 1375(w), 1330(w), 1260(m), 1185(w), 1090(s), 1025(s) cm^{-1}. ^1H NMR (C_6D_6): δ 7.51 (m, 8H, Ph-*o*), 7.02 (m, 12H, Ph-*m*, *p*), 2.01 (s, 12H, CH_3), 1.90 (s, 12H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -19.0. *Anal.* Calc. for $C_{42}H_{44}Cl_2P_2Ti$: C, 65.14; H, 6.07; Ti, 6.57. Found: C, 65.83; H, 5.82; Ti 6.90%.

(η^5-Cyclopentadienyl)[η^5-(diphenylphosphino)tetramethylcyclopentadienyl]dicarbonyltitanium (4)

A 100 ml Schlenk flash was charged with 0.80 g (1.63 mmol) of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5Me_4P(C_6H_5)_2]TiCl_2$, 0.2 g (7.4 mmol) of aluminium turnings and 0.1 g (0.4 mmol) of mercuric chloride. The flask was fitted with a gas outlet valve and flushed with carbon monoxide. THF (30 ml) was added and the reaction mixture was stirred overnight at room temperature under CO atmosphere (about 30 mb superpressure). The solvent was then removed under vacuum and 40 ml of toluene was added to the residue. The mixture was cooled to −10 °C and filtered through a plug (4 cm) of alumina. The solvent was evaporated on a vacuum line at +30 °C. The residue was washed two times with pentane and dried under vacuum yielding 0.26 g (33%) of **4** as a red–brown powder. This material is of about 95% purity by ^{1}H and ^{31}P NMR. IR (THF): ν(CO) 1952, 1882 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.53 (m, 4H, Ph-*o*), 7.13 (m, 6H, Ph-*m*, *p*), 4.47 (s, 5H, C_5H_5), 1.65 (s, 6H, CH_3), 1.55 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −20.0.

Bis[η^5-(diphenylphosphino)tetramethylcyclopentadienyl]dicarbonyltitanium (5)

The reaction of **3** (0.63 g, 0.86 mmol) with carbon monoxide in the presence of aluminium (0.1 g, 3.7 mmol) and mercuric chloride (0.05 g, 0.2 mmol) was performed following a procedure similar to that described for **4**. Compound **5** was isolated (0.19 g, 30%) as a pale brown solid, which was almost pure according to ^{1}H NMR and ^{31}P NMR spectroscopy. Attempts to obtain further purification of **4** and **5** failed, probably because of their instability. IR (THF): ν(CO) 1955, 1882 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.45 (m, 8H, Ph-*o*), 7.05 (m, 12H, Ph-*m*, *p*), 1.79 (s, 12H, CH_3), 1.59 (s, 12H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −20.6.

Tetracarbonyl[[P,P′-bis((diphenylphosphino)tetramethylcyclopentadienyl)]dichlorotitanium(IV)]-molybdenum(0) (6), a variant made with use of Mo(CO)$_5$THF

A solution of $Mo(CO)_5THF$ in THF (65 ml), prepared by photolyzing 1.06 g (4 mmol) of $Mo(CO)_6$, was added via syringe to a stirred solution of **3** (1.38 g, 1.9 mmol) in THF (10 ml). The infrared control of the reaction mixture shows a growing of four CO stretching bands at 2020, 1965, 1913 and 1882 cm^{-1}, and the lowering of the two bands characteristic of $Mo(CO)_5THF$ (1942, 1894 cm^{-1}) over a period of 8 h. The mixture was allowed to stir overnight. The solvent was removed under vacuum and 20 ml of toluene was added to the residue. A solution was filtered through *c.* 3 cm of degassed silica gel and the solvent evaporated under vacuum. The resulting solid was washed three times with pentane yielding **6** as a brown powder (1.44 g, 81%). Analytically pure material was obtained by recrystallization from methylene chloride/hexane. A crystal of **6** suitable for X-ray analysis was grown from 2/1 CH_2Cl_2/hexane for *c.* 24 h, while a minimal stream of argon gives rise to about 50% concentration of the solvent. The steel grey platelets of **6** are moderately air-stable. They should be kept under argon for extended periods. m.p. 248 °C dec. IR (THF): ν(CO) 2020, 1965, 1913, 1882 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.71 (m, 8H, Ph-*o*), 6.98 (m, 12H, Ph-*m*, *p*), 1.97 (s, 12H, CH_3), 1.84 (s, 12H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ +35.7. *Anal.* Calc. for $C_{46}H_{44}Cl_2O_4P_2MoTi$: C, 58.93; H, 4.73; Ti, 5.11; Mo, 10.23. Found: C, 57.95; H, 4.66; Ti, 4.99; Mo, 10.33%.

