ELSEVIER

Journal of Organometallic Chemistry 654 (2002) 109–116

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of new half sandwich tetrachloro derivatives of molybdenum(V) and tungsten(V). X-ray structures of $(C_5HPr^i_4)W(CO)_3(CH_3)$ and $(C_5Et_5)WCl_4$

Matthias Bastian [a,b], Dolores Morales [b], Rinaldo Poli [b,*], Philippe Richard [b], Helmut Sitzmann [a,*]

[a] *Fachbereich Chemie, Universität Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany*
[b] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté de Science Gabriel, Université de Bourgogne, 6 boulevard Gabriel, 21000 Dijon, France*

Abstract

The new synthetic intermediates (Ring)MCl_4 [Ring = $C_5HPr^i_4$ or ^4Cp, M = Mo, **2**; Ring = C_5Et_5 or ^VCp, M = W, **4**, Ring = ^4Cp, M = W, **6**] containing sterically protecting cyclopentadienyl ligands have been synthesized. Along the synthetic pathway to **2**, it was found that the treatment of $[^4CpMo(CO)_3]^-$ with an aqueous ferric solution according to the well established Manning procedure affords the hydride compound $^4CpMo(CO)_3H$ (**1**) by hydrolysis rather than the expected neutral dimer by oxidation. Compound **1** could be converted, however, to **2** upon oxidation with $PhICl_2$ in good yields. Compound **4** is shown by a single crystal X-ray analysis to adopt a monomeric four-legged piano stool structure. The precursors to compounds **4** and **6**, (Ring)$W(CO)_3(CH_3)$ (Ring = ^VCp, **3**; ^4Cp, **5**) have also been characterized, including an X-ray structure for **5**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Tungsten; Bulky cyclopentadienyl ligands; Organometallic synthesis; X-ray structure

---

1. Introduction

Half-sandwich halide compounds are useful intermediates for the preparation of a large variety of organometallic products [1]. Cyclopentadienyl ligands carrying large substituents have been used to study the influence of steric bulk on metallocenes of the transition metals [2–10]. They are capable of stabilizing unusual unsaturated configurations and of tuning the reactivity of other co-ligands via their control of the steric environment around the metal [11–15]. It is, therefore, desirable to develop new half-sandwich halide derivatives containing sterically encumbering cyclopentadienyl rings. The pentaethylcyclopentadienyl (^VCp) ligand [16,17] has recently been utilized for the preparation of ferrocene and ferrocenium analogues [8] and the half-sandwich Mo(V) complex $(^VCp)MoCl_4$ [18]. In the latter report, it was shown that while the electronic effect of the ^VCp ligand is equivalent to that of the pentamethyl analogue Cp*, the greater steric encumberance exerts a kinetic control of the protonation reaction of hydride derivatives and on the dihydrogen elimination reaction from the protonated products. We are, therefore, interested in the development of a larger variety of half sandwich Mo(V) species, and also their W(V) counterparts, for the further development of this sterically protected hydride chemistry.

In this contribution, we report the synthesis of the tetrachloro Mo(V) complex containing the tetraisopropylcyclopentadienyl (^4Cp) ligand and of both the ^VCp and ^4Cp analogues of tetrachloro W(V), including the X-ray structure of $^VCpWCl_4$.

2. Experimental

All manipulations were carried out under an inert atmosphere of argon. Solvents were dried by standard methods (THF, Et_2O, toluene and pentane over Na–

---

* Corresponding authors. Tel.: +33-38-39-6881; fax: +33-38-39-3720.

E-mail address: poli@u-bourgogne.fr (R. Poli).

PII: S0022-328X(02)01392-X

benzophenone, CH_2Cl_2 over P_2O_5, CH_3CN over molecular sieve), followed by distillation under argon. The instrumentation used for the spectroscopic characterization was as follows: ^{1}H-NMR, Bruker AC 200 or AMX 400; IR, Perkin–Elmer IFS 66 and Perkin–Elmer 16 PC; EPR, Bruker ESP 300 (X band). Elemental analyses were performed by the LSEO analytical services with a Fisons EA 1108 apparatus and by the Fachbereich Chemie Kaiserslautern analytical service with a Perkin–Elmer 240 or 400 CHN analyzer. Compounds $PhICl_2$ [19], Li^{V}Cp [16], and Na^{4}Cp [6] were prepared by literature methods.

2.1. *Synthesis of ^{4}CpMo(CO)$_3$H (**1**)*

Hexacarbonylmolybdenum (4.51 g, 17.1 mmol) and sodium tetraisopropylcyclopentadienide (4.817 g, 18.7 mmol) were suspended together in 100 ml of THF. The mixture was refluxed for 16 h, during which time it transformed into an orange solution. The IR spectrum of this solution showed bands at 1889, 1785s and 1734s cm^{-1} and the complete consumption of the starting material. This solution was subsequently added slowly to an aqueous solution of $Fe_3(SO_4)_2$ (6.8 g, 17 mmol, in 2 l of degased water). After stirring for 1 h, the resulting orange precipitate was filtered in air through a Buchner funnel. The solid was purified by dissolution in pentane and filtration through alumina, leaving a brown insoluble deposit on the column. Subsequent removal of the solvent by evaporation under reduced pressure and prolonged drying left a spectroscopically pure oil. Yield: 4.09 g (58%). The spectroscopic (IR, ^{1}H-NMR) properties match those previously reported in the literature [20].

