

Electrophilic addition of CCl_4 to a cyclopentadienyl ligand in the tungstenocene carbonyl $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})]$ to give $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$ ¹

Peter Jernakoff², James R. Fox, N. John Cooper^{*}

Department of Chemistry and Materials Research Center, University of Pittsburgh, Pittsburgh, PA 15260, USA

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Abstract

Reaction of the tungstenocene monocarbonyl complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})]$ with an excess of CCl_4 at room temperature gives a 50% yield of an adduct which crystallizes in the monoclinic space group $P 2_1/n$ with $a = 12.938(2) \text{ \AA}$, $b = 6.724(1) \text{ \AA}$, $c = 16.226(3) \text{ \AA}$, $\beta = 93.29(1)^\circ$. A single crystal X-ray diffraction study ($R_F = 3.36\%$, $R_w = 3.32\%$) has established that the adduct is $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$, with a trichloromethyl group bonded exo to the saturated carbon of an η^4 -cyclopentadiene ligand and a dihedral angle between the plane containing this carbon and the mean plane of the butadiene residue of 35.3° . The $^1J_{\text{C-H}}$ coupling constants of the four carbon atoms of the butadiene residue indicate an average hybridization of $sp^{1.9}$. The first step in the addition is proposed to involve electron transfer from the metal to fragment the CCl_4 into the trichloromethyl radical and the chloride anion. Exo addition of the trichloromethyl radical to an $\eta^5\text{-C}_5\text{H}_5$ ligand would then be followed by trapping of the 16-electron cationic intermediate by the Cl^- anion.

Keywords: Tungsten; Metallocenes; Electrophilic addition; Cyclopentadienyl; Cyclopentadiene

1. Introduction

Electrophilic modification of cyclopentadienyl ligands has been a central thread within organotransition metal chemistry since the first report of ferrocene substitution under Friedel–Crafts conditions [1]. Rausch has been an important contributor to this area, and his early reports [2] include one of the first electrophilic alkylations of ferrocene [3], the synthesis of osmocene and a comparison of its aromatic reactivity with that of its congeners ruthenocene and ferrocene [4]. His group made major contributions to the area of functionally substituted cyclopentadienyl complexes which developed from these studies [5], and most recently he has

been one of those who have developed a new generation of α -olefin polymerization catalysts which use substituted cyclopentadienyl and indenyl complexes of the early transition metals [6].

Our own work on derivatized cyclopentadienyl ligands has centered on the nucleophilic substitution of cyclopentadienyl ligands in bent tungstenocene complexes [7], with the primary purpose of using differentially substituted and hence chiral tungstenocene complexes to study the stereochemistry of reactions occurring at the metal center [8]. We have also, however, had occasion to examine the reactions of complexes in this system with electrophiles, and we now wish to report an unprecedented electrophilic approach to the functionalization of bent tungstenocene complexes in which the reaction of CCl_4 with the electron-rich tungstenocene carbonyl $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})]$ [9] gives the crystallographically characterized cyclopentadienyl/cyclopentadiene complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$, in a reaction for which we propose an electron transfer mechanism as summarized in Scheme 1.

^{*} Corresponding author.

¹ Dedicated to Marv Rausch in celebration of his 65th birthday.

² Current address: E.I. du Pont de Nemours, Jackson Laboratory, Deepwater, NJ 08023, USA.

2. Experimental details

2.1. Materials and methods

All transformations and manipulations involving air-sensitive compounds were performed under an atmosphere of prepurified nitrogen or argon unless otherwise noted, using either standard Schlenk techniques or a Vacuum Atmospheres drybox. Glassware was flame dried under vacuum or dried in an oven (> 4 h, 120°C) before use. Diethyl ether was predried over sodium wire and then distilled from sodium/benzophenone ketyl under nitrogen. Pentane was first stirred for a minimum of two days over concentrated sulfuric acid, and then over KCO₃ for a minimum of 6 h, before being distilled from LiAlH₄. CH₂Cl₂ was distilled from CaH₂. Reagent grade CCl₄ was used as received from Mallinckrodt. The carbonyl complex [W(η⁵-C₅H₅)₂(CO)] was prepared from [W(η⁵-C₅H₅)₂Cl₂] by a literature procedure in 40% yield, [9] but in our hands was always contaminated by 5–10% [W(η⁵-C₅H₅)₂H₂]. [W(η⁵-C₅H₅)₂Cl₂] was prepared from WCl₆ by established procedures [10].

¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 or WM 300-WB (300 MHz) NMR spectrometer. Perdeuteroacetone (99.5 + atom %) was purchased from Merck, Sharpe, and Dohme or from Cambridge Isotopes and used as received. ¹H NMR chemical shifts are reported in δ using the residual proton resonances of the acetone d₅ at δ 2.04 as an internal standard. ¹³C NMR chemical shifts are reported in δ using the ¹³C chemical shift of the perdeuteroacetone solvent at δ 29.5 as an internal standard. Infrared spectra were obtained on a Perkin Elmer 683 grating infrared spectrometer with the 1601 cm⁻¹ band of polystyrene as an external reference. Mass spectra were recorded on a

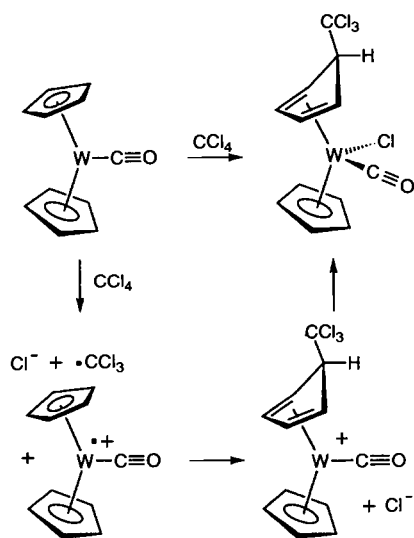
Kratos MS-9 spectrometer. Mass spectral patterns which exhibited the W isotope envelope are reported as the values of m/e corresponding to the ion containing ¹⁸⁴W. Microanalyses were carried out by Galbraith Microanalytical Laboratory, Knoxville, Tennessee.

2.2. Synthesis of [W(η⁵-C₅H₅)(η⁴-C₅H₅-exo-CCl₃)(CO)Cl]

Carbon tetrachloride (5.0 ml, 7.95 g, 51.6 mmol) was added to a stirred dark green solution of [W(η⁵-C₅H₅)₂(CO)] (1.88 g, 5.50 mmol) in CH₂Cl₂. The solution immediately turned a dark cherry-red and gradually became cloudy over the course of 1 h. The solvent was removed under reduced pressure and the resulting brown-gold solid extracted with diethyl ether (6 × 100 ml). The combined extracts were filtered, reduced in volume to approx. 250 ml under reduced pressure, and filtered again. Slow cooling of this solution to -70°C over a 20 h period led to the deposition of spectroscopically pure [W(η⁵-C₅H₅)(η⁴-C₅H₅-exo-CCl₃)(CO)Cl] as yellow irregular needles and dark yellow granular nuggets (1.37 g, 2.76 mmol = 50%). Analytically pure material could be obtained (approx. 90% recovery) by an additional low temperature diethyl ether recrystallization. Anal. Calc. for C₁₂H₁₀Cl₄OW: C, 29.07; H, 2.03. Found: C, 29.34; H, 2.22. ¹H NMR (300 MHz, -60°C, acetone-d₆): δ 5.87 (c, 1H, η⁴-C₅H₅ {H(3) or H(4)}), 5.53 (s, 5H, η⁵-C₅H₅), 5.10 (c, 1H, η⁴-C₅H₅ {H(4) or H(3)}), 4.43 (c, 1H, η⁴-C₅H₅ {H(1)}), 3.09 (c, 1H, η⁴-C₅H₅ {H(2) or H(5)}), 2.65 (c, 1H, η⁴-C₅H₅ {H(5) or H(2)}). ¹³C NMR (75.5 MHz, gated decoupled, -20°C, acetone-d₆): δ 216.7 (s, 1C, W-CO), 112.5 (s, 1C, CCl₃), 92.5 (d, 5C, ¹J_{C-H} = 183.3 Hz, η⁵-C₅H₅), 83.0 (d, 1C, ¹J_{C-H} = 182.6 Hz, η⁴-C₅H₅), 70.8 (d, 1C, ¹J_{C-H} = 186.9 Hz, η⁴-C₅H₅), 70.7 (d, 1C, ¹J_{C-H} = 150.7 Hz, η⁴-C₅H₅), 64.1 (d, 1C, ¹J_{C-H} = 181.7 Hz, η⁴-C₅H₅), 41.4 (d, 1C, ¹J_{C-H} = 175.8 Hz, η⁴-C₅H₅). IR (KBr): 3130 m, 3085 m, 3048 w, 2940 mw, 1930 vs br, 1431 m, 1413 m, 1381 m, 1351 m, 1319 ms, 1242 m, 1220 ms, 1111 mw, 1073 ms, 1057 ms, 1046 m sh, 1020 m, 994 m, 967 w, 934 ms, 865 m, 838 s, 805 s, 762 ms, 735 s, 660 m, 629 ms, 585 mw, 517 ms, 491 ms, 446 ms, 410 m, 361 m, 325 mw br cm⁻¹. Mass spectrum (parent ion, ¹⁸⁴W) m/e 496.

