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CYCLOPENTADIENYLTUNGSTEN(IV) CHEMISTRY: SYNTHESIS AND CHARACTERIZATION OF (η-RING)WX$_3$(CO)$_2$ (RING = C_5H_5, C_5H_4Me, C_5Me_5) AND X-RAY STRUCTURE OF (η-C_5Me_5)WBr$_3$(CO)$_2$

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Abstract—The W^{IV} carbonyl compounds [(Ring)WX$_3$(CO)$_2$](Ring = C_5H_5, C_5H_4Me, C_5Me_5; X = Cl, Br, I) have been prepared by a one-step oxidation of the corresponding [(Ring)W(CO)$_3$]$_2$ with PhICl$_2$, Br$_2$ and I$_2$, respectively, in high yields. The structure of Cp*WBr$_3$(CO)$_2$ has been elucidated by X-ray methods. It exhibits a distorted, pseudo octahedral arrangement of the Cp*, two CO and three Br ligands in a *facial* configuration.

Carbon monoxide is undoubtedly the most important ligand in organometallic chemistry, forming stable compounds in combination with almost every metal of the *d*-block.[1] Its properties as a strong π acid optimize bonding in systems where the metal has a low oxidation state, whereas no stable adduct is formed or the interaction leads to metal reduction when the oxidation state is high. The highest-valent stable CO complexes reported so far have the metal in the oxidation state IV, for instance the molybdenum compounds of general formula [(η-Ring)MoX$_3$(CO)$_2$] (Ring = C_5H_5 and substituted derivatives; X = halide).[2] Although the latter complexes can be isolated under ordinary laboratory conditions, the lability of the Mo—CO bond is manifested by their facile thermal decarbonylation, which we have recently exploited for the high yield synthesis of previously unknown '(η-Ring)MoX$_3$' materials.[3,4]

We are now extending this synthetic strategy to the analogous compounds of tungsten. For this reason, we have prepared a series of dicarbonyl W^{IV} compounds analogous to those of Mo^{IV} mentioned above. The complexes with the unsubstituted Cp ring, CpWX$_3$(CO)$_2$ (X = Cl, Br, I), have been prepared before by oxidation of the corresponding isolated CpW(CO)$_3$X precursor with Cl$_2$, Br$_2$ and I$_2$, respectively.[2b] Another compound of this type, e.g. (η-C_5H_4-*i*-Pr)WBr$_3$(CO)$_2$, has been synthesized more recently by a less logical route, i.e. from carbonylation of the W^{III} precursor [(η-C_5H_4-*i*-Pr)WBr$_2$]$_2$, and structurally characterized.[5] Finally, the formation of compound Cp*WI$_3$(CO)$_2$ from Cp*W(SnPh$_3$)[=C(OEt)Ph](CO)$_2$ and I$_2$ has been reported, but the product was not analytically and spectroscopically characterized.[6] Here we report the synthesis and properties of a more extensive series of (η-Ring)WX$_3$(CO)$_2$ complexes (Ring = Cp, Cp′, Cp*; Cp = C_5H_5; Cp′ = C_5H_4Me, Cp* = C_5Me_5; X = Cl, Br, I) by a novel, simple and high yield method, and the X-ray structure of Cp*WBr$_3$(CO)$_2$. The results of the decarbonylation studies, currently under investigation, will be reported in due course.

EXPERIMENTAL

All operations were carried out under dinitrogen with standard Schlenk-line techniques. Toluene and heptane were refluxed over sodium at least 12 h before being distilled. Dichloromethane was refluxed over P$_4$O$_{10}$ under dinitrogen, distilled, and then freeze–pump–thaw degassed (three cycles)