Tetracarbonyl[[P,P′-bis((diphenylphosphino)tetramethylcyclopentadienyl)]-di(p-tolylthiolate)titanium-(IV)]molybdenum(0) (7)

A solution of **6** (0.37 g, 0.39 mmol) in THF (15 ml) was added via syringe to a stirred solution of sodium *p*-methylthiophenoxide* (0.16 g, 1.1 mmol) in 8 ml of THF at room temperature. The reaction mixture became dark green rapidly. After 1 h at room temperature the mixture was concentrated to about 5 ml, and 20 ml of toluene added. The suspension was then filtered under argon through a fine porosity jacketed frit. The solvent was removed under vacuum and the residue washed twice with pentane yielding **7** (0.31 g, 72%) as a dark green solid. An analytically pure sample was obtained by recrystallization from pentane/ether at −20 °C. m.p. 262 °C dec. IR (THF): ν(CO) 2020, 1966, 1912, 1879 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.80 (m, 8H, PPh-*o*), 7.47 (d, $J = 7.9$ Hz, 4H, Ph-tol), 7.03 (dd, $J \cong 8$ Hz, 8H, PPh-*m*), 6.93 (m, 4H, PPh-*p*), 6.68 (d, $J = 7.9$ Hz, 4H, Ph-tol), 2.18 (br s, 18H, CH_3-Cp + CH_3-tol), 1.98 (s, 12H, CH_3-Cp). *Anal.* Calc. for $C_{60}H_{58}O_4P_2S_2MoTi$: Ti, 4.30; Mo, 8.62. Found: Ti, 4.06; Mo, 8.34%.

Pentacarbonyl[[(η^5-cyclopentadienyl)(η^5-(diphenylphosphinotetramethylcyclopentadienyl)]dichlorotitanium(IV)]chromium(0) (8)

A solution of $Cr(CO)_5$ THF in THF (30 ml) prepared by photolyzing 0.45 g (2 mmol) of $Cr(CO)_6$, was added via syringe to a stirred solution of **2** (0.92 g, 1.88 mmol) in THF (20 ml). After 20 h at room temperature in the dark the mixture was filtered through Celite, yielding a brown solution. The solvent was removed under vacuum. A total of 3 ml of ethanol-free CH_2Cl_2 and 8 ml of pentane was added to the residue. When the solution was stirred in the dark at −20 °C for 0.5 h the precipitate formed. The precipitate was collected by filtration under argon and washed with pentane to give **8** as a grey–green powder (0.92 g, 72%). m.p. 206 °C dec. IR (THF): ν(CO) 2060, 1983, 1929 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.80 (m, 4H, Ph-*o*), 6.98 (m, 6H, Ph-*m*, *p*), 5.99 (s, 5H, C_5H_5), 1.97 (s, 6H, CH_3), 1.62 (s, 6H, CH_3). ^{31}P{1H} NMR (C_6D_6): δ +42.4. MS: *m*/*e* 681 (M^+).

X-ray structure determination

A deep red crystal (0.40×0.25×0.20 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections (CAD4 routines). Crystal data: triclinic, space group $P\bar{1}$, $a = 11.716(1)$, $b = 11.753(2)$, $c = 16.110(2)$ Å, $\alpha = 99.06(1)$, $\beta =$

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*Prepared from the freshly recrystallized *p*-thiocrésol and sodium in THF.