2.3. X-ray diffraction study of [W(η⁵-C₅H₅)(η⁴-C₅H₅-exo-CCl₃)(CO)Cl]

Bright yellow parallelepipeds of [W(η⁵-C₅H₅)(η⁴-C₅H₅-exo-CCl₃)(CO)Cl] were grown by slow vapor diffusion (5 days) of pentane into a saturated diethyl ether solution of the complex. A crystal of dimensions 0.1 × 0.3 × 0.4 mm mounted in a 0.3 mm glass capillary tube under nitrogen was used for the diffraction



Scheme 1.

Table 1
Crystal data, data collection parameters, and agreement factors

	[W(η^5 -C ₅ H ₅)- (η^4 -C ₅ H ₅ -exo-CCl ₃)- (CO)Cl]
Crystal data	
Molecular Formula	C ₁₂ H ₁₀ Cl ₄ O _W
Molecular Weight (g mol ⁻¹)	495.88
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.938(2)
<i>b</i> (Å)	6.724(1)
<i>c</i> (Å)	16.226(3)
β (°)	93.29(1)
<i>V</i> (Å ³)	1409.1(4)
<i>Z</i>	4
<i>d</i> _c (g ml ⁻¹)	2.34
Data collection	
μ (cm ⁻¹)	91.23
<i>T</i> (°C)	25
λ (Å)	0.71069
Scan type	2 θ : θ
Max 2 θ (deg)	60
Min 2 θ (deg)	3
Scan range (°)	2.0 (symmetrical)
Scan speed (deg min ⁻¹)	3.5–19.5
Background/scan ratio	0.75
Total reflections	4847
Unique reflections	3374
(<i>I</i> > 3 σ (<i>I</i>), <i>F</i> > 3 σ (<i>F</i>))	Agreement factors
Final <i>R</i> (%) ^a	3.36
Final <i>R</i> _w (%) ^b	3.32
Goodness of fit (GOF) ^c	1.111
<i>g</i> value	0.00060

$$^a R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|$$

$$^b R_w = \sum |w|^{1/2} (F_{\text{obs}} - F_{\text{calc}}) / \sum |w|^{1/2} F_{\text{obs}}$$

$$^c \text{GOF} = [\sum w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

study. Data were collected on a Nicolet R3 diffractometer using graphite monochromatized Mo K α radiation (50 kV, 30 mA). Data collection was controlled by the Nicolet p3 program [11] and the structure was solved and refined using SHELXTL [12]. Diffractometer data were processed with FOXTAPE, a local modification of the Nicolet program XTAPE. Empirical absorption corrections were performed by the program XEMP (Nicolet) while drawings were generated by the program SNOOPI (part of the Oxford University CHEMGRAF Suite package) [13] or by XPLOT (Nicolet). All molecular calculations were performed with the aid of the program XP (Nicolet). Atomic scattering factors were based on literature values [14]. Weights were taken as $[\sigma^2(F) + gF^2]^{-1}$. Crystal data, details of the data collection, and final agreement parameters are summarized in Table 1.

