Simple and effective synthesis of pentamethylcyclopentadienyl oxo-peroxo and dioxo tungsten acetylide complexes

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Abstract

The pentamethylcyclopentadienyl tungsten carbonyl acetylide complexes $(C_5Me_5)W(CO)_3(CCR)$, (1) R = Ph, CH_2OMe, Pr^n and $C(Me) = CH_2$, reacted with an acidic solution of hydrogen peroxide at room temperature, giving the oxo-peroxo acetylide complexes $(C_5Me_5)W(O)(O_2)(CCR)$ (2) in good yields. Upon treatment with triphenylphosphine the complexes (2) lost one oxygen atom to afford the corresponding dioxo complexes $(C_5Me_5)W(O)_2(CCR)$ (3). These oxo-peroxo and dioxo complexes were characterized by spectroscopic methods and, for $(C_5Me_5)W(O)_2(CCPh)$ (3a), was further identified by single crystal X-ray diffraction study. © 1997 Elsevier Science S.A.

1. Introduction

The study of high oxidation state organometallic compounds having metal-oxygen multiple bonds is currently in a period of rapid growth [1]. Such compounds are of particular interest both as a distinctive class of compounds and as catalysts for various organic transformations. For instance, the dioxo Mo(VI) complex $(C_5Me_5)Mo(O)_2Cl$ has been invoked as catalyst for the reaction of alkyl hydroperoxides with olefins to yield the epoxides and alcohols [2]. The related peroxo molybdenum or tungsten species also appear to be a useful reagent in alcohol oxidation and other catalytic processes [3]. Investigation on the reactivity of the mononuclear rhenium complexes such as $(C_5Me_5)Re(O)_3$ and $CpRe(O)_3$ has led to the discovery of the methyl rhenium trioxo complex $MeRe(O)_3$ [4], which has been shown to display profound activity as catalysts for oxidation, olefin metathesis and other reactions [5].

The wide spread usage of oxo metal compounds as catalytic precursors prompts us to examine the bonding and reactivity of the oxo ligand on the polynuclear carbonyl cluster compounds. In continuation of this goal

we have prepared some transition metal carbonyl oxide complexes by direct oxidation [6] and C–O bond scission [7] or through addition of $CpW(CO)_3(CCPh)$ to the unsaturated oxo complex $[(C_5Me_5)Re(O)(\mu\text{-}O)]_2$ [8]. These preparations pose some problem because most of the oxo carbonyl cluster compounds have formed adventitiously. It was, therefore, of interest to develop a more systematic methodology of generating these compounds through combination of metal oxo complex and carbonyl cluster template. One target molecule which can be applied in assembling such cluster molecules, is the dioxo acetylide compounds with formula $LM(O)_2(CCR)$, M = Mo or W; L = Cp or C_5Me_5; R = alkyl or aryl groups, as the acetylide group can provide an initial attachment to the alkyne accepting cluster, a requisite prior to the building of the desired cluster framework [9]. In this article, we describe the direct syntheses of the oxo and the peroxo complexes $(C_5Me_5)W(O)(O_2)(CCR)$ and $(C_5Me_5)W(O)_2(CCR)$ from tricarbonyl complexes $(C_5Me_5)W(CO)_3(CCR)$, which have the potential to serve for this propose.

2. Results and discussion

The oxidation of pentamethylcyclopentadienyl tungsten tricarbonyl acetylide derivatives