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under dinitrogen to remove any residual oxygen. Deuterated NMR solvents were also degassed with the freeze–pump–thaw method (three cycles) under dinitrogen and stored over type 4A molecular sieves (Fischer). NMR spectra were obtained using Bruker WP200 and AF200 spectrometers. The spectra were referenced with internal residual solvent peaks for ^1H and external 85% H_3PO_4 for ^{31}P. The H_3PO_4 standard solution was contained in a sealed capillary and immersed in the same solvent used for the measurement. Peaks are reported with positive shifts at lower fields from TMS(^1H) and H_3PO_4(^{31}P). All glassware was silylated with a 1 : 10 v/v solution of dichlorodimethylsilane in CCl_4 and the treated equipment was thoroughly rinsed with solvent grade dichloromethane and dried in a 110°C oven for at least 1 h prior to use. Elemental analyses were obtained from MHW Laboratories, Phoenix, Arizona. $PhICl_2$,[7] $[CpW(CO)_3]_2$ and $[Cp'W(CO)_3]_2$[8] were prepared as described in the literature. $[Cp^*W(CO)_3]_2$ was prepared by an adaptation of the procedure described for the Cp and Cp′ analogues in 85% yields on a 10 g scale. Its spectroscopic properties are identical with those reported in the literature.[9]

Preparation of $(Ring)WX_3(CO)_2$ (Ring = Cp, Cp′, Cp*; X = Cl, Br, I)

The preparation of these nine compounds (a–i) follows the same general procedure as described in detail for compound $CpWCl_3(CO)_2$. The compounds are only sparingly soluble in all common solvents and cannot be easily recrystallized. The spectroscopic and analytical properties have been obtained on the crude materials and are collected in Table 1.

(a) $CpWCl_3(CO)_2$. $[CpW(CO)_3]_2$ (529 mg, 0.794 mmol) was added to dichloromethane (20 cm^3) and to the resulting red suspension was added $PhICl_2$ (657 mg, 2.38 mmol). An immediate effervescence was observed as well as the formation of a flocculent yellow–green precipitate and a change in colour of the solution from red to orange–brown. The solution was monitored by IR. The IR patterns in the CO stretching region show only two bands of the product (Table 1). The solution was evaporated under reduced pressure to ca 2–3 cm^3 and the precipitation of the product was completed by the addition of heptane (50 cm^3). After filtration, the solid was washed with heptane (3×10 cm^3) until the washings were colourless. The washings were cannulated off and discarded. The solid was then dried *in vacuo* and stored in flame-sealed vials under dinitrogen. Yield 575 mg, 88%.

(b) $CpWBr_3(CO)_2$. $[CpW(CO)_3]_2$ (1.042 g, 1.564 mmol) was added to dichloromethane (20 cm^3) and to the resulting cherry red suspension was added Br_2 (242 μl, 4.69 mmol). An immediate effervescence was observed as well as the formation of a flocculent yellow–brown precipitate and a change in colour of the solution from red to yellow–orange. Work up as decribed in (a) gave 869 mg of product (57% yield).

(c) $CpWI_3(CO)_2$. $[CpW(CO)_3]_2$ (305 mg, 0.458 mmol) was added to dichloromethane (20 cm^3) and to the resulting cherry red suspension was added I_2 (349 mg, 1.37 mmol). An immediate effervescence was observed as well as the formation of a flocculent orange precipitate and a change in colour of the solution from red to brown. Work up as described in (a) gave 524 mg of product (83% yield).

(d) $Cp'WCl_3(CO)_2$. $[Cp'W(CO)_3]_2$ (744 mg, 1.07 mmol) was added to dichloromethane (20 cm^3) and to the resulting red suspension was added $PhICl_2$ (887 mg, 3.21 mmol). An immediate effervescence was observed as well as the formation of a flocculent light tan precipitate and a change in colour of the solution from red to dark yellow–brown. Work up as described in (a) gave 726 mg of product (80% yield).

(e) $Cp'WBr_3(CO)_2$. $[Cp'W(CO)_3]_2$ (1.05 g, 1.51 mmol) was added to dichloromethane (20 cm^3) and to the resulting red suspension was added Br_2 (234 cm^3, 4.54 mmol). An immediate effervescence was observed as well as the formation of a flocculent yellow precipitate and a change in colour of the solution from red to orange. Work up as described in (a) gave 1.32 g of product (78% yield).