The unit cell was indexed using 15 reflections obtained from a rotation photograph. Two angles were near 90°, and a lattice determination using both the p3 program and TRACER [15] yielded a monoclinic cell. A trial data collection revealed systematic absences which uniquely determined the space group of the cell to be *P*

2₁/*n* (nonstandard setting of *P* 2₁/*c*). Final unit cell parameters were obtained by a least squares refinement of the angles obtained from 12 selected Friedel pairs in the range 20° ≤ 2 θ ≤ 30°.

The intensities of three check reflections (1, 0, -9), (7, 0, -3), and (0, 4, 0) were measured after every 60 reflections. The final intensities, *I*_f, were related to the initial intensities, *I*₀, and the initial standard deviations, σ_0 , as follows: (1, 0, -9), *I*_f = *I*₀ - 3.5 σ_0 ; (7, 0, -3), *I*_f = *I*₀ - 5.0 σ_0 ; (0, 4, 0), *I*_f = *I*₀ - 8.0 σ_0 . A linear decay correction based on the intensity changes of the check reflections (to correct for an approx. 6% average decrease in intensity after 96 h of exposure) and Lorentz and polarization corrections were applied to the data. The crystal suffered from severe absorption and a semi-empirical absorption correction based on ψ scans from 10 reflections in the range 6° ≤ 2 θ ≤ 57° was applied.

A sharpened Patterson map readily revealed the position of the W atom. A difference map calculated after refining the scale factor, the isotropic temperature factor, and the positional parameters of the W atom revealed the positions of the 4 chlorine atoms. Further least squares refinement of the positional and isotropic temperature parameters of these atoms revealed the positions of the oxygen atom and all 12 of the carbon atoms. Hydrogen atoms were placed in calculated positions on the η^5 -cyclopentadienyl carbon atoms (*U*_{iso}(H) = 1.2 × *U*_{iso}(C); *d*_{C-H} = 0.96 Å) and all non-hydrogen

Table 2

Fractional coordinates (× 10⁴) for the non-hydrogen atoms and the refined (cyclopentadiene) hydrogen atoms of [W(η^5 -C₅H₅)(η^4 -C₅H₅-exo-CCl₃)(CO)Cl]

Atom	<i>X/A</i>	<i>Y/B</i>	<i>Z/C</i>
W	2244.6(1)	1464.3(3)	222.2(1)
Cl(1)	1668(1)	-1979(2)	-84(1)
Cl(2)	5320(1)	2710(3)	-1410(1)
Cl(3)	3788(1)	2303(4)	-2755(1)
Cl(4)	4140(1)	6102(3)	-1970(1)
C(1)	1220(4)	2535(9)	-607(3)
C(2)	3185(4)	3018(8)	-1214(3)
C(3)	4064(4)	3479(10)	-1801(3)
C(11)	2467(7)	3276(15)	1419(5)
C(12)	2584(7)	1263(16)	1684(4)
C(13)	1665(9)	319(13)	1510(5)
C(14)	971(6)	1641(5)	1149(5)
C(15)	1439(7)	3480(12)	1116(5)
C(21)	3341(4)	3795(9)	-338(3)
C(22)	3897(4)	2313(10)	131(3)
C(23)	3718(4)	455(9)	-270(3)
C(24)	3051(4)	876(8)	-980(3)
O(1)	628(4)	3256(8)	-1058(3)
H(2)	2581(51)	3578(92)	-1514(41)
H(21)	3271(40)	5200(81)	-170(32)
H(22)	4330(47)	2330(105)	648(38)
H(23)	3878(49)	-780(108)	-67(41)
H(24)	2740(53)	10(115)	-1347(46)