92.61(1), $\gamma=104.20(1)^\circ$, $Z=2$, $\mu=7.190$ cm^{-1}. Intensities were measured with filtered Mo radiation, $\lambda=0.71073$ Å, ω–2θ scan, $2^\circ<\theta<25^\circ$ in the range 0 to 8 for h ($h_{\max}$ value for $\theta_{\max}=25^\circ$ is 13), -14 to 14 for k and -19 to 19 for l. During data collection we encountered some problems with the hardware of our VAX 730 computer. A total of 4176 intensity data measured up to h equal to 8 was stored in three different files, each independently treated by Lorentz–polarization corrections and then merged by the DATA program of the Enraf–Nonius SDP library giving a common file of data. Structure determination with 2827 independent reflections ($I>3\sigma(I)$) showed it to be closely similar to that reported by Tikkanen for $[(C_5H_4PPh_2)_2ZrCl_2]$-$Mo(CO)_4$, so we did not attempt to complete the data set-up to h equal to 13. The structure was solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares methods with neutral atom scattering factors. Fourteen atoms (metals, chlorines, phosphorus and carbonyls) were refined with anisotropic temperature factors, whereas all carbon atoms of methylcyclopentadienyl and phenyl groups were refined isotropically. No attempt was made to locate the hydrogen atoms. Final residuals were $R=0.048$ and $R_w=0.051$, weighting scheme $w^{-1}=[\sigma(I)^2+(0.04I)^2]^{1/2}$. The final atomic coordinates are given in Table 1.

TABLE 1. Positional and equivalent thermal parameters for **6**

Atom	x	y	z	B (Å^2)[a]
Mo	0.5915(1)	0.39430(5)	0.83931(4)	2.29(3)
TI	0.9014(2)	0.2525(1)	0.65688(7)	2.64(6)
Cp1	0.7791	0.0915	0.6736	
Cp2	0.9879	0.4236	0.7300	
Cl1	0.8412(3)	0.2904(2)	0.5269(1)	4.64(9)
Cl2	1.0590(4)	0.1886(2)	0.6022(2)	5.7(1)
P1	0.6238(3)	0.1825(1)	0.8010(1)	2.25(8)
P2	0.7728(3)	0.5049(1)	0.7760(1)	2.25(9)
O1	0.503(1)	0.6275(5)	0.8676(5)	6.4(3)
O2	0.3748(8)	0.2981(5)	0.9356(3)	3.9(2)
O3	0.4269(9)	0.3515(6)	0.6703(3)	5.1(3)
O4	0.7373(9)	0.4745(5)	1.0189(3)	5.7(3)
C1	0.539(1)	0.5453(6)	0.8591(5)	3.5(3)
C2	0.456(1)	0.3301(6)	0.8980(4)	3.2(3)
C3	0.490(1)	0.3633(6)	0.7290(4)	2.6(3)
C4	0.688(1)	0.4428(6)	0.9536(4)	3.5(3)
C11	0.734(1)	0.1468(5)	0.7268(4)	2.5(1)*
C12	0.830(1)	0.0974(6)	0.7415(4)	2.7(1)*
C13	0.854(1)	0.0358(6)	0.6624(4)	3.3(2)*
C14	0.776(1)	0.0544(6)	0.5995(4)	2.9(1)*
C15	0.702(1)	0.1235(5)	0.6378(4)	2.3(1)*
C121	0.902(1)	0.0891(6)	0.8220(5)	3.6(2)*
C131	0.937(1)	−0.0474(8)	0.6517(6)	5.4(2)*
C141	0.764(1)	−0.0013(6)	0.5067(5)	3.6(2)*
C151	0.599(1)	0.1489(6)	0.5923(4)	3.3(2)*
C21	0.887(1)	0.4388(5)	0.7367(4)	2.2(1)*
C22	0.953(1)	0.3868(6)	0.7921(4)	2.6(1)*
C23	1.062(1)	0.3801(6)	0.7606(4)	3.2(1)*
C24	1.068(1)	0.4363(6)	0.6865(4)	2.8(1)*
C25	0.970(1)	0.4762(5)	0.6743(4)	2.5(1)*
C221	0.923(1)	0.3664(6)	0.8812(4)	3.0(1)*
C231	1.162(1)	0.3386(8)	0.7990(5)	4.9(2)*
C241	1.181(1)	0.4618(8)	0.6402(5)	4.7(2)*
C251	0.959(1)	0.5569(6)	0.6112(4)	3.4(2)*
C31	0.486(1)	0.0658(6)	0.7497(4)	2.7(1)*
C32	0.501(1)	−0.0452(7)	0.7089(5)	3.9(2)*
C33	0.397(1)	−0.1360(8)	0.6780(5)	4.6(2)*
C34	0.287(1)	−0.1129(8)	0.6871(5)	4.8(2)*
C35	0.270(1)	−0.0021(8)	0.7262(6)	5.4(2)*
C36	0.377(1)	0.0903(7)	0.7577(5)	4.0(2)*
C41	0.648(1)	0.1081(6)	0.8918(4)	2.8(1)*
C42	0.638(1)	0.1681(6)	0.9724(4)	3.1(2)*
C43	0.644(1)	0.1101(7)	1.0428(5)	3.8(2)*
C44	0.655(1)	−0.0056(7)	1.0293(5)	4.3(2)*
C45	0.659(1)	−0.0679(7)	0.9503(5)	4.1(2)*
C46	0.653(1)	−0.0100(7)	0.8795(5)	3.9(2)*
C51	0.721(1)	0.5678(6)	0.6890(4)	2.9(1)*
C52	0.682(1)	0.4910(7)	0.6112(5)	3.6(2)*
C53	0.638(1)	0.5349(7)	0.5437(5)	4.1(2)*
C54	0.633(1)	0.6543(8)	0.5533(6)	5.1(2)*
C55	0.667(1)	0.7297(8)	0.6297(6)	5.1(2)*
C56	0.713(1)	0.6841(7)	0.6987(5)	4.1(2)*
C61	0.869(1)	0.6395(6)	0.8448(4)	2.6(1)*
C62	0.821(1)	0.6959(6)	0.9147(4)	3.0(1)*
C63	0.896(1)	0.7990(7)	0.9653(5)	3.6(2)*
C64	1.008(1)	0.8444(7)	0.9476(5)	3.8(2)*
C65	1.057(1)	0.7905(8)	0.8792(6)	5.5(2)*
C66	0.983(1)	0.6867(8)	0.8273(5)	4.7(2)*