2.2. *Synthesis of ^{4}CpMoCl$_4$ (**2**)*

To a solution of ^{V}CpMo(CO)$_3$H (4.09 g, 9.86 mmol) in 40 ml of dichloromethane was added in small portions a solution of $PhICl_2$ (6.78 g, 24.7 mmol) in 50 ml of CH_2Cl_2 by cannula. During the addition, the color of the solution changed to purple, while vigorous gas evolution ensued and a purple solid precipitated. The reaction mixture was further stirred for 1 h at room temperature (r.t.) After filtration, the solid was washed with pentane (5×20 ml) and dried under vacuum. Yield: 1.97 g (42.4%). EPR (CH_2Cl_2): singlet with Mo satellites, $g = 1.989$, $a_{Mo} = 38.9$. Anal. Calc. for $C_{17}H_{29}Cl_4Mo$: C, 43.34; H, 6.20. Found: C, 43.81; H, 6.25%.

2.3. *Synthesis of ^{V}CpW(CO)$_3$(CH$_3$) (**3**)*

To a suspension of hexacarbonyltungsten (2.287 g, 6.5 mmol) in 50 ml of THF was added by cannula a solution of lithium pentaethylcyclopentadienide in 25 ml of THF at r.t. The yellow–brown reaction mixture was refluxed to yield a red–orange solution after ca. 12 h. After cooling down to r.t. methyl iodide (0.40 ml, 0.92 g, 6.5 mmol) was added with a syringe. During the addition, the color immediately changed to red–brown. The reaction mixture was refluxed for an additional hour. The solvent was then removed to obtain a brown precipitate, which was extracted into CH_2Cl_2 and filtered through Celite. Evaporation of the filtrate to dryness yielded 3.016 g (95%) of an orange–yellow solid. IR (pentane, cm^{-1}): 2008.3 m, 1917.3 s. ^{1}H-NMR (C_6D_6, δ): 1.98 (q, $J = 7.51$ Hz, 10H, CH_2CH_3), 0.87 (t, $J = 7.51$ Hz, 15H, CH_2CH_3), 0.40 (s, 3H, W–CH_3). Anal. Calc. for $C_{19}H_{28}O_3W$: C, 46.74; H, 5.78. Found: C, 46.13; H, 6.65%.

2.4. *Synthesis of ^{V}CpWCl$_4$ (**4**)*

To a solution of compound **3** (2.09 g, 4.28 mmol) in 20 ml of dichloromethane was added in small portions a solution of $PhICl_2$ (4.12 g, 15.0 mmol) in 40 ml of CH_2Cl_2 by cannula. During the addition, the color of the solution changed from brown to dark green, while vigorous gas evolution ensued. The reaction mixture was refluxed for 5 h yielding an orange–brown solution. The solution was then treated with 25 ml of THF to destroy the excess of $PhICl_2$. The solvents were then removed by evaporation under reduced pressure and the olive precipate was extracted into dichloromethane and filtered over Celite. Evaporation of the filtrate to dryness left a brown solid (1.17 g, 51.5%). Single crystals of this compound were obtained from a dichloromethane solution at -80 °C in 12 h. Anal. Calc. for $C_{15}H_{25}Cl_4W$: C, 33.93; H, 4.75. Found: C, 33.57; H, 4.57%. EPR (CH_2Cl_2): broad singlet, $g = 1.958$, width (peak-to-peak) = 13 G, $a_W = 64$ G.

2.5. *Synthesis of ^{4}CpW(CO)$_3$(CH$_3$) (**5**)*

To a suspension of hexacarbonyltungsten (1.76 g, 5.0 mmol) in 30 ml of THF was added dropwise a solution of sodium tetraisopropylcyclopentadienide (1.282 g, 5 mmol) in 10 ml of THF at r.t. The yellow–brown reaction mixture was refluxed to yield a red–brown solution after ca. 14 h. After cooling down to r.t., methyl iodide (0.31 ml, 0.71 g, 5.0 mmol) was added with a syringe. The reaction mixture was refluxed for an additional hour. The solvent was then removed to obtain a brown precipitate, which was extracted into CH_2Cl_2 and filtered. Evaporation of the filtrate to dryness yielded 2.151 g (4.2 mmol, 83.3%) of a yellow solid. IR (THF, cm^{-1}): 2001.7 vs, 1907.9 vs. ^{1}H-NMR (C_6D_6, δ): 4.73 (s, 1H, ring CH), 2.61 (septet, $J = 6.8$ Hz, 2H, $CHMe_2$), 2.29 (septet, $J = 7.2$ Hz, 2H, $CHMe_2$), 1.23 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$), 1.07 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.05 (d, $J = 7.0$ Hz, 6H,