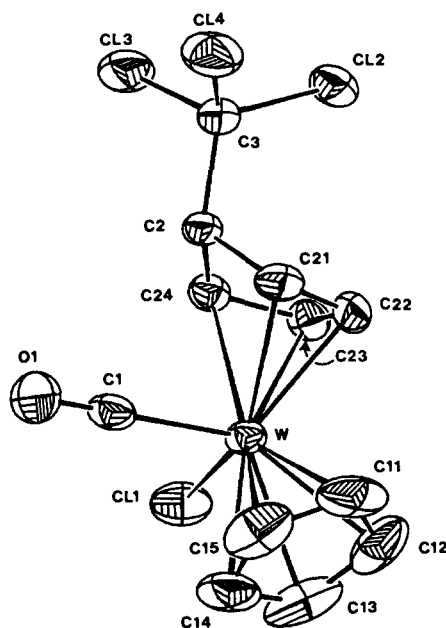


Fig. 1. Molecular structure of $[W(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$ (50% probability ellipsoids).

atoms were allowed to refine anisotropically. Additional refinement of the positional and anisotropic temperature parameters of these atoms yielded a discrepancy index of 3.5%. A low angle difference map then revealed the positions of the 5 hydrogen atoms on the η^4 -cyclopentadiene ligand (the positional and isotropic thermal parameters of these atoms were refined without restraint to reasonable distances and U_{iso} values). Continued blocked cascade least squares refinement was performed to convergence ($\Delta/\sigma(\text{max}) \leq 0.1$). The weighting scheme used was $w = [\sigma^2(F) + gF^2]^{-1}$. The value of the F^2 multiplier was adjusted so that a normal probability plot [16] gave a slope as close to 1.0 as possible. The largest peak in the final difference map had a density of $0.97 \text{ e}^-/\text{\AA}^3$ and was located 1.44 \AA from the tungsten atom. Final atomic coordinates for the non-hydrogen atoms and the refined (cyclopentadiene) hydro-

gen atoms of $[W(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$ are listed in Table 2.

Tables listing the anisotropic displacement coefficients for the non-hydrogen atoms, the isotropic displacement coefficients for the refined (cyclopentadiene) hydrogen atoms, calculated fractional coordinates and isotropic displacement coefficients for the cyclopentadienyl hydrogen atoms, and more complete bond lengths and angles, have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis and structural characterization of $[W(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$

Treatment of a dark green dichloromethane solution of the tungstenocene monocarbonyl complex $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})]$ with an excess of carbon tetrachloride at room temperature resulted in an immediate solution color change to dark red. Removal of the reaction solvent, followed by extraction with diethyl ether, yielded a yellow solution which deposited yellow crystals upon slow cooling to -70°C . A mass spectrum of the complex contained a tungsten pattern corresponding to the molecular ion of the 1:1 adduct $W(\text{C}_5\text{H}_5)_2(\text{CO}) \cdot \text{CCl}_4$, and formulation as the 1:1 adduct was confirmed by elemental analysis. The adduct was isolated in 50% yield.

A single crystal X-ray diffraction study (see section 2) established that the adduct is $[W(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$, in which one of the cyclopentadienyl ligands has been converted into a cyclopentadiene ligand with an exo trichloromethyl group bonded to the saturated carbon. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are listed in Tables 3 and 4 respectively.