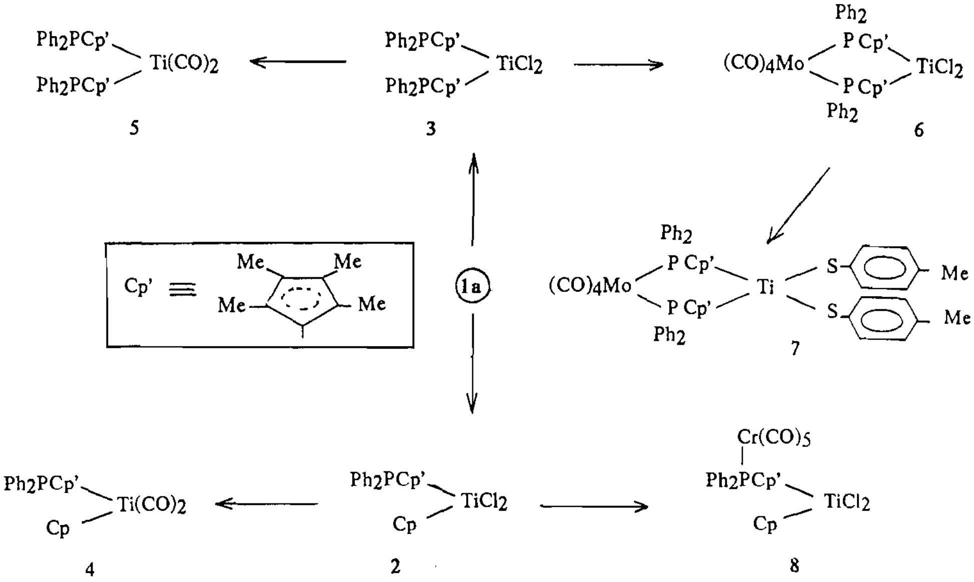
[a] Starred atoms were refined isotropically.

Results and discussion

The ligand **1a** has been used to synthesize two titanium complexes **2** and **3** (Scheme 2) bearing one C_5H_5 and one $C_5Me_4PPh_2$, or two $C_5Me_4PPh_2$ units, respectively.