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Scheme 1.
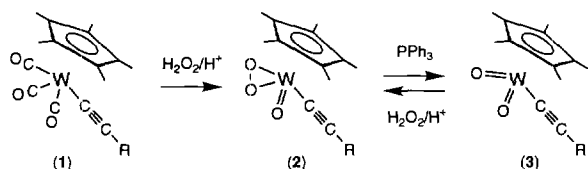
$(C_5Me_5)W(CO)_3(CCR)$ (**1a**, R = Ph; **1b**, CH_2OMe; **1c**, Pr^n; **1d**, $C(Me) = CH_2$) was carried out in hydrogen peroxide at room temperature with addition of trace amount of concentrated sulfuric acid. The employed conditions are modified in accord with the preparative procedure for rhenium trioxo complex $(C_5Me_5)Re(O)_3$, using both $(C_5Me_5)Re(CO)_3$ and hydrogen peroxide as starting materials [10]. The oxo-peroxo complexes $(C_5Me_5)W(O)(O_2)(CCR)$ (**2a**, R = Ph; **2b**, CH_2OMe; **2c**, Pr^n; **2d**, $C(Me) = CH_2$) were obtained in 65–80% yields (Scheme 1) after the routine workup by washing with deionized water, followed by recrystallization in acetone at $-20°C$. The reactions were executed in an open reaction flask and the products showed no significant decomposition even on extending the reaction time to three days. However, it is important to stir the toluene/hydrogen peroxide mixture thoroughly, as the efficient mixing reduced the reaction time by at least two folds. The successful isolation of (**2**) is remarkable, because this result is in contrast to the well documented instability of the mononuclear acetylide complexes during their preparation [11].

The corresponding dioxo complexes $(C_5Me_5)W(O)_2(CCR)$ (**3a**, R = Ph; **3b**, CH_2OMe; **3c**, Pr^n; **3d**, $C(Me) = CH_2$) were prepared by treatment of the oxo-peroxo complexes (**2**) with slightly excess triphenylphosphine. The reactions occurs rapidly at room temperature with formation of triphenylphosphine oxide as the co-product, which can be easily removed by flash chromatography eluted with dichloromethane. The oxo-peroxo complexes (**2**) can be regenerated in nearly quantitative yield by reoxidation of dioxo complexes (**3**) with hydrogen peroxide solution under similar conditions.

These oxo-peroxo and dioxo acetylide complexes were fully characterized by spectroscopic methods. The

IR spectra of complexes (**2**) and (**3**) show typically strong W = O stretching bands between 942 and 893 cm^{-1}, which are akin to those reported for $(C_5Me_5)W(O)(O_2)R$ and $(C_5Me_5)W(O)_2R$, R = Me and CH_2SiMe_3 [12], and can be assigned accordingly. In addition, the ^{13}C NMR data are of particular interest. The ^{13}C NMR chemical shifts and coupling constants of the acetylide α- and β-carbon atoms, along with the data of their precursors (**1**), are listed in Table 1.

Assignments are based on J_{WC} coupling constants; the C_α carbons always show a larger J_{WC} coupling constant than the respective C_β carbons. As can be seen from this table, the C_α resonances move to their C_β carbon resonances in the lower field region following the sequence (**2**) > (**3**) > (**1**). The net effect is to reduce the chemical shift difference between the C_α and C_β atoms. In certain extremes, the C_α resonance appears in the same spectral region with its C_β carbon. Deshielding of C_α is probably attributed to the development of a positive charge density on the carbon atoms of the oxo-peroxo complexes (**2**) and the dioxo complexes (**3**) due to the electron withdrawing effect of tungsten atom at the formal oxidation state (VI). The acetylide C_β signals change in the same trend, but the variation of chemical shifts are less obvious as it is further away from the tungsten atom. Interestingly, the J_{WC} coupling constants change in a distinct order (**3**) > (**2**) > (**1**). This suggests that the s-character of the tungsten atom involved in the bonding with the terminal acetylide is the greatest for the dioxo complexes (**3**), followed by the oxo-peroxo complexes (**2**) and then the carbonyl complexes (**1**).

Attempts in establishing the molecular structure of oxo-peroxo complexes (**2**) were unsuccessful. The single crystals can be obtained by cooling a diluted acetone solution to $-20°C$ slowly or grown from a saturated solution at room temperature. However, after the crystals were removed from the mother liquor, cracks and other defects rapidly developed over the surface of crystals at room temperature, changing the transparent crystals into opaque solids. In one case, i.e., complex (**2d**), we managed to collect a set of satisfactory X-ray diffraction data [13], but the crystal suffers a severe disorder for the positions of the tungsten atom and the ligated oxo and peroxo atoms, which reduced the accu-

Table 1

^{13}C NMR chemical shifts (ppm) and J_{W-C} coupling constants (Hz) of the acetylide complexes $(C_5Me_5)W(CO)_3(CCR)$ (**1**), $(C_5Me_5)W(O)(O_2)(CCR)$ (**2**) and $(C_5Me_5)W(O)_2(CCR)$ (**3**)