The complex can be viewed as a four legged piano-stool [17] with the CO, the Cl and the two coordinated

Table 3
Selected bond lengths (\AA) within $[W(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{-exo-CCl}_3)(\text{CO})\text{Cl}]$

W–C(11)	2.297(8)	C(24)–C(2)	1.502(8)	C(1)–O(1)	1.136(7)
W–C(12)	2.391(7)	C(21)–C(2)	1.517(7)	C(2)–C(3)	1.556(7)
W–C(13)	2.388(8)	C(21)–C(22)	1.423(8)	C(3)–Cl(2)	1.787(6)
W–C(14)	2.297(8)	C(22)–C(23)	1.422(9)	C(3)–Cl(3)	1.756(6)
W–C(15)	2.280(8)	C(23)–C(24)	1.428(7)	C(3)–Cl(4)	1.788(7)
W–C(21)	2.332(6)				
W–C(22)	2.226(5)				
W–C(23)	2.215(5)				
W–C(24)	2.299(5)				
W–C(1)	1.970(5)				
W–Cl(1)	2.474(2)				
C(2)–H(2)	0.973(65)	C(21)–H(21)	0.989(54)	C(22)–H(22)	0.983(59)
C(23)–H(23)	0.913(71)	C(24)–H(24)	0.910(76)		

Table 4
Selected bond angles (deg) within $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$

W–C(1)–O(1)	175.9(5)	C(21)–C(2)–C(24)	96.0(4)
Cl(1)–W–C(1)	91.2(2)	C(21)–C(2)–C(3)	116.3(4)
C(2)–C(21)–C(22)	107.2(5)	C(24)–C(2)–C(3)	116.4(5)
C(21)–C(22)–C(23)	107.9(5)	C(2)–C(3)–Cl(2)	114.0(4)
C(22)–C(23)–C(24)	105.7(5)	C(2)–C(3)–Cl(3)	109.3(4)
C(2)–C(24)–C(23)	108.7(4)	C(2)–C(3)–Cl(4)	109.8(4)

double bonds of the η^4 -cyclopentadiene ligand as the legs. This suggests comparison with the archetypal W(II) piano-stool $[W(\eta^5-C_5H_5)(CO)_3Cl]$, crystallographically characterized by Churchill [18], and many structural parameters of the molecules are indeed similar. The W-carbonyl (W–C(1)) bond distance of 1.970(5) Å is, however, slightly shorter than the average of 1.998 [5] observed in $[W(\eta^5-C_5H_5)(CO)_3Cl]$, suggesting somewhat more focused π -back donation to the solitary carbonyl ligand.

The saturated carbon atom of the cyclopentadiene ligand (C(2)) carries the *exo*-trichloromethyl group and lies 0.584 Å out of the diene plane; this results in a W...C(2) non bonded distance of 2.886 Å. The hydrogen atoms of the η^4 -cyclopentadiene ligand (located via a low angle difference map calculation) are on average 0.954(29) Å from the carbon to which they are bonded; the W...H(2) non-bonded distance is 3.208 Å.

Folding of the ligand at C(21) and C(24) is such that the dihedral angle between the plane defined by C(21), C(2), and C(24) and the mean plane of the butadiene residue is 35.3°. This can be compared with the 32–41° range observed for the analogous angle in other crystallographically characterized η^4 -cyclopentadiene complexes: 32.7° in $[Mn(\eta^4-C_5H_5-exo-CH_3)(CO)(NO)(PPh_3)]$ [19]; 34.7° in $[Fe(\eta^4-C_5H_5-exo-CH_2Ph)(CO)_2(PPh_3)]$ [20]; 36.5° in $[Co(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-C_6H_5)]$ [21]; 38.7° in $[Mo(\eta^5-C_5H_5)(\eta^4-C_5H_5-endo-C_2H_5)(PC_2H_5)_3Cl]$ [22]; and 40.9° in $[Re(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CH_3)(CH_3)_2]$ [23].

Folding of a coordinated cyclopentadiene ring has been rationalized in terms of rehybridization of the terminal carbons of the butadiene residue from sp^2 to sp^3 [21,23], but this was proposed in the context of the long-short-long sequence of butadiene C–C bond distances reported for early η^4 -cyclopentadiene complexes and this pattern has not turned out to be typical ([19,20,22]). In the present case the C–C bond lengths within the diene residue of $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$ are equal within experimental error and average 1.424(5) Å; none of the distances differs significantly from this mean value.