(f) $Cp'WI_3(CO)_2$. $[Cp'W(CO)_3]_2$ (1.04 g, 1.50 mmol) was added to dichloromethane (20 cm^3) and to the resulting red suspension was added I_2 (1.14 g, 4.50 mmol). An immediate effervescence was observed as well as the formation of a flocculent dark yellow precipitate and a change in colour of the solution from red to dark orange–brown. Work up as described in (a) gave 1.88 g of product (90% yield).

(g) $Cp^*WCl_3(CO)_2$. $[Cp^*W(CO)_3]_2$ (547 mg, 0.678 mmol) was added to dichloromethane (15 cm^3) and to the resulting bright orange suspension was added $PhICl_2$ (561 mg, 2.04 mmol). An immediate effervescence was observed as well as the formation of a flocculent maize yellow precipitate and a change in colour of the solution from orange to orange–brown. Work up as described in (a) gave 437 mg of product (67% yield).

(h) $Cp^*WBr_3(CO)_2$. $[Cp^*W(CO)_3]_2$ (0.500 g, 0.610 mmol) was added to dichloromethane (20 cm^3) and to the resulting bright orange suspension was added Br_2 (95 μl, 1.86 mmol). An immediate effervescence was observed as well as the formation

Table 1. Spectroscopic and analytical data for compounds (Ring)$WX_3(CO)_2$

Compound		IR[a]	^{1}H NMR[b]		Elemental analysis	
Ring	X	ν_{CO} (cm^{-1})	δ (ppm)	J_{HH} (Hz)	Calc.	Obs.
C_5H_5	Cl[c]	2048 2098	6.37 (s)		C 20.4 H 1.2	20.5 1.3
	Br[d]	2043 2088	6.42 (s)		C 15.4 H 0.9	15.6 0.7
	I[e]	2026 2068	6.40 (s)		C 12.3 H 0.7	12.4 0.8
C_5H_4Me	Cl	2040 2090	6.25 (t, $C_5\mathit{H}_4$Me, 2H) 5.97 (t, $C_5\mathit{H}_4$Me, 2H) 2.53 (s, $C_5H_4\mathit{Me}$, 3H)	2.42 2.37	C 22.6 H 1.7	22.4 1.6
	Br	2036 2083	6.26 (t, $C_5\mathit{H}_4$Me, 2H) 6.07 (t, $C_5\mathit{H}_4$Me, 2H) 2.68 (s, $C_5H_4\mathit{Me}$, 3H)	2.56 2.54	C 17.2 H 1.3	17.6 1.2
	I	2021 2064	6.28 (t, $C_5\mathit{H}_4$Me, 2H) 6.14 (t, $C_5\mathit{H}_4$Me, 2H) 2.75 (s, $C_5H_4\mathit{Me}$, 3H)	2.50 2.56	C 13.7 H 1.0	14.3 1.3
C_5Me_5	Cl	2023 2077	2.25 (s)		C 29.9 H 3.1	29.6 3.1
	Br	2017 2068	2.36 (s)		C 23.4 H 2.5	23.6 2.3
	I	2002 2048	2.38 (s)		C 19.1 H 2.0	19.5 2.0

[a] Solvent = CH_2Cl_2.
[b] Solvent = acetone-d_6.
[c] Lit. (ref. 2b): 2099 and 2043 cm^{-1} (Nujol mull); δ 6.34 (acetone-d_6).
[d] Lit. (ref. 2b): 2096 and 2041 cm^{-1} (Nujol mull); δ 6.40 (acetone-d_6).
[e] Lit. (ref. 2b): 2068 and 2027 cm^{-1} (Nujol mull); δ 6.40 (acetone-d_6).

of a flocculent orange–brown precipitate and a change in colour of the solution from bright orange to orange–brown. After a few minutes, the mixture was filtered; crystals formed on the walls of the receiving vessel upon standing at room temperature. One of these crystals was used for the X-ray analysis. The combined yield was 485 mg of product (65%).