Table 1
Crystal data and structure refinement parameters for compounds **4** and **5**

Compound	^{4}CpW(CH$_3$)(CO)$_3$ (**5**)	^{V}CpWCl$_4$ (**4**)
Empirical formula	$C_{21}H_{32}O_3W$	$C_{15}H_{25}Cl_4W$
M	516.3	531.00
T (K)	110(2)	110(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbca* (see text)
a (Å)	14.388(5)	14.2596(9)
b (Å)	16.962(5)	15.7854(9)
c (Å)	8.490(5)	16.0106(7)
V (Å^3)	2072.0(15)	3603.9(3)
Z	4	8
F(000)	1024	2056
D_{calc} (g cm^{-3})	1.655	1.957
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Scan type	ϕ rotation and ω scans	ϕ rotation and ω scans
λ (Å)	0.71073	0.71073
μ (mm^{-1})	5.591	6.992
Crystal size (mm^3)	0.37 × 0.25 × 0.12	0.15 × 0.12 × 0.12
Sin(θ)/λ max; (Å^{-1})	0.65	0.53
Index ranges	$-17 \leq h \leq 18$, $-21 \leq k \leq 20$, $-11 \leq l \leq 9$	$-9 \leq h \leq 15$, $-16 \leq k \leq 16$, $-13 \leq l \leq 17$
Reflections collected	8501	9119
Independent reflections collected	2417 [$R_{int} = 0.0372$]	2263 [$R_{int} = 0.082$]
IRCGT = IRC and [$I > 2\sigma(I)$]	1920	1896
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	2417/0/170	2263/0/106
R for IRCGT	R_1 [a] $= 0.026$, wR_2 [b] $= 0.059$	R_1 [a] $= 0.048$, wR_2 [b] $= 0.109$
R for IRC	R_1 [a] $= 0.037$, wR_2 [b] $= 0.064$	R_1 [a] $= 0.055$, wR_2 [b] $= 0.1127$
Goodness-of-fit [c]	1.051	1.139
$\Delta\rho$, max/min (e Å^{-3})	1.15 and −1.74	1.09 and −1.61

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2+(0.00P)^2+75.12P]$ for **4** and $w = 1/[\sigma^2(F_o^2+(0.027P)^2+1.47P]$ for **5** where $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$.

[c] Goodness-of-fit $= [\Sigma\, w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$.

CH(CH_3)$_2$), 0.96 (d, $J = 6.8$ Hz, 6H, CH(CH_3)$_2$), 0.61 (s with satellites, $J_{WH} = 1.8$ Hz, 3H, W–CH_3). ^{13}C-NMR (C_6D_6, δ): 233.6 (s with satellites, $J_{WC} = 66.18$ Hz, 1C, W–*C*O), 220.4 (s with satellites, $J_{WC} = 77.21$ Hz, 2C, W–*C*O), 117.2 (s, 2C, ring), 112.7 (s, 2C, ring), 91.3 (s, 1C, ring), 26.9 (s, *i*-Pr), 26.6 (s, *i*-Pr), 26.0 (s, *i*-Pr), 25.2 (s, *i*-Pr), 24.4 (s, *i*-Pr), 23.9 (s, *i*-Pr), −29.8 (s with satellites, $J_{WC} = 15.16$ Hz, W–*C*H_3). Anal. Calc. for $C_{21}H_{32}O_3W$: C, 48.89; H, 6.25. Found: C, 48.30; H, 6.10%. Single crystals of this compound were grown from benzene at r.t.

2.6. Synthesis of ^{4}CpWCl$_4$ (**6**)

Compound **5** (1.033 g, 2 mmol) was dissolved in 20 ml of dichloromethane. A solution of PhICl$_2$ (1.375 g, 5 mmol) in 30 ml of dichloromethane was added dropwise during 15 min while stirring at r.t. A strong gas evolution ensued and the color of the reaction mixture changed from brown to dark red–brown. The solution was stirred at r.t. overnight, during which time the color became green. A small amount (5 ml) of THF was added to destroy the excess of PhICl$_2$. Then, the solution was evaporated to dryness leaving a dark-green solid (0.845 g, 1.5 mmol, yield: 75.6%). Anal. Calc. for $C_{17}H_{29}WCl_4$: C, 36.52; H, 5.23. Found: C, 37.02; H, 4.83%. The product is extremely soluble in dichloromethane, toluene and diethylether and could be recrystallized by cooling concentrated solutions in these three solvents to −70 °C. EPR (THF, r.t.): $g = 1.958$, width (peak-to-peak) = 13.5 G, $a_W = 64.2$ G. ^{1}H-NMR (at 200 MHz, CDCl$_3$, δ): nine signals of varying intensity between 7.15 and 7.85 (C*H*Me$_2$, $\Delta\nu_{1/2} \sim 20$ Hz), four overlapping signals at 2.10, 1.55, 0.77, and 0.44 with $\Delta\nu_{1/2}$ ca. 400–600 Hz.