(η^5-Cyclopentadienyl)[η^5-(diphenylphosphino)-tetramethylcyclopentadienyl]dichlorotitanium (**2**) was obtained by the reaction of the lithium salt of **1a** with $CpTiCl_3$ in THF at room temperature, and isolated as a brick-red powder in 85% yield. The reaction between $TiCl_3$ and two equivalents of metallated **1a** in refluxing THF, followed by a CCl_4 oxidation produced bis[η^5-(diphenylphosphino)tetramethylcyclopentadienyl]dichlorotitanium (**3**) as a brown powder in 90% yield. Both complexes are solids stable under argon and well soluble in tetrahydrofuran, methylene chloride and toluene, moderately soluble in ethyl ether and almost insoluble in pentane.

The structure characterization of **2** and **3** was based upon their elemental analysis, ^1H and ^{31}P NMR spectral data. The ^1H NMR spectra of **2** and **3** display two singlets at 1.82, 1.92 and 1.90, 2.01 ppm, respectively, assignable to protons of the two methyl pairs of the titanium-complexed tetrame-



Scheme 2.

thylcyclopentadienyl ring. Indeed, these values are intermediate between two methyl resonances of the $Ph_2PCp'^-$ anion **1a** (2.24, 2.33 ppm) and the protonated ligand $Ph_2PCp'H$ (1.54, 1.79 ppm) [8].

The ^{31}P NMR chemical shifts of **2** and **3** of −17.1 and −19.0 ppm were consistent with the phosphine ligands not coordinated to a metal atom. These values are closely similar to those reported for a non-substituted analogue $[(C_6H_5)_2P(C_5H_4)]_2TiCl_2$ (−17.3 ppm) [9], as well as for the one of two ^{31}P resonances exhibited by a diphenylphosphine titanocene, $[(C_5H_4PPh_2)(C_7H_6PPh_2)]Ti$ ($\delta = -18.8$ ppm) [12].

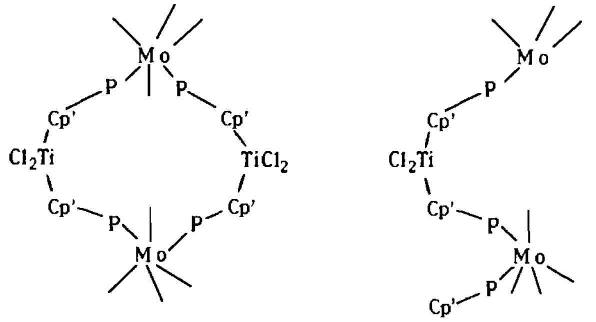
Using a method employed for the reductive carbonylation of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [13], **2** and **3** were converted to their dicarbonyl–titanium analogues **4** and **5** (Scheme 2) in 33 and 30% yields, respectively. Both compounds are air-sensitive red–brown powders of about 95% purity by ^1H NMR.

The proton NMR spectra of **4** and **5** display 0.2–0.3 ppm upfield shifts of the two methyl singlet resonances, compared to their dichloro–titanium precursors **2** and **3**. However, the ligand effect on the titanium atom has only a small repercussion on the electronic density of the phosphorus. Indeed, the ^{31}P chemical shifts only vary over about 3–1.5 ppm within the series **4**–**5** and **2**–**3**, respectively. In turn, the presence of the diphenylphosphine substituent does not significantly perturb the electronic environment about the titanium atom in **4** and **5**, as can be seen from their infrared spectra. The IR spectra of **4** and **5** exhibit two carbonyl stretching bands at 1952, 1882 and 1955, 1882 cm^{-1}, respectively, i.e. very similar to those observed for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ [14]. The above infrared data are in agreement with those obtained by Rausch *et al.* [2a] for a non-substituted $(\eta^5\text{-}C_5H_5)[(\eta^5\text{-}C_5H_4P(C_6H_5)_2]Ti(CO)_2$ (1960, 1880 cm^{-1}).

In order to test the chelating properties of the diphosphine metalloligand **3**, we coordinated it to the $Mo(CO)_4$ fragment, using initially (cyclooctadiene-1,5)tetracarbonylmolybdenum(0), ($Mo(CO)_4$(cod)). Addition of a THF solution of $Mo(CO)_4$(cod) to a stirred solution of **3** in THF at room temperature produces a dark greenish mixture. The IR examination reveals a growing of four CO stretching bands at 2020, 1965, 1913 and 1882 cm^{-1}. The reaction was stopped after a 5 h period, and the complex **6** (Scheme 2) isolated with 81% yield. It crystallized readily from CH_2Cl_2/pentane giving steel grey platelets.