Gated decoupled ^{13}C NMR spectra also argue against the appropriateness of the diene rehybridization model for the bonding in $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-$

$CCl_3)(CO)Cl]$. These spectra established $^1J_{C-H}$ coupling constants between 175 Hz and 187 Hz, similar to the $^1J_{C-H}$ value of 183 Hz for the $\eta^5-C_5H_5$ ligand, for the butadiene carbon atoms. Since $^1J_{C-H}$ values for sp^2 hybridized carbon centers are usually in excess of 155 Hz, and are not usually affected much by complexation to a metal [24], it seems probable that these carbons are best regarded as sp^2 hybridized; their average hybridization was determined to be $sp^{1.9}$ through the use of Newton's semi-empirical rule relating $^1J_{C-H}$ values to the % s character of the carbon atom in question [25].

These arguments imply that the interaction of the butadiene residue with the metal involves essentially pure carbon p orbitals, consistent with a theoretical analysis by Hoffmann and co-workers of the interaction between η^4 -cyclopentadiene and η^5 -cyclohexadienyl ligands with the $M(CO)_3$ fragment ([26]). In the case of the model complex $[Fe(\eta^4-C_5H_6)(CO)_3]$ used in these calculations the folding of the η^4 -cyclopentadiene ligand was ascribed to the need to avoid a secondary anti-bonding interaction between a donor orbital on the metal and the η^4 -cyclopentadiene ligand LUMO which includes a hyperconjugative contribution from the saturated carbon bridge.

3.2. NMR spectroscopy of $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$

At $-60^\circ C$ the 1H NMR spectrum of $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$ in perdeuteroacetone contains a singlet attributable to the $\eta^5-C_5H_5$ ligand and five complex multiplets with intensities 1/5 that of the singlet and with chemical shifts and coupling constants consistent with assignment to the five inequivalent η^4 -cyclopentadiene protons, as detailed in the experimental. Resonances in gated decoupled ^{13}C NMR spectra at $-20^\circ C$ were also fully consistent with assignment to the carbon atoms of the molecule characterized crystallographically in the solid state. There is no evidence in either spectrum for the existence of rotamers involving different orientations of the η^4 -cyclopentadiene ligand, as has been proposed for the related complex $[Mo(\eta^5-C_5H_5)(\eta^4-C_5H_5-endo-C_2H_5)(PPh_3)Cl]$ on the basis of 1H NMR data [22b].

Both the 1H and ^{13}C NMR spectra exhibited unusual temperature dependence when warmed to room temperature. In both cases the resonances broadened markedly but with only slight changes in chemical shifts ($< \delta 0.15$ shifts in 1H spectra and negligible shifts in ^{13}C spectra). The broadening applied fairly uniformly to all the resonances associated with the complex and there were no indications in either set of spectra of incipient coalescence of any groups of resonances as would be expected if the broadening reflected the onset of an intramolecu-

lar fluxional process. A preliminary spin population transfer experiment indicated that the hydrogen on the saturated carbon bridge of the η^4 -cyclopentadiene ligand is not exchanging with any other proton at room temperature, and an Evans susceptibility measurement [27] confirmed that the bulk of the material in solution is diamagnetic at room temperature. The broadening was fully reversible when the temperature was lowered.

The origin of this temperature-dependent behavior is unclear. One obvious possibility is that the endo-hydrogen on the bridgehead is migrating reversibly to the metal, a process which is synthetically facile in a related complexes [7], but if this is happening it is unclear why any broadening effect would extend to the cyclopentadienyl ligand. A more reasonable possibility is that the molecule is in equilibrium with a coordinatively unsaturated derivative by, for example, dissociation of one of the double bonds of the diene ligand. It is also possible that the broadening is a consequence of electron exchange between the complex and a small quantity of a paramagnetic one-electron oxidation or reduction product; we have previously observed such effects with tungstenocene dialkyls [28].