2.7. X-ray crystallography for compounds **4** and **5**

2.7.1. General

Both intensity data were collected on a Nonius Kappa CCD diffractometer at 110 K. The structures were solved by a Patterson search program and refined by full-matrix least-square methods (SHELX-97) [21] with the aid of the WINGX program [22]. The crystal data and refinement parameters for both compounds are collected in Table 1.

Table 2
Bond lengths (Å) and angles (°) for compounds **4** and **5** [a]

Compound **4**		Compound **5**	
Bond lengths			
W–CNT	2.053(4)	W–CNT	2.010(3)
W–Cl(1)	2.2894(16)	W–C(1)	2.288(5)
W–Cl(2)	2.3381(15)	W–C(2)	1.987(3)
W–Cl(3)	2.3403(12)	W–C(3)	2.000(5)
W–Cl(4)	2.3380(12)	C(2)–O(1)	1.148(3)
		C(3)–O(2)	1.111(6)
Bond angles			
CNT–W–Cl(1)	112.5(3)		
CNT–W–Cl(2)	110.9(2)	CNT–W–C(1)	112.2(4)
CNT–W–Cl(3)	110.2(2)	CNT–W–C(2)	125.9(4)
CNT–W–Cl(4)	110.4(2)	CNT–W–C(3)	117.0(4)
Cl(1)–W–Cl(2)	84.12(6)	C(1)–W–C(2)	72.95(12)
Cl(1)–W–Cl(3)	137.29(5)	C(1)–W–C(3)	130.80(19)
Cl(1)–W–Cl(4)	82.86(5)	C(2)–W–C(3)	78.65(11)
Cl(2)–W–Cl(3)	81.49(5)	C(2)–W–C(2) [b]	107.55(18)
Cl(2)–W–Cl(4)	138.62(4)		
Cl(3)–W–Cl(4)	81.99(4)		

[a] CNT, cycopentadienyl ring centroid.

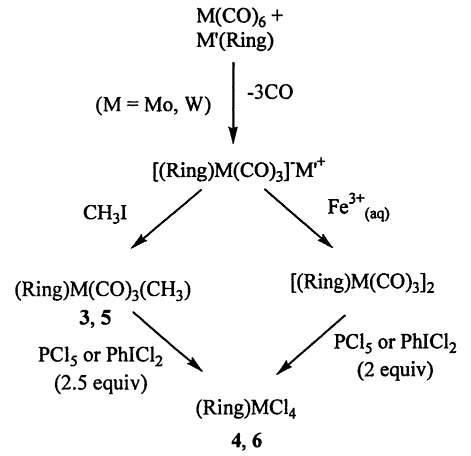
[b] Symmetry transformation used to generate equivalent atom: x; $-y+1/2$; z.

2.7.2. Compound ^{V}CpWCl$_4$ (**4**)

A single crystal was selected from the −80° crystallization solution after removing the mother liquor by cannula transfer. The crystals were washed with cold pentane and dried by purging with argon. Prior to mounting on the diffractometer, the crystal was stored at −80 °C to avoid decomposition. The refinement was rather unstable and led to non-positive defined adp for some atoms. A careful inspection of the data set indicated that the *hkl* layers with *k* odd exhibited a much lower mean intensity than the even ones. For example: $(k, \langle F^2 \rangle) = (0, 189)$, (1, 6), (2, 256), (3, 5), (4, 253), (5, 6) etc. Skipping these odd layers led to the new space group *Pbcm* with cell parameters $a = 7.8925(5)$ Å, $b = 16.0106(7)$ Å, $c = 14.2596(9)$ Å. In this space group, the molecule is located on a mirror plane, which could explain the pseudo-symmetry problem encountered. Nevertheless, a refinement in this group led to non-realistic adp and strong residual peaks in the last Fourier difference map. We present the results in the *Pbca* space group with an isotropic refinement of the carbon atoms. Hydrogen atoms were included in a riding model. Selected bond distances and angles are listed in Table 2.

2.7.3. Compound ^{4}CpW(CO)$_3$(CH$_3$) (**5**)

A single crystal could be obtained from a benzene solution at r.t. The mother liquor was decanted off and the crystals were dried in a nitrogen purge. Non-hydrogen atoms were anisotropically refined and hydrogen atoms, found in the last Fourier difference maps, were refined freely. Selected bond distances and angles are listed in Table 2.



Scheme 1.

3. Results and discussion

The synthetic scheme for the tetrachloro compounds reported in this paper parallel those reported previously by Schrock [23], Green [24] and ourselves [25,26] for the Cp* and other cyclopentadienyl derivatives of Mo and W, including ^{V}CpMoCl$_4$ [18] These are illustrated in Scheme 1, where (Ring) is a generic cyclopentadienyl ligand and M′ is an alkali metal, usually Li, Na or K. Salts of the appropriate cyclopentadienyl derivative react with the hexacarbonyl starting material to afford the corresponding cyclopentadienyltricarbonyl anion. In the Schrock method, the latter anion is quenched by methyl iodide to afford a tricarbonyl methyl product which is subsequently transformed to the tetrachloro product by use of 2.5 equivalents of PCl$_5$. In the method used by Green and us, on the other hand, the anion is transformed to the neutral dimer by the ferric oxidation, which was first illustrated by Manning [27]. This neutral species can then be transformed to the tetrachloro product by the use of only two equivalents of either PCl$_5$ or the convenient alternative chlorinating agent PhICl$_2$.