The structural features of **6** have been supported by their ^{31}P, ^1H NMR and IR spectra. The proton-decoupled ^{31}P NMR spectrum of **6** exhibits only one singlet at +35.7 ppm. The downfield shifts of about 55 ppm, relatively to the original bis-diphenylphosphine **3** is indicative of coordination of both phosphorus atoms. In accordance with that, the ^1H NMR spectrum of **6** shows marked downfield shifts of the diphenylphosphine *ortho*-protons resonances compared to **3**. Almost the same chemical shifts of the $-CH_3$ proton resonances for **6** and **3** confirm our above remarks about the relative independance of the PPh_2 and Cp coordination centers. These results are in agreement with those obtained by Tikkanen *et al.* [6a] for the zirconocene series. Compound **6** has also been characterized chemically by the substitution of its two linked-to-titanium chlorine atoms by the thiolate groups. Thus the reaction of **6** with the sodium *p*-methylthiophenoxide in THF produced **7** (Scheme 2) as green crystals with 72% yield. The infrared spectrum in the CO stretching region of **7** is nearly identical with that of **6**. The proton NMR spectrum of **7** displays two doublets at 6.68–6.70 and 7.46–7.48 ppm assignable to the *para*-substituted phenyl system. About 0.2 ppm downfield shifts compared to **6** of the two methyl pair resonances can be observed.

The four carbonyl stretching frequencies observed in the IR spectra of **6** are similar to those reported for different *cis*-diphosphine tetracarbonylmolybdenum(0) complexes [15]. This suggests that complex **6** may be monomeric with the bidentate bis(phosphinocyclopentadienyl)titanium metalloligand like in the analogous Zr complex. However, because of the smaller size of Ti, other structures, e.g. cyclic or chain non-chelated ones, satisfying a *cis*-$P_2Mo(CO)_4$ configuration like those depicted below may be expected.



The results of the single-crystal X-ray analysis carried out on **6** confirm that its molecular structure (Fig. 1) is similar to that of $[(Ph_2PC_5H_4)_2ZrCl_2]Mo(CO)_4$ reported by Tikkanen *et al.* [6a]. Figure 2 shows that as in the Zr analogue the Mo atom does not lie in the open portion of the pocket formed by the bent C_5 rings but is located to the side of this pocket. The substituted Cp rings are staggered (Fig. 2) thus allowing the $P_2Mo(CO)_4$ unit for a geometry without excessive deformation (Table 2).

However there is some significant difference between both structures. The Mo–P distances (2.593(2), 2.549(3) Å), P–Mo–P (97.15(9)°) and Mo–P–C(C_5) (122.9(2), 124.5(2)°) angles in **6** are greater than the corresponding parameters observed in the structure of the zirconium complex — 2.547(1), 2.558(1) Å; 93.96(2)°; 118.3(1) and 122.9(1)°, respectively. The equatorial Mo–C(CO) bonds (mean 1.97 Å) are shorter than the axial ones (mean 2.03 Å) as expected (*trans* influence of the phosphorus atoms) and are the same as in the structure of the zirconium complex.

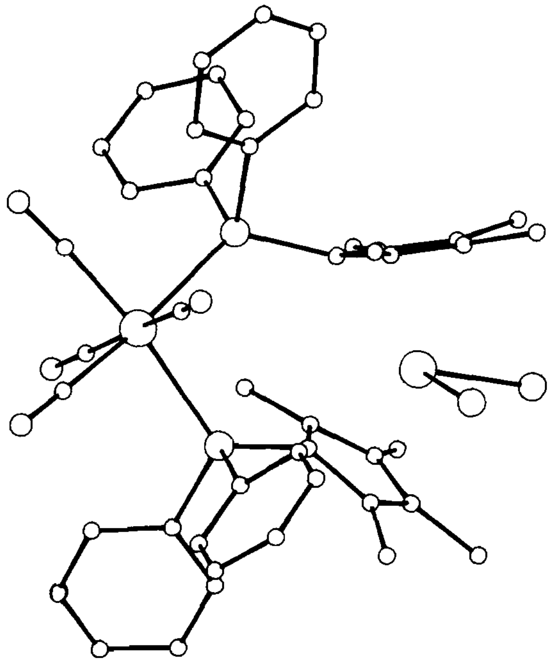


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5Me_4PPh_2)_2\text{-}TiCl_2]Mo(CO)_4$.