(i) $Cp^*WI_3(CO)_2$. $[Cp^*W(CO)_3]_2$ (500.0 mg, 0.620 mmol) was added to dichloromethane (20 cm^3) and to the resulting bright orange suspension was added I_2 (470.0 mg, 1.852 mmol). An immediate effervescence was observed as well as the formation of a flocculent orange precipitate and a change in colour of the solution from bright orange to orange–brown. Work up as described in (a) gave 497 mg of product (53% yield).

X-ray crystallography

A single crystal was glued to the inside of a thin-walled glass capillary which was then sealed under dinitrogen and mounted on the diffractometer. The unit cell and crystal orientation matrix were obtained from a least-squares fit on the setting angles of 25 reflections in the $9.5 < \theta < 11.5°$ range. The cell dimensions and Laue symmetry were confirmed by axial photographs. The data were collected at room temperature in the *hkl* octant. The periodic monitoring of three standard reflections showed no significant variation in intensity, therefore a decay correction was not applied. At the end of data collection, nine ψ-scan reflections were collected at 10° intervals showing significant absorption, therefore an absorption correction, as well as Lorentz and polarization corrections, were applied to the data.

The structure was solved by direct methods (MITHRIL), which located the two independent tungsten atoms. Subsequent alternating full-matrix least-squares refinements located the position of all the other non-hydrogen atoms. Convergence was achieved first with all the non-hydrogen atoms treated isotropically, then with the heavy atoms (W and Br) anisotropic, and finally including the hydrogen atoms in calculated positions. The latter were used for structure factor calculations but their position was not refined. All calculations were carried out with the TEXSAN package of programs on a MicroVax computer. Crystal and refinement parameters are shown in Table 2 and selected bond distances and angles are collected in Table 3. (The atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre.)

Table 2. Crystal data for $Cp^*WBr_3(CO)_2$

Chemical formula	$C_{12}H_{15}O_2Br_3W$
Formula weight	614.81
Space group	*Pbca* (No. 61)
Syst. abs.	$0kl$: $k = 2n$; $h0l$: $l = 2n$; $hk0$: $h = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$
a (Å)	15.048 (4)
b (Å)	17.26 (1)
c (Å)	24.39 (2)
V (Å^3)	6335
Z	16
d_{calc} (g cm^{-3})	2.58
Crystal size (mm)	$0.40 \times 0.35 \times 0.25$
μ (Mo-K_α) (cm^{-1})	157.20
Data collection instrument	Enraf/Nonius CAD4
Radiation (monochromated in incident beam)	Mo-K_α ($\lambda = 0.71073$ Å)
Orientation reflections (no., range (2θ) (°))	25, 19–23
Temperature (°C)	23
Scan method	$\omega - 2\theta$
Data collection range (2θ) (°)	2–43.9
No. of unique data (total collected)	4331
No. of observed data ($F_o^2 > 3\sigma(F_o^2)$)	1936
No. of parameters refined	185
Transmission factors (max., min)	0.6009–1.0900
R^a	0.058
$R_w{}^b$	0.074
Quality-of-fit indicator^c	1.47
Largest shift/esd, final cycle	0.31
Largest peak (e Å^{-3})	1.53

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.
[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs.} - N_{par.})]^{1/2}$.

RESULTS AND DISCUSSION

The compounds described in this paper (Table 1) have all been obtained directly from the corresponding W^I tricarbonyl dimers according to eqs (1) and (2):

$$[(Ring)W(CO)_3]_2 + 3PhICl_2 \rightarrow 2(Ring)WCl_3(CO)_2 + 3PhI + 2CO \quad (1)$$

$$[(Ring)W(CO)_3]_2 + 3X_2 \rightarrow 2(Ring)WX_3(CO)_2 + 2CO \quad (X = Br, I) \quad (2)$$