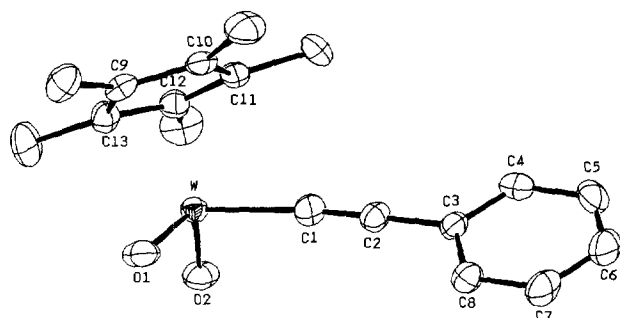|	C_α (ppm)/J_{WC} (Hz)			C_β (ppm)/J_{WC} (Hz)		
	(1)	(2)	(3)	(1)	(2)	(3)
(a) RPh	88.1/89	125.9/204	122.9/266	127.3/21	124.2/38	122.5/50
(b) R = CH_2OMe	82.4/89	121.2/203	118.2/266	121.8/20	119.7/40	125.6/50
(c) R = Pr^n	69.6/87	116.3/203	113.6/264	126.7/20	125.2/41	131.4/51
(d) R = $C(Me) = CH_2$	86.5/89	126.3/203	128.2/266	129.0/20	125.0/40	130.0/52

Fig. 1. Molecular structure of $(C_5Me_5)W(O)_2(CCPh)$ (3a) showing the atomic labeling scheme and the thermal ellipsoids at 30% probability level. Selected bond lengths (Å): $W-O(1) = 1.721(8)$, $W-(2) = 1.725(8)$, $W-C(1) = 2.08(1)$, $C(1)-C(2) = 1.19(2)$, $W-C(9) = 2.43(1)$, $W-C(10) = 2.497(9)$, $W-C(11) = 2.48(1)$, $W-C(12) = 2.43(1)$ and $W-C(13) = 2.32(1)$. Bond angles (°): $W-C(1)-C(2) = 175(1)$, $O(1)-W-O(2) = 109.0(4)$, $O(1)-W-C(1) = 103.7(5)$ and $O(2)-W-C(1) = 101.6(5)$.

racy of the bond angles and distances obtained. Thus, despite the gross geometry of complex (2d) confirms the identity of these oxo-peroxo complexes, the detailed structure is not presented in this article. The rapid crystal decay of these oxo-peroxo complexes are in common with the physical behaviour of the analogous peroxo complexes $LW(O)(O_2)(CH_2SiMe_3)$, $L = Cp$ and C_5Me_5 [12].

On the other hand, the single crystals of the dioxo complexes (3) are more stable as they remains unchanged over the period of several days, which allow us to identify their structure unambiguously. As indicated in Fig. 1, complex (3a) exhibits the expected structural features of metal acetylide complexes [14]. The acetylide ligand is nearly linear with angle 175(1)°. The local environment of the tungsten atom adopts the three-legged piano stool geometry. The short W−O distances (1.721(8)−1.725(8) Å) resembles that observed in $CpW(O)(N-o-tolyl)(o-tolyl)$, $[HB(Me_2pz)_3]W(O)_2R$ and other related oxo complexes [15], consisting with the formal $W = O$ multiple bond. Finally, the W−C(13) distance (2.32(1) Å) of the pentamethylcyclopentadienyl ligand is much shorter than other four W−C distances, which are in the range (2.43(1)−2.50(1) Å). Such variation of W−C distance is clearly due to the strong *trans* influence of the oxo ligands which increases the distance to the carbon atoms located opposite to the oxo ligands [16].