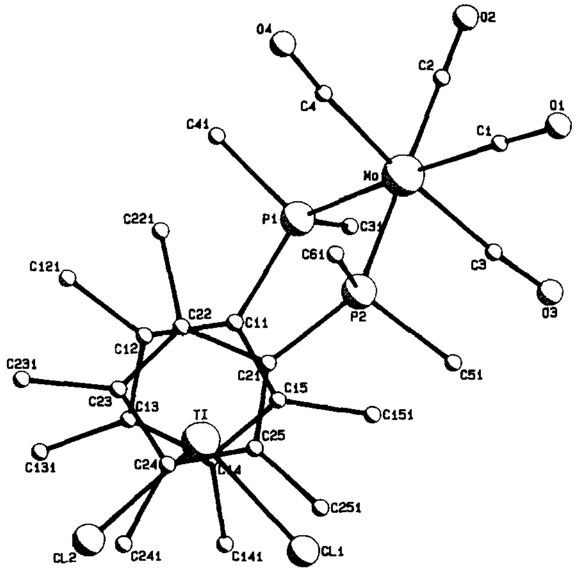


Fig. 2. Projection of the structure of $[(\eta^5\text{-}C_5Me_4PPh_2)_2\text{-}TiCl_2]Mo(CO)_4$ onto the Cl1–Ti–Cl2 plane with the atom labelling scheme. The phenyl rings are omitted for clarity.

The non-bonding Mo–Ti distance of 5.194(1) Å is longer than the Mo–Zr separation of 4.8524(3) Å in spite of the smaller size of Ti compared to that of Zr. It is the most significant difference between the structures which confirms the statement that the smaller metals cause the steric effects to be more pronounced [16]. The parameters observed in the bis-cyclopentadienyl titanium part of the molecule

TABLE 2. Selected interatomic distances (Å) and angles (°) for **6**

Mo...Ti	5.194(1)	P1–C11	1.874(11)
Mo–P1	2.593(2)	P1–C31	1.899(10)
Mo–P2	2.549(3)	P1–C41	1.863(8)
Mo–C1	2.002(10)	P2–C21	1.801(12)
Mo–C2	1.940(11)	P2–C51	1.828(9)
Mo–C3	2.022(9)	P2–C61	1.860(8)
Mo–C4	2.039(9)	C1–O1	1.14(1)
Ti–CP1[a]	2.136	C2–O2	1.17(1)
Ti–CP2	2.147	C3–O3	1.15(1)
Ti–C11	2.323(3)	C4–O4	1.14(1)
Ti–C12	2.317(5)		
P1–Mo–P2	97.15(9)	Mo–P1–C11	122.9(2)
P1–Mo–C1	170.2(3)	Mo–P1–C31	113.5(4)
P1–Mo–C2	89.7(3)	Mo–P1–C41	115.8(2)
P1–Mo–C3	88.6(3)	C11–P1–C31	99.9(4)
P1–Mo–C4	97.8(3)	C11–P1–C41	104.1(5)
P2–Mo–C1	88.8(3)	C31–P1–C41	96.4(4)
P2–Mo–C2	172.2(2)	Mo–P2–C21	124.5(2)
P2–Mo–C3	92.1(4)	Mo–P2–C51	108.0(4)
P2–Mo–C4	87.9(3)	Mo–P2–C61	116.4(3)
C1–Mo–C2	84.9(4)	C21–P2–C51	105.5(4)
C1–Mo–C3	83.4(4)	C21–P2–C61	98.1(5)
C1–Mo–C4	90.2(4)	C51–P2–C61	102.0(3)
C2–Mo–C3	91.7(4)	Mo–C1–O1	176(1)
C2–Mo–C4	87.6(5)	Mo–C2–O2	176.2(6)
C3–Mo–C4	173.6(4)	Mo–C3–O3	174(1)
CP1–Ti–CP2	138.4	Mo–C4–O4	176(1)
CP1–Ti–C11	105.6	CP2–Ti–C11	105.5
CP1–Ti–C12	103.8	CP2–Ti–C12	102.1
C11–Ti–C12	91.7(1)		