For reasons of atom economy, we initially adopted the dimer route for the preparation of ^{4}CpMoCl$_4$. We were surprised, however, to find that the product of the aqueous ferric oxidation was not the expected dimer but rather the corresponding Mo(II) hydride species, ^{4}CpMo(CO)$_3$H (**1**), which was recovered in a relatively good yield. No trace of the dimer was evident from the IR spectrum of the crude product. This reactivity pattern may result from the steric shielding exerted by the bulky cyclopentadienyl, which slows down the rate of thermodynamically favorable processes. This effect is apparently stronger for the outer sphere electron transfer from

$Fe^{3+}_{(aq)}$ with respect to the metal protonation process. The protonation should be a favorable process also for less encumbered anions, since the pK_a of, for instance, $CpMo(CO)_3H$ is 13.9 in acetonitrile [28] (corresponding to ca. 6.4 in water) [29] and derivatives with alkyl-substituted cyclopentadienyl ligands are naturally expected to be less acidic. However, the success of the Manning procedure for the synthesis of the Cp and even Cp* dimers shows that the electron transfer process is faster in those cases.

The properties of the hydride compound **1** are as expected, with a typical pattern of CO stretching vibrations in the IR and a highly shielded ^{1}H-NMR resonance for the hydride proton [30,31]. The clean conversion shown by Schrock for the methyl compound to the tetrachloro product made us suspect that the hydride compound could also be a convenient starting material for the same transformation according to the same stoichiometry, with elimination of HCl (see Eq. (1)). Indeed, this turned out to be the case, compound $^4CpMoCl_4$ (**2**), being recovered in a 42% yield by this procedure. A similar conversion of $CpWH(CO)_3$ to $CpWCl_4$ was reported recently by Royo et al. [32]. Compound **2** has EPR properties analogous to those of the previously reported compounds with other rings and fully consistent with a monomeric structure, showing a sharp singlet with Mo satellites at $g = 1.989$ with $a_{Mo} = 38.9$ G.

$$\begin{aligned} &{}^4\underset{\mathbf{1}}{\mathrm{CpMo(CO)_3H}} + 2.5\ \mathrm{PhICl_2} \\ &\quad \rightarrow {}^4\underset{\mathbf{2}}{\mathrm{CpMoCl_4}} + 2.5\ \mathrm{PhI} + \mathrm{HCl} \qquad (1) \end{aligned}$$

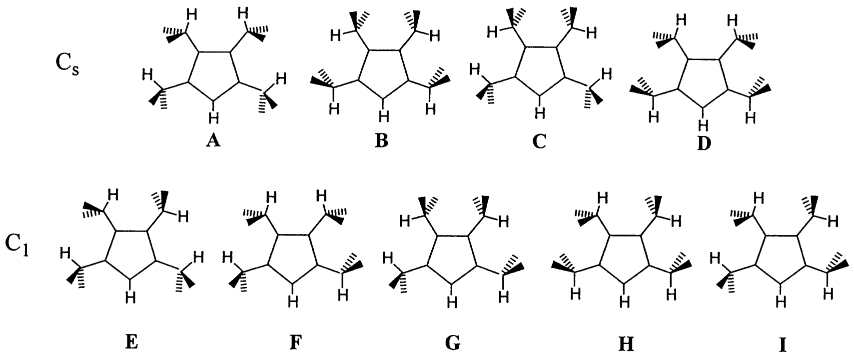
In view of the above complications, the synthesis of the tungsten compounds (Ring)WCl_4 [Ring = ^{V}Cp, **4**, ^{4}Cp, **6**] was carried out by returning to the original Schrock procedure via the tricarbonyl methyl intermediates (Ring)$W(CO)_3(CH_3)$ [Ring = ^{V}Cp, **3**, ^{4}Cp, **5**]. Compounds **3** and **5** show, like the hydride complex **1**, the typical properties of this four-legged piano stool half-sandwich class of complexes, notably the CO stretching frequencies are characteristic of this stoichiometry, as can be seen from the data in Table 3. Conversion of **3** and **5** to the tetrachloro complexes **4** and **6** proceeded as expected according to Scheme 1. The W(V) tetrachloro compounds are characterized by an EPR signal whose parameters are independent on the nature of the ring. Their linewidth (ca. 13 G peak-to-peak) is sharper than that observed previously for the Cp* analogue (50 G) [23], allowing the clear observation of the metal satellites. The hyperfine coupling constant to the ^{183}W nucleus (14.4% abundance) is 62 G.