3.3. Reactivity of $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$

When stored in the dark, the complex possessed surprising air stability both in the solid state and in solution. Solid samples of the complex kept under reduced light conditions showed no apparent signs of decomposition after 4 months exposure to the atmosphere. Diethyl ether solutions of the complex were stable for weeks in air under reduced illumination. The molecule is, however, quite light sensitive, and diethyl ether solutions under argon deposited an NMR silent, intractable black powder after approx. 15 h of exposure to normal laboratory lighting.

An attempt to convert the adduct to a bis-cyclopentadienyl complex with a CCl_3 substituent on one of the rings using trityl hexafluorophosphate to abstract the endo hydrogen from the η^4 -cyclopentadiene ligand [29] was unsuccessful; no reaction was observed. An attempt to abstract the tungsten bound chlorine atom with $Tl[PF_6]$ [30] was also unsuccessful. A reaction did occur when the complex was treated with an excess of n-butyl lithium at room temperature (in tetrahydrofuran), but no tractable products were obtained after an ethanol quench.

3.4. Mechanism of formation of $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$

The observation that the CCl_3 fragment adds exo to the cyclopentadienyl ligand while the halide adds to the metal implies that the reaction of CCl_4 with $[W(\eta^5-$

$C_5H_5)_2(CO)]$ must occur in at least two steps to allow the two fragments to separate. This can be readily accounted for by a mechanism (see Scheme 1) in which the first step is electron transfer from the metal to fragment the halocarbon into the trichloromethyl radical and the chloride anion. Exo addition of the trichloromethyl radical to an η^5 -cyclopentadienyl ring of the 17-electron radical cation complex $[W(\eta^5-C_5H_5)_2(CO)]^+$ would then give a 16-electron cationic intermediate which would be expected to have a high affinity for the Cl^- anion, generating the product $[W(\eta^5-C_5H_5)(\eta^4-C_5H_5-exo-CCl_3)(CO)Cl]$. Such a mechanism is consistent with the very low ionization energy of approx. 6.0 eV anticipated for $[W(\eta^5-C_5H_5)_2(CO)]$ from examination of PES data for related tungstenocene and molybdenocene complexes [31], and with the observation that $[W(\eta^5-C_5H_5)_2(CO)]$ undergoes a facile and partly reversible one-electron electrochemical oxidation in THF at -0.74 V vs SCE [32].

A mechanism involving an organic radical which moves a significant distance in solution is more plausible with highly halogenated alkyls capable of giving rise to stabilized radical intermediates than it would be with mono-haloalkyls, and access to a unique reaction pathway for such substrates could account for the otherwise surprising contrast between the cyclopentadienyl regiochemistry for the addition of CCl_4 to $[W(\eta^5-C_5H_5)_2(CO)]$ and the metal regiochemistry observed for the addition of other alkylhalides [33] and of heteroalkenes [34] to the same substrate.

4. Conclusion

There are a few earlier reports of related electrophilic additions of CCl_4 to cyclopentadienyl ligands in cobaltocene [35] and in $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(PPhCl)]$ [36] to give cyclopentadiene ligands with *exo*- CCl_3 substituents, and Bitterwolf has recently reported a related example of a photochemically driven addition of a $CHCl_2$ radical derived from chloroform to a cyclopentadienyl ligand of a derivative of Fp dimer as a step in the formylation of the cyclopentadienyl ligand [37]. All of these reactions have been proposed to involve electron transfer mechanisms similar to that in Scheme 1 [36,37,38], but in the cobaltocene case two equivalents of the metal complex are required (one to act as the electron source and one as the CCl_3 acceptor), while in the Re case the Cl atom is added to the phosphido ligand. The addition of CCl_4 to $[W(\eta^5-C_5H_5)_2(CO)]$ is the only example in which the CCl_3 radical ends up on the ring while the halide ion generated in the electron transfer step is trapped on the metal. It is also the only example of electrophilic activation of a cyclopentadienyl ligand in the tungstenocene system, and the steric accessibility and probable reactivity of the CCl_3 group

in the product offers an intriguing approach to the attachment of this molecule to polymer supports.

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