[a] CP are the gravity centers of C_5 rings.

agree well with this statement. In the compounds available for direct comparison (**6**, $(C_5Me_5)_2TiCl_2$ [17] and $(C_5H_5)_2TiCl_2$ [18]) the Ti–C(C_5 rings), Ti–CP (centroid of C_5 ring) distances and CP–Ti–CP angles show the regular changes directly corresponding to steric demands. All these parameters decrease on going from **6** through C_5Me_5 to C_5H_5 derivatives. Thus Ti–C distances are equal to 2.46, 2.44 and 2.366 Å, Ti–CP ones are equal to 2.14, 2.13 and 2.06 Å and CP–Ti–CP angles are equal to 138.4, 137.4 and 131.0°, respectively. Generally, the X–M–X angles in bent Cp_2MX_2 complexes decrease with the opening of the CP–M–CP angle [19]. As expected, the corresponding Cl–Ti–Cl angles are equal to 91.7(1) in **6**, 92.94(4) in C_5Me_5 and 94.53(6)° in C_5H_5 complexes.

The methyl groups in **6** are bent considerably out of the cyclopentadienyl best least-squares planes and away from the titanium atom (0.02 to 0.40 Å). These deviations which are generally observed in permethylated cyclopentadienyl rings arise through steric rather than through electronic factors. The deviations of phosphorus atoms from these planes are still greater (0.55 and 0.66 Å) and should be due not only to the differences of P–C_5 and CH_3–C_5 bond lengths (Table 2) but also to the deformations resulting from chelation to the $Mo(CO)_4$ unit.

It appears that the steric influence may favour the insertion of a $Mo(CO)_4$ unit into the parent molecule **3** owing to the expected opening of the C_5–Ti–C_5 angle and to the greater Ti–ring distances compared to the monosubstituted C_5H_5 ring.

The easy formation of the canted bimetallic complex **6** prompted us to check the chelating abilities of the metalloligand **3** by using penta and hexacarbonyls of Mo instead of $Mo(CO)_4$(cod).

Compound **3** reacts with $Mo(CO)_5$THF in THF at room temperature and with $Mo(CO)_6$ in refluxing toluene to give **6** in a good yield. It is worth noting that no trace of the trinuclear acyclic complex $[(Cp'PPh_2)_2TiCl_2][Mo(CO)_5]_2$ could be detected. The entropically favoured intramolecular cyclization step seems to control the overall chelation process.

We note that the treatment of the monophosphine metalloligand **2** with the polycarbonylmolybdenum(0) reagents $Mo(CO)_6$, $Mo(CO)_5$THF and $Mo(CO)_4$(cod) in different temperatures gave rise to complex reaction mixtures. Even in the case of $Mo(CO)_5$THF no defined product could be isolated from these. Moreover, when **2** was treated with $Cr(CO)_5$THF in THF at room temperature, a bimetallic compound **8**, $\{[CpCp'PPh_2]TiCl_2\}$ $Cr(CO)_5$, could be isolated as a grey-green powder with 72% yield.

The reasons for the presumed reactivity (instability) of the pentacarbonylmolybdenum species, $[(Cp'PPh_2)TiCl_2L_n][Mo(CO)_5]_x$ (L_n = Cp'PPh$_2$ and $x=2$ for **3**; L_n = Cp and $x=1$ for **2**), are not clear but may be of electronic nature. However, that may be, the –$Mo(CO)_5$ mono-coordinated intermediate derived from the chelating diphosphine **3** was obviously transformed into **6** by the rapid ligand substitution–cyclization process. This reaction occurs readily probably due to the above-mentioned steric effect of the methyl groups. On the other hand, the thermodynamic stability of the canted heterobimetallic chelate **6** would be assured by the possible conformational arrangement in the titanocene species. Further studies on complexes containing the (diphenylphosphino)tetramethylcyclopentadienyl ligands **1a** and **1b** are currently in progress.

Supplementary material

Tables of anisotropic thermal parameters, least-squares planes and structure factors may be obtained from the authors.

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