

Journal of Organometallic Chemistry 545-546 (1997) 151-156



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

Chin-Wei Shiu ^a, Chi-Jung Su ^a, Chih-Wei Pin ^a, Yun Chi ^{a,*}, P. Shie-Ming Peng ^b, Gene-Hsiang Lee ^b

^a Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, ROC ^b Department of Chemistry and Instrumentation Center, National Taiwan University, Taipei 10764, Taiwan, ROC

Received 29 January 1997; received in revised form 19 March 1997

Abstract

The pentamethylcyclopentadienyl tungsten carbonyl acetylide complexes $(C_5Me_5)W(CO)_3(CCR)$, (1) R = Ph, CH₂OMe, Prⁿ and C(Me) = CH₂, 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 $(C_5Me_5)Mo(O)$, Cl 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 (C₅Me₅)Re(O)₃ and CpRe(O)₃ has led to the discovery of the methyl rhenium trioxo complex MeRe(O), [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 $[(C_5Me_5)Re(O)(\mu-O)]_2$ [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 $LM(O)_{2}(CCR), M = Mo \text{ or } W; L = Cp \text{ or } C_{5}Me_{5}; R =$ 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, Me,)W(CO), (CCR), which have the potential to serve for this propose.

2. Results and discussion

The oxidation of pentamethylcyclopentadienyl tungsten tricarbonyl acetylide derivatives

^{&#}x27;Corresponding author. Fax: +886-3-5720864; e-mail: ychi@faculty.nthu.edu.tw.



 $(C_5Me_5)W(CO)_3(CCR)$ (1a, R = Ph; 1b, CH₂OMe; 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 $(C_{s}Me_{s})Re(O)_{3}$, 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, CH₂OMe; 3c, Prⁿ; 3d, C(Me) = CH₂) 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 complexits 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 CH₂SiMe₃ [12], and can be assigned accordingly. In addition, the ¹³C NMR data are of particular interest. The ¹³C 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

¹³C NMR chemical shifts (ppm) and J_{W-C} coupling constants (Hz) of the acetylide complexes (C₅Me₅)W(CO)₃(CCR) (1), (C₅Me₅)W(O)(O₂)(CCR) (2) and (C₅Me₅)W(O)₂(CCR) (3)

	$C_{\alpha} (\text{ppm})/J_{WC} (\text{Hz})$			$C_{\beta} \text{ (ppm)}/J_{WC} \text{ (Hz)}$		
	(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) $R = CH, OMe$	82.4/89	121.2/203	118.2/266	121.8/20	119.7/40	125.6/50
$(\mathbf{c}) \mathbf{R} = \mathbf{Pr}^{\mathbf{n}}$	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 two-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)(O₂)(CH₂SiMe₃), L = Cp and C₅Me₅ [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 threelegged 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 B-hydrogen atom on the alkyl substituent. However, treatment of hydrogen peroxide with the analogous molybdenum complex (C₅Me₅)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

Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on either a Bruker AM-400 or a Varian Unity-400 instrument. ¹H and ¹³C NMR chemical shifts are quoted with respect to internal standard TMS. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. The acetylide complexes (C_5Me_5)W(CO)₃(CCR), R = Ph, CH₂OMe, Pr^a, C(Me) = CH₂, were prepared according to literature procedures [11a]. Reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F₂₅₄, E. Merck). Elemental analyses were carried out at the regional instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

4.1. Synthesis of $(C_5 Me_5)W(O)(O_2)(CCPh)$

To a toluene solution (50 mL) of $(C_5 \text{Me}_5)W(\text{CO})_3(\text{CCPh})$ (1.00 g, 1.98 mmol) was added a mixture of 35% H₂O₂ (10 mL) and concentrated H₂SO₄ (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 \times 3) to remove the excess H₂O₂. The organic layer was separated and dried with Na₂SO₄, 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 (C₅Me₅)W(O)(O₂)(CCPh) (2a, 1.61 mmol, 81%) as light yellow crystals.

Spectral data for (2a): MS (EI, ¹³⁴W): m/z 468 (M⁺). IR (KBr): ν (W = O) 942 (s); ν (O–O) 856 (s); ν (W–O) 569 (m), 556 (m) cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂, 253 K): δ 7.56 ~ 7.54 (m, 2H), 7.38 ~ 7.37 (m, 3H), 2.25 (s, 15H). ¹³C NMR (100 MHz, CD₂Cl₂, 253 K): δ 132.0 (2C, o-C₆H₅), 129.2 (1C, p-C₆H₅), 129.1 (2C, m-C₆H₅), 125.9 (C_β, J_{WC} = 204 Hz), 124.2 (C_α, J_{WC} = 38 Hz), 124.0 (1C, i-C₆H₅), 121.6 (C_5 Me₅), 11.3 (C₅Me