The reactions proceed through the intermediate compounds of partial halogenation, the known (for Ring = Cp)[10] tricarbonyltungsten(II) species $(Ring)WX(CO)_3$, as shown by monitoring the halogenation reactions by IR spectroscopy. the W^{IV} products are much less soluble than the W^{II} intermediates and precipitate directly from the reaction medium, from which they can be easily isolated as analytically and spectroscopically pure microcrystalline powders. The reaction between $[CpW(CO)_3]_2$ and X_2 (X = Cl, Br, I) has been previously described,[11] although emphasis there was given to the formation and reactivity of the intermediates and not to the isolation of the final W^{IV} dicarbonyl products. The synthetic method shown in eqs (1) and (2) has the advantage over the previously reported synthesis from $CpW(CO)_3X$ and X_2 of being a single step procedure from easily accessible W starting materials. In addition, for the specific syntheses of the chloro derivatives, eq. (1), the use of the air stable, solid crystalline $PhICl_2$, a mild Cl_2 delivering agent, allows a better control of the stoichiometry and avoids problems of overoxidation with possible formation of the known[12] $(Ring)WCl_4$ materials. This reagent has previously been used for the preparation of analogous $(Ring)MoCl_3(CO)_2$ complexes.[3,4]

The spectroscopic properties of the compounds reported here are collected in Table 1. The CO stretching vibrations in the IR spectrum show the expected red shifts on going from Cl to Br to I and from Cp to Cp′ to Cp*, reflecting a decrease in electronegativity and/or an increase in electron releasing power. They also show, as expected, a red shift compared to the vibration of the corresponding Mo compounds.

The structure of the $Cp^*WBr_3(CO)_2$ has been elucidated by single-crystal X-ray crystallography. The asymmetric unit contains two independent but substantially equivalent molecules (distances and angles for the two molecules are compared in Table 3). One of the two molecules is shown in Fig. 1. The molecular geometry is identical to that of

Table 3. Selected bond distances (Å) and angles (°) for $Cp^*WB_3(CO)_2$[a]

W(1)—Br(11)	2.600(5)	W(2)—Br(21)	2.594(5)
W(1)—Br(12)	2.590(5)	W(2)—Br(22)	2.646(4)
W(1)—Br(13)	2.638(4)	W(2)—Br(23)	2.591(4)
W(1)—C(11)	1.99(3)	W(2)—C(21)	2.04(4)
W(1)—C(12)	2.11(5)	W(2)—C(22)	1.97(4)
C(11)—O(11)	1.11(4)	C(21)—O(21)	1.15(4)
C(12)—O(12)	1.04(5)	C(22)—O(22)	1.19(4)
W(1)—CNT(1)	2.021(4)	W(2)—CNT(2)	2.024(4)
Br(11)—W(1)—Br(12)	85.8(2)	Br(21)—W(2)—Br(22)	80.8(2)
Br(11)—W(1)—Br(13)	80.3(2)	Br(21)—W(2)—Br(23)	85.8(2)
Br(11)—W(1)—C(11)	89(1)	Br(21)—W(2)—C(21)	88(1)
Br(11)—W(1)—C(12)	147(1)	Br(21)—W(2)—C(22)	150(1)
Br(12)—W(1)—Br(13)	82.0(2)	Br(22)—W(2)—Br(23)	82.2(1)
Br(12)—W(1)—C(11)	153.9(9)	Br(22)—W(2)—C(21)	71(1)
Br(12)—W(1)—C(12)	82(1)	Br(22)—W(2)—C(22)	71(1)
Br(13)—W(1)—C(11)	71.9(9)	Br(23)—W(2)—C(21)	153(1)
Br(13)—W(1)—C(12)	68(1)	Br(23)—W(2)—C(22)	83(1)
C(11)—W(1)—C(12)	89(1)	C(21)—W(2)—C(22)	90(2)
CNT(1)—W(1)—Br(11)	108(1)	CNT(2)—W(2)—Br(21)	108(1)
CNT(1)—W(1)—Br(12)	107(1)	CNT(2)—W(2)—Br(22)	167(1)
CNT(1)—W(1)—Br(13)	167(1)	CNT(2)—W(2)—Br(23)	106(1)
CNT(1)—W(1)—C(11)	98(1)	CNT(2)—W(2)—C(21)	99(1)
CNT(1)—W(1)—C(12)	105(1)	CNT(2)—W(2)—C(22)	101(1)
W(1)—C(11)—O(11)	176(3)	W(2)—C(21)—O(21)	179(3)
W(1)—C(12)—O(12)	168(4)	W(2)—C(22)—O(22)	177(3)