Table 3
Comparison of CO stretching frequencies for substituted cyclopentadienyl complexes of tungsten

Compound	ν(CO) (cm^{-1})		Solvent	Reference
$CpW(CO)_3Me$	2020vs	1930vs	CCl_4	[52]
$^4CpW(CO)_3Me$ (**5**)	2001.7vs	1907.9vs	THF	This work
	2010.1vs	1919.2vs	Pentane	
$^VCpW(CO)_3Me$ (**3**)	2008.3s	1917.3vs	Pentane	This work
$Cp^*W(CO)_3Me$	2013s	1920vs	Pentane	[53]

The ^{1}H-NMR data on the three ^{4}Cp compounds **1**, **5** and **6** shows interesting features concerning the mobility of the isopropyl substituents. For compounds **1** and **5**, only two methyne peaks are observed, indicating that either only one rigid C_s conformer is present in solution (this could correspond to the structure observed in the solid state for compound **5**, vide infra) or that the various possible conformers are rapidly equilibrating. Four C_s-symmetric (2:2, **A**–**D**) and five C_1-symmetric (of which four 3:1, **E**–**H**, and one 4:0, **I**) conformers are possible in principle (see Scheme 2), if we restrict the possibilities to having the methyne proton on the ring plane. The n:($4-n$) nomenclature indicates the number of methyne H atoms that are oriented in the two opposite (clockwise and anti-clockwise) directions. All determined solid state structures, including the one reported in this work, show either a 2:2 or a 3:1 conformation. The structure of compound **5** (vide infra) corresponds to the arrangement **A**, like many other previously determined structures [2,15,33–39]. Among the alternative arrangements shown in Scheme 2, only **E** is precedented [2,15,34–36,38–42]. Moreover, three bis(tetraisopropylcyclopentadienyl) complexes exhibiting both arrangements **A** and **E** within the same molecule have also been structurally characterized [2,35,39].

Hindered rotation of isopropyl groups is not commonly observed in tetraisopropylcyclopentadienyl complexes at room temperature, except for the extremely congested octaisopropylferrocene [6]. Therefore, it seems more likely that the isopropyl groups are freely rotating in solution for compounds **1** and **5**. This hypothesis is equally in agreement with the observation of four distinct doublet resonances of equal intensity for the isopropyl methyl protons in these compounds. For compound **6**, on the other hand, two distinct regions of resonances can be identified as originating from the methyne and methyl protons (see Fig. 1). The peaks are broad and paramagnetically shifted but still sufficiently sharp to provide useful structural information (this is not the case for the analogous Mo complex **2**). Incidentally, the NMR spectrum also shows that the compound is not contaminated by significant amount of diamagnetic impurities. The relative intensities of the two regions at δ 7–8 and -1 to 4 allows their relative assignment to the methyne and methyl protons, respectively. The methyne region shows at least nine peaks of various intensities, consistent with the population of several conformations and with the slow interconversion



Scheme 2.

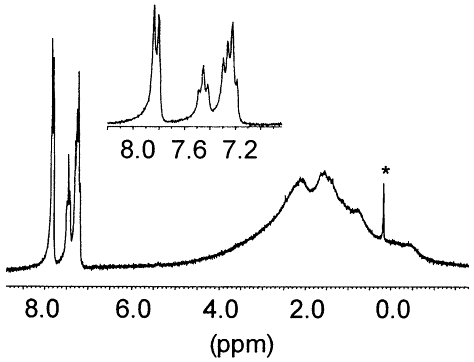


Fig. 1. ^{1}H-NMR spectrum of compound $(C_5Pr^i_4H)WCl_4$. The starred peak is due to a minor diamagnetic contaminant (probably silicone grease).

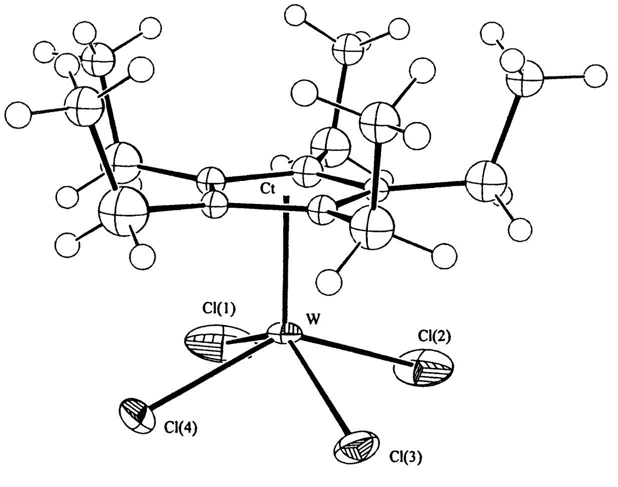


Fig. 2. ORTEP view of compound $(C_5Et_5)WCl_4$.