3. Conclusion

This synthetic route provides simple and effective access to mononuclear metal acetylide complexes with oxo or peroxo ligands. As for the possibility of extending this reaction to other group 6 mononuclear metal complexes we encountered with a mixed result. Thus,

the reaction of hydrogen peroxide with the tungsten methyl complex $(C_5Me_5)W(CO)_3Me$ occurred smoothly at room temperature to afford the corresponding $(C_5Me_5)W(O)(O_2)Me$ in slightly lower yield. This result indicates that this methodology of using hydrogen peroxide as oxygen transfer reagent can be further applied to the preparation of other oxo complexes with no β-hydrogen atom on the alkyl substituent. However, treatment of hydrogen peroxide with the analogous molybdenum complex $(C_5Me_5)Mo(CO)_3(CCPh)$ or the cyclopentadienyl compound $CpW(CO)_3(CCPh)$, produced a rather rapid exothermic reaction even at 0°C, giving only decomposition. These significant difference in reactivity can be explained by the weak tolerance of the molybdenum atom against the uncontrollable oxidation by the relatively stronger oxidant such as hydrogen peroxide, and the poor steric shielding provided by the less electron donating and smaller cyclopentadienyl ligand.

Despite these limitations we still believe that the facile introduction of the oxygen atoms to such tungsten acetylide complexes is noteworthy because of the effectiveness of the method. Further studies in searching for a milder oxygen atom transfer reagent to accomplish the direct synthesis of $CpW(O)(O_2)(CCPh)$ and $(C_5Me_5)Mo(O)(O_2)(CCPh)$ from $CpW(CO)_3(CCPh)$ and $(C_5Me_5)Mo(CO)_3(CCPh)$ are in progress.

4. Experimental details

4.1. Synthesis of $(C_5Me_5)W(O)(O_2)(CCPh)$

To a toluene solution (50 mL) of $(C_5Me_5)W(CO)_3(CCPh)$ (1.00 g, 1.98 mmol) was added a mixture of 35% H_2O_2 (10 mL) and concentrated H_2SO_4 (0.35 mL). The solution was then stirred at room temperature for 24 h, during which the color changed from yellow orange to milky yellow. After the reaction was completed, the solution was washed with

deionized water three times (50 mL × 3) to remove the excess H_2O_2. The organic layer was separated and dried with Na_2SO_4, and solvent was removed under vacuum to produce a yellow powdery residue. This residue was then further recrystallized in hot acetone solution, giving 752 mg of $(C_5Me_5)W(O)(O_2)(CCPh)$ (**2a**, 1.61 mmol, 81%) as light yellow crystals.

Spectral data for (**2a**): MS (EI, ^{184}W): m/z 468 (M^+). IR (KBr): $\nu(W = O)$ 942 (s); $\nu(O–O)$ 856 (s); $\nu(W–O)$ 569 (m), 556 (m) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 253 K): δ 7.56 ~ 7.54 (m, 2H), 7.38 ~ 7.37 (m, 3H), 2.25 (s, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2, 253 K): δ 132.0 (2C, o-C_6H_5), 129.2 (1C, p-C_6H_5), 129.1 (2C, m-C_6H_5), 125.9 (C_β, J_{WC} = 204 Hz), 124.2 (C_α, J_{WC} = 38 Hz), 124.0 (1C, i-C_6H_5), 121.6 (C_5Me_5), 11.3 (C_5Me_5). Elemental analysis: Found: C, 45.59; H, 4.30. $C_{18}H_{20}O_3W$ calc.: 46.18; H, 4.31.

Spectral data for (**2b**): MS (EI, ^{184}W): m/z 436 (M^+). IR (KBr): $\nu(W = O)$ 940 (s); $\nu(O–O)$ 856(s); $\nu(W–O)$ 562 (s) cm^{-1}. ^1H NMR (300 MHz, d^6-acetone, 297 K): δ 4.35 (s, 2H), 3.50 (s, 3H), 2.35 (s, 15H). ^{13}C NMR (75 MHz, d^6-acetone, 297 K): δ 121.2 (C_α, J_{WC} = 203 Hz), 120.9 (C_5Me_5), 119.7 (Cp, J_{WC} = 40 Hz), 60.7 (CH_2), 57.0 (CH_3), 10.1 (C_5Me_5). Elemental analysis: Found: C, 38.32; H, 4.63. $C_{14}H_{20}O_4W$ calc.: C, 38.55; H, 4.62.