[a] Equivalent parameters for the two independent molecules are compared on each line.

the previously described $(C_5H_4\text{-}i\text{-Pr})WBr_3(CO)_2$ analogue.[5] In particular, the same pseudo-octahedral configuration with a *facial* arrangement of the ligands is observed. This is a point of interest because of the three possible configurations for the $CpMX_3L_2$ stoichiometry, e.g. *fac* (**I**), *trans,mer* (**II**) and *cis,mer* (**III**), have all been observed experimentally: **I** for $CpMoCl_3[P(OCH_2)_3CEt]_2$,[13] $(C_5H_4\text{-}i\text{-Pr})WBr_3(CO)_2$,[5] and the compound described here; **II** for $CpMoCl_3(PMe_2Ph)_2$;[14] **III** for $CpMoCl_3(L\text{–}L)$ (L–L = $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$).[15,16] The trend that seems to emerge is that small, π-acidic ligands such as CO and $P(OCH_2)_3CEt$ prefer to occupy *cis*-equatorial coordination sites.

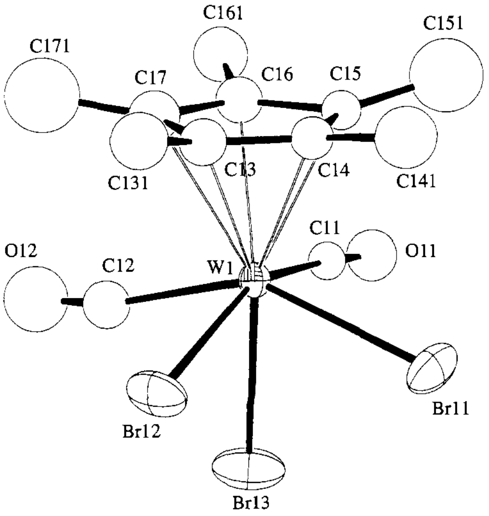
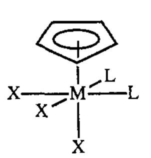


Fig. 1. ORTEP view of one of the two independent $Cp^*WBr_3(CO)_2$ molecules. The other molecule has an identical geometry. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.



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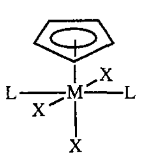
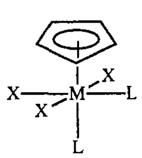


II



III

The geometry of $Cp^*WBr_3(CO)_2$ shows the same distortions previously described for the $C_5H_4\text{-}i\text{-Pr}$ analogue. In particular, the equatorial (*cis* to Cp*) ligands are pushed away from the ring and toward the opposite bromine atom as shown by the CNT–W–ligand angles. The three bromine atoms that occupy the same triangular face in each independent molecule also experience a mutual repulsion which is manifested in the displacement of the axial bromine from its ideal position toward the two CO ligands (CNT—Mo—Br_{trans} = 167(1)°; *cf* 167.5° for the C_5H_4-*i*-Pr analogue[5]). The axial Mo—Br bond is substantially longer than the equatorial ones (averages over the two independent molecules are 2.642(4) Å for Mo—$\mathrm{Br}_{\mathrm{ax}}$ and 2.594(5) Å for Mo—$\mathrm{Br}_{\mathrm{eq}}$), suggesting a greater *trans* influence of the Cp* ligand with respect to CO. The average W—C and C—O distances are 2.03(6) Å and 1.12(6) Å, respectively.

The strength of the W—CO interaction cannot be quantitatively evaluated from the above structural data, especially considering the large uncertainties on the bond parameters. The high CO stretching frequencies, however, indicate that the W atom in these molecules is not a strong π donor and the CO ligands should therefore be relatively labile. Preliminary studies indicate that indeed these materials can be completely decarbonylated by thermal treatment in solvents with relatively low boiling points such as toluene. The nature of these decarbonylated products is currently under study and will be reported separately.

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