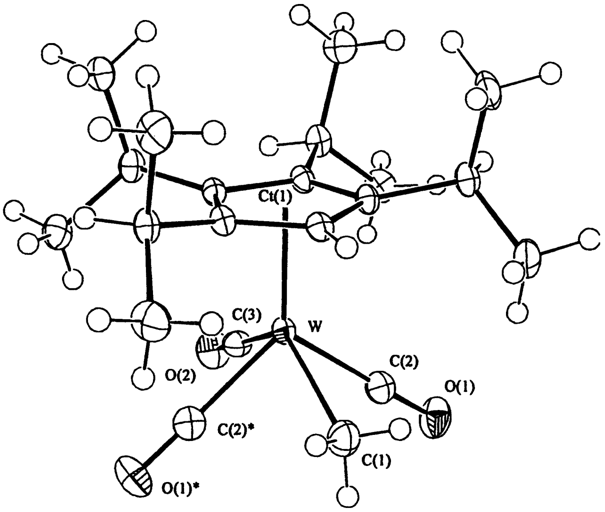


Fig. 3. ORTEP view of compound $(C_5Pr^i_4H)W(CO)_3(CH_3)$.

of these on the NMR time scale. At a first glance, it seems strange that the fast exchange limit for the isopropyl group rotation is observed for **1** and **5** while the slow exchange limit is observed for **6**, since all systems have similar four-legged piano stool geometries, thus the rotation barriers should be similar. In fact, the NMR observation of fast and slow exchange depends not only on the rate constant for the exchange process but also on the frequency difference between the resonances in the slow exchange limit. The much greater resonance spread for paramagnetic **6** is the likely cause for the observation of the slow exchange limit, even if the exchange rate may be similar to that in the diamagnetic compounds. It seems to us that this is the first report, for a ^{4}Cp derivative, where a restricted rotation of the isopropyl groups is directly evidenced. We are aware, however, of a similar situation for another paramagnetic complex, namely $[^4CpNi(\mu\text{-}Br)]_2$ [43].

In the solid state (see Fig. 2) **4** exhibits a four-legged piano stool geometry with a ring centroid—metal distance of 2.05 Å, which is ca. 3% longer than the 1.99 Å found for $[(C_5H^i_4Pr)WCl_4]$ [24]. The W–Cl bonds of **4** (see Table 2, average bond length 2.326 Å) are slightly shorter than those of the literature precedent (2.343 Å) and less uniform. Four chloro ligands arrange with five ethyl-substituted ring carbon atoms such that Cl(3) is fully eclipsed with one ring carbon atom and consequently displays the longest W–Cl bond (2.340 Å), whereas Cl(1) in transposition exhibits the shortest W–Cl distance of 2.289 Å.

The crystal structure of **5** (Fig. 3) reveals a molecule sitting on a crystallographic mirror plane which contains the tungsten–methyl and the C(3)–O(2) bonds as well as the ring CH unit and the ring center. The distance between the ring center and the tungsten atom (see Table 3) is in the middle of the 2.00–2.02 Å range usually found for tricarbonyl(cyclopentadienyl)tungsten methyl complexes [44–51]. The W–CH_3 distance is among the relatively short bonds within the 2.23–2.44 Å range reported in the literature. The methyl ligand is in an eclipsed position with regard to the unsubstituted ring carbon atom C(4), while the *trans*-CO ligand is accommodated between the two isopropyl groups turned away from each other on the opposite side of the ring.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 178173 and 178174. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the French Ministry of Research and to the CNRS for funding, and the French and German Ministries of Foreign Affairs for a bilateral travel grant (Procope program).