Spectral data for (**2c**): MS (EI, ^{184}W): m/z 434 (M^+). IR (KBr): $\nu(W = O)$ 940 (s); $\nu(O–O)$ 856 (s); $\nu(W–O)$ 564 (s) cm^{-1}. ^1H NMR (300 MHz, d^6-acetone, 297 K): δ 2.50 (t, 2H, J_{HH} = 7.2 Hz), 2.33 (s, 15H), 1.74 (m, 2H, J_{HH} = 7.2 Hz), 1.16 (t, 3H, J_{HH} 7.2 Hz). ^{13}C NMR (75 MHz, d^6-acetone, 297K): δ 125.2 (C_β, J_{WC} = 41 Hz), 120.6 (C_5Me_5), 116.3 (C_α, J_{WC} = 203 Hz), 22.9 (CH_2), 22.6 (CH_2), 13.3 (CH_3), 10.1 (C_5Me_5). Elemental analysis: Found: C, 41.09; H, 5.03. $C_{15}H_{22}O_3W$ calc.: C, 41.49; H, 5.11.

Spectral data for (**2d**): MS (EI, ^{184}W): m/z 432 (M^+). IR (KBr): $\nu(W = O)$ 939 (s); $\nu(O–O)$ 856 (s); $\nu(W–O)$ 563 (s) cm^{-1}. ^1H NMR (400 MHz, d^6-acetone, 293 K): δ 5.60 (s, 1H), 5.56 (s, 1H), 2.47 (s, 15H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, d^6-acetone, 294K): δ 129.0 (C = CH_2), 126.3 (C_α, J_{WC} = 203 Hz), 125.0 (C_β, J_{WC} = 40 Hz), 122.3 (CH_2), 121.9 (C_5Me_5), 24.0 (CH_3), 11.1 (C_5Me_5). Elemental analysis: Found: C, 40.97; H, 4.67. $C_{15}H_{20}O_3W$ calc.: C, 41.69; H, 4.66.

4.2. Synthesis of $(C_5Me_5)W(O)_2(CCPh)$

A toluene solution (35 mL) of (**2a**) (500 mg, 1.07 mmol) and PPh_3 (280 mg, 1.07 mmol) was stirred at room temperature for 30 min, during which the color changed from yellow to yellowish green. Solvent was evaporated in vacuo and the residue dissolved in a minimum quantity of CH_2Cl_2. The solution was passed through a short silica gel column using CH_2Cl_2 as

eluent to remove the $OPPh_3$ formed, giving $(C_5Me_5)W(O)_2(CCPh)$ (**3a**, 464 mg, 1.03 mmol, 96%) as yellow powder on evaporation of the CH_2Cl_2 solvent. Samples of $(C_5Me_5)W(O)_2(CCPh)$ were further purified by recrystallization in acetone solution at −20°C.

Spectral data for (**3a**): MS (EI, ^{184}W): m/z 452 (M^+). IR (KBr): $\nu(W = O)$ 934 (s), 893 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.43 (d, 2H, J_{HH} = 7.4 Hz), 7.29 ~ 7.26 (m, 3H), 2.24 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$, 294 K): δ 131.4 (2C, o-C_6H_5), 128.9 (1C, p-C_6H_5), 128.7 (1C, i-C_6H_5), 128.1 (2C, m-C_6H_5), 122.9 (C_α, J_{WC} = 266 Hz), 122.5 (C_β, J_{WC} = 50 Hz), 119.7 (C_5Me_5), 10.8 (C_5Me_5). Elemental analysis: Found: C, 47.62; H, 4.45. $C_{18}H_{20}O_2W$ calc.: C, 47.81; H, 4.46.

Spectral data for (**3b**): MS (EI, ^{184}W): m/z 420 (M^+). IR (KBr): $\nu(W = O)$ 933 (s), 897 (s) cm^{-1}. ^1H NMR (300 MHz, d^6-acetone, 297 K): δ 4.30 (s, 2H), 3.47 (s, 3H), 2.35 (s, 15H). ^{13}C NMR (75 MHz, d^6-acetone, 297 K): δ 125.6 (C_β, J_{WC} = 50Hz), 119.7 (C_5Me_5), 118.2 (C_α, J_{WC} = 266 Hz), 60.5 (CH_2), 57.1 (CH_3), 10.5 (C_5Me_5). Elemental analysis: Found: C, 40.41; H, 4.78. $C_{14}H_{20}O_3W$ calc.: 30.02; H, 4.8.

Spectral data for (**3c**): MS (EI, ^{184}W): m/z 418 (M^+). IR (KBr): $\nu(W = O)$ 934 (s), 897 (s) cm^{-1}. ^1H NMR (300 MHz, d^6-acetone, 297 K): δ 2.45 (t, 2H, J_{HH} = 7.2 Hz), 2.33 (s, 15H), 1.71 (m, 2H, J_{HH} = 7.2 Hz), 1.13 (t, 3H, J_{HH} = 7.2 Hz). ^{13}C NMR (75 MHz, d^6-acetone, 297 K): δ 131.4 (C_β, J_{WC} = 51 Hz), 119.2 (C_5Me_5), 113.6 (C_α, J_{WC} = 264 Hz), 22.8 (CH_2), 22.2 (CH_2), 13.2 (CH_3), 10.5 (C_5Me_5). Elemental analysis: Found: C, 43.11; H, 5.36. $C_{15}H_{22}O_2W$ calc.: C, 43.08; H, 5.3.

Spectral data for (**3d**): MS (EI, ^{184}W): m/z 416 (M^+). IR(KBr): $\nu(W = O)$ 937 (s), 898 (s) cm^{-1}. ^1H NMR (400 MHz, d^6-acetone, 293K): δ 5.68 (s, 1H), 5.66 (s, 1H), 2.50 (s, 15H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, d^6-acetone, 294K): δ 130.0 (C_β, J_{WC} = 52 Hz), 128.2 (C_α, J_{WC} = 266 Hz), 124.1 (CH_2), 123.1 (C = CH_2), 120.8 (C_5Me_5), 23.6 (CH_3), 11.5 (C_5Me_5). Elemental analysis: Found: C, 42.99; H, 4.80. $C_{15}H_{20}O_2W$ calc.: C, 43.29; H, 4.84.

4.3. X-ray Crystallography

The X-ray diffraction measurement of (**3a**) was carried out on a Nonius CAD-4 diffractometer. Lattice parameters were determined from 25 high-angle reflections with 2θ angles in the range 22.0–39.0°. Three standard reflections (6, 0, 0; 0, 12, 0; 0, 0, 7) were monitored every 3600 s. No significant change in intensities (≤ 1%) due to crystal decay, was observed over the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz, polariza-

Table 2
Crystal data for the X-ray diffraction studies of (**3a**)

Formula = $C_{18}H_{20}O_2W$	mol. wt. = 452.20
Crystal system, Space group	monoclinic, $P2_1$
$a = 7.8004(8)$ Å	$b = 13.417(2)$ Å
$c = 8.216(1)$ Å	$\beta = 103.64(1)°$
Vol. = 835.6(2) Å^3	$Z = 2$
$D_c = 1.797$ g/cm^3	$F(000) = 434$
2θ (max)	60°
h, k, l ranges	$-10\ 10, 0\ 18, 0\ 11$
Crystal size, mm.	$0.12 \times 0.40 \times 0.45$
$\mu(\text{Mo-K}_\alpha)$ cm^{-1}	70.61
Transmission: max, min.	1.000, 0.281
No. of unique data	2522
data with $I > 2\sigma I)$	2231
No. of atoms and parameters	41, 190
Maximum Δ/σ ratio	0.009
R_F; R_W	0.032; 0.036
G.O.F.	1.58
D-map, max./min, e/Å^3	$2.18/-1.55$

tion and absorption effects (ψ scans). The structure was solved by using the NRCC-SDP-VAX package. All non-hydrogen atoms had anisotropic thermal parameters, while the hydrogen atoms of the organic substituents were placed at the idealized positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters are summarized in Table 2, while the atomic positional parameters are given in Table 3. Tables of bond distances and angles, tables of anisotropic thermal parameters and listings of the observed and calculated structural factors are available from the author (YC).

Table 3
Atomic coordinates and isotropic displacement coefficients for complex (**3a**); e.s.ds. refer to the last digit printed

	x	y	z	B_{eq}
W	0.32991(4)	0.50000	0.07975(4)	2.788(22)
O1	0.3332(10)	0.5668(7)	$-0.0983(10)$	4.6(4)
O2	0.1512(11)	0.4204(7)	0.0379(11)	4.5(4)
C1	0.2527(16)	0.6044(9)	0.2352(14)	3.7(5)
C2	0.1961(14)	0.6647(9)	0.3141(14)	3.5(4)
C3	0.1279(13)	0.7396(8)	0.4071(14)	3.3(4)
C4	0.1297(15)	0.7266(10)	0.5745(15)	4.2(5)
C5	0.0598(17)	0.7993(14)	0.6604(16)	5.3(7)
C6	$-0.0146(19)$	0.8819(12)	0.5799(20)	5.6(7)
C7	$-0.0200(18)$	0.8956(10)	0.4130(20)	5.4(7)
C8	0.0499(16)	0.8237(10)	0.3260(16)	4.1(5)
C9	0.6475(13)	0.4837(9)	0.1212(14)	3.4(5)
C10	0.6246(12)	0.5213(9)	0.2770(12)	3.4(5)
C11	0.5290(13)	0.4494(9)	0.3496(13)	3.2(4)
C12	0.4964(15)	0.3657(9)	0.2411(14)	3.5(4)
C13	0.5588(15)	0.3878(9)	0.0949(14)	3.6(4)
C14	0.7434(17)	0.5313(10)	0.0079(18)	5.1(6)
C15	0.6952(18)	0.6176(12)	0.3579(20)	5.6(7)
C16	0.4918(20)	0.4565(12)	0.5201(15)	5.2(7)
C17	0.4015(22)	0.2707(10)	0.2666(21)	5.6(7)
C18	0.5579(24)	0.3200(11)	$-0.0483(19)$	5.7(8)