References

[1] R. Poli, Chem. Rev. 91 (1991) 509.
[2] D.J. Burkey, M.L. Hays, R.E. Duderstadt, T.P. Hanusa, Organometallics 16 (1997) 1465.
[3] J.S. Overby, T.P. Hanusa, S.P. Sellers, G.T. Yee, Organometallics 18 (1999) 3561.
[4] J.S. Overby, N.J. Schoell, T.P. Hanusa, J. Organomet. Chem. 560 (1998) 15.
[5] M.L. Hays, D.J. Burkey, J.S. Overby, T.P. Hanusa, S.P. Sellers, G.T. Yee, V.G. Young, Organometallics 17 (1998) 5521.
[6] H. Sitzmann, J. Organometal. Chem. 354 (1988) 203.
[7] D. Stein, H. Sitzmann, R. Boese, J. Organometal. Chem. 421 (1991) 275.
[8] D. Stein, H. Sitzmann, E. Dormann, H. Winter, J. Organometal. Chem. 412 (1991) 143.
[9] H. Sitzmann, M. Schar, E. Dormann, M. Kelemen, Z. Anorg. Allg. Chem. 623 (1997) 1609.
[10] H. Sitzmann, M. Schar, E. Dormann, M. Kelemen, Z. Anorg. Allg. Chem. 623 (1997) 1850.
[11] O.J. Scherer, Chem. Unserer Zeit 34 (2001) 374.
[12] O.J. Scherer, J. Meiers, M. Regitz, M.A. Hofmann, K. Karaghiosoff, G. Wolmershäuser, Z. Anorg. Allg. Chem. 627 (2001) 1532.
[13] C. Eichhorn, O.J. Scherer, T. Sögding, G. Wolmershäuser, Angew. Chem. Int. Ed. Engl. 43 (2001) 2859.
[14] H. Sitzmann, T. Dezember, W. Kaim, F. Baumann, D. Stalke, J. Kärcher, E. Dormann, H. Winter, C. Wachter, M. Kelemen, Angew. Chem. Int. Ed. Engl. 35 (1996) 2872.
[15] F. Baumann, E. Dormann, Y. Ehleiter, W. Kaim, J. Kärcher, M. Kelemen, R. Krammer, D. Saurenz, D. Stalke, C. Watcher, G. Wolmershäuser, H. Sitzmann, J. Organomet. Chem. 587 (1999) 267.
[16] D. Stein, H. Sitzmann, J. Organomet. Chem. 402 (1991) 249.
[17] D. Stein, H. Sitzmann, J. Organomet. Chem. 402 (1991) C1.
[18] D. Morales, R. Poli, J. Andrieu, Inorg. Chim. Acta 300–302 (2000) 709.
[19] H.J. Lucas, E.R. Kennedy, Org. Synth. 22 (1942) 482.
[20] H. Sitzmann, Chem. Ber. 123 (1990) 2311.
[21] G.M. Sheldrick, SHELX97 (Includes SHELXS97 and SHELXL97), Release 97–2, Programs for Crystal Structure Analysis', University of Göttingen, 1998.
[22] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[23] R.C. Murray, L. Blum, A.H. Liu, R.R. Schrock, Organometallics 4 (1985) 953.
[24] M.L.H. Green, J.D. Hubert, P. Mountford, J. Chem. Soc. Dalton Trans. (1990) 3793.
[25] D.W. Keogh, R. Poli, Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer), vol. 8, Georg Thieme Verlag, Stuttgart, 1997, p. 98.
[26] J.C. Gordon, R. Poli, Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer), vol. 8, Georg Thieme Verlag, Stuttgart, 1997, p. 97.
[27] R. Birdwhistell, P. Hackett, A.R. Manning, J. Organometal. Chem. 157 (1978) 239.
[28] R.F. Jordan, J.R. Norton, J. Am. Chem. Soc. 104 (1982) 1255.
[29] E.J. Moore, J.M. Sullivan, J.R. Norton, J. Am. Chem. Soc. 108 (1986) 2257.
[30] S.P. Nolan, C.D. Hoff, J.T. Landrum, J. Organomet. Chem. 282 (1985) 357.
[31] H.G. Alt, H.E. Engelhardt, W. Kläui, A. Müller, J. Organomet. Chem. 331 (1987) 317.
[32] P.G. Sal, I. Jiménez, A. Martín, T. Pedraz, P. Royo, A. Sellés, A. Vásquez de Miguel, Inorg. Chim. Acta 273 (1998) 270.
[33] H. Sitzmann, G. Wolmershäuser, Z. Naturforsch. Sect. B 50 (1995) 750.
[34] D.J. Burkey, T.P. Hanusa, Organometallics 15 (1996) 4971.
[35] D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, M. Visseaux, Eur. J. Inorg. Chem. (2000) 2333.
[36] H. Sitzmann, G. Wolmershäuser, R. Boese, D. Blaser, Z. Anorg. Allg. Chem. 625 (1999) 2103.
[37] H. Sitzmann, O. Schmitt, F. Weber, G. Wolmershäuser, Z. Anorg. Allg. Chem. 627 (2001) 12.
[38] H. Sitzmann, G. Wolmershäuser, Chem. Berlin 127 (1994) 1335.
[39] V. Quindt, D. Saurenz, O. Schmitt, M. Shär, T. Dezember, G. Wolmershäuser, H. Sitzmann, J. Organomet. Chem. 579 (1999) 376.
[40] H. Sitzmann, D. Saurenz, G. Wolmershäuser, A. Klein, R. Boese, Organometallics 20 (2001) 700.
[41] R.A. Williams, K.F. Tesh, T.P. Hanusa, J. Am. Chem. Soc. 113 (1991) 4843.
[42] H. Sitzmann, T. Dezember, O. Schmitt, F. Weber, G. Wolmershäuser, M. Ruck, Z. Anorg. Allg. Chem. 626 (2000) 2241.
[43] F.H. Kohler, H. Sitzmann, in press.
[44] R. Boese, R.L. Myrabo, D.A. Newman, K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 29 (1990) 549.
[45] J.A. Kim, T.M. Chung, Y.K. Chung, J.H. Jung, S.W. Lee, J. Organomet. Chem. 486 (1995) 211.

[46] T.M. Chung, Y.K. Chung, Organometallics 11 (1992) 2822.
[47] H.G. Alt, S.J. Palackal, R.D. Rogers, J. Organomet. Chem. 388 (1990) 105.
[48] J.K. Stille, C. Smith, O.P. Anderson, M.M. Miller, Organometallics 8 (1989) 1040.
[49] C. Lo Sterzo, J.K. Stille, Organometallics 9 (1990) 687.
[50] H. Plenio, Chem. Berlin 124 (1991) 2185.
[51] H.G. Alt, J.S. Han, R.D. Rogers, J. Organomet. Chem. 445 (1993) 115.
[52] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.
[53] R.B. King, A. Efraty, J. Am. Chem. Soc. 94 (1972) 3773.