References

[1] (a) J. Xiao, J.J. Vittal, R.J. Puddephatt, L. Manojlovic-Muir, K.W. Muir, J. Am. Chem. Soc. 115 (1993) 7882; (b) M.J. Carney, P.J. Walsh, F.J. Hollander, R.G. Bergman, Organometallics 11 (1992) 761; (c) F. Bottomley, L. Sutin, Adv. Organomet. Chem. 28 (1988) 339; (d) C.K. Schauer, E.J. Voss, M. Sabat, D.F. Shriver, Am. Chem. Soc. 111 (1989) 7662; (e) J.T. Park, Y. Chi, J.R. Shapley, M.R. Churchill, J.W. Ziller, Organometallics 13 (1994) 813; (f) M.H. Dickman, M.T. Pope, Chem. Rev. 94 (1994) 569; (g) S.N. Brown, J.M. Mayer, J. Am. Chem. Soc. 118 (1996) 12119; (h) S. Thomas, E.R.T. Tiekink, C.G. Young, Organometallics 15 (1996) 2428; (i) M. O'Donoghue, R.R. Schrock, A.M. LaPointe, W.M. Davis, Organometallics 15 (1996) 1334.
[2] M.K. Trost, R.G. Bergman, Organometallics 10 (1991) 1172.
[3] (a) W.P. Griffith, A.M.Z. Slawin, K.M. Thompson, D.J. Williams, J. Chem. Soc. Chem. Commun. (1994) 569; (b) J. Belgacem, J. Kress, J.A. Osborn, J. Mol. Catal. 86 (1994) 267.
[4] (a) W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 27 (1988) 1297; (b) F.E. Kuehn, W.A. Herrmann, R. Hahn, M. Elison, J. Bluemel, E. Herdtweck, Organometallics 13 (1994) 1601; (c) W.A. Herrmann, W.R. Thiel, F.E. Kuehn, R.W. Fischer, M. Kleine, E. Herdtweck, W. Scherer, J. Mink, Inorg. Chem. 32 (1993) 5188; (d) C. De Meric de Bellefon, W.A. Herrmann, P. Kiprof, C.R. Whitaker, Organometallics 11 (1992) 1072.
[5] (a) W.A. Herrmann, J.D.G. Correia, F.E. Kuehn, G.R.J. Artus, C.C. Romao, Chem. Eur. J. 2 (1996) 168; (b) W.A. Herrmann, J. Organomet. Chem. 500 (1995) 149; (c) W.A. Herrmann, R.W. Fischer, M.U. Rauch, W. Scherer, J. Mol. Catal. 86 (1994) 243; (d) J.H. Espenson, O. Pestovsky, P. Huston, S. Staudt, J. Am. Chem. Soc. 116 (1994) 2869; (e) M.M. Abu-Omar, J.H. Espenson, Organometallics 15 (1996) 3543; (f) A.M. Al-Ajlouni, J.H. Espenson, J. Org. Chem. 61 (1996) 3969.
[6] (a) Y. Chi, L.-S. Hwang, G.-H. Lee, S.-M. Peng, J. Chem. Soc., Chem. Commun. (1988) 1456; (b) S.-M. Peng, G.-H. Lee, Y. Chi, Polyhedron 9 (1990) 1491; (c) Y. Chi, P.-S. Cheng, H.-L. Wu, D.-K. Hwang, S.-M. Peng, G.-H. Lee, J. Chem. Soc. Chem Commun. (1994) 1839; (d) H.-L. Wu, G.-L. Lu, Y. Chi, L.J. Farrugia, S.-M. Peng, G.-H. Lee, Inorg. Chem. 35 (1996) 6015.
[7] (a) C.-J. Su, P.-C. Su, Y. Chi, S.-M. Peng, G.-H. Lee, J. Am. Chem. Soc. 118 (1996) 3289; (c) J.-H. Gong, D.-K. Hwang, C.-W. Tsay, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 13 (1994) 1720.
[8] N.-S. Lai, W.-C. Tu, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 13 (1994) 4652.
[9] P. Blenkiron, A.J. Carty, S.-M. Peng, G.-H. Lee, C.-J. Su, C.-W. Shiu, Y. Chi, Organometallics 16 (1997) 519.
[10] W.A. Herrmann, J. Okuda, J. Mol. Catal. 41 (1987) 109.
[11] (a) M.I. Bruce, M.G. Humphrey, J.G. Matison, S.K. Roy, A.G. Swincer, Aust. J. Chem. 37 (1984) 1955; (b) E. Viola, L.C. Sterzo, R. Crescenzi, G. Frachy, J. Organomet. Chem. 493 (1995) 55.
[12] (a) J.W. Faller, Y. Ma, Organometallics 7 (1988), 559; (b) J.W. Faller, Y. Ma, J. Organomet. Chem. 368 (1989) 45; (c) P. Legzdins, E.C. Phillips, S.J. Rettig, L. Sánchez, J. Trotter, V.C. Yee, Organometallics 7 (1988) 1877.

[13] Selected structural data for complex (**2d**): $C_{15}H_{20}O_3W$, M = 432.17, orthorhombic, space group P na2$_1$, $a = 18.078(4)$, $b = 12.485(3)$, $c = 6.464(3)$ Å, $V = 1459.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.968$ gcm^{-3}, $F(000) = 828$, $\lambda(Mo - K_\alpha) = 0.7107$ Å, T = 298 K, $\mu = 30.79$ cm^{-1}.

[14] J. Manna, K.D. John, M.D. Hopkins, Adv. Organomet. Chem. 38 (1995) 79.

[15] (a) P. Legzdins, S.J. Rettig, K.J. Ross, J.E. Veltheer, J. Am. Chem. Soc. 113 (1991) 4361; (b) P. Legzdins, E.C. Phillips, J. Trotter, V.C. Yee, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. C51 (1995) 2498; (c) A.A. Eagle, E.R.T. Tiekink, C.G. Young, J. Chem. Soc. Chem. Commun. (1991) 1746; (d) A.A. Eagle, C.G. Young, E.R.T. Tiekink, Organometallics 11 (1992) 2934; (e) Z. Xiao, R.W. Gable, A.G. Wedd, C.G. Young, J. Am. Chem. Soc. 118 (1996) 2912.

[16] W.A. Herrmann, E. Werdtweck, M. Floel, J. Kulpe, U. Kusthardt, J. Okuda, Polyhedron 6 (1987) 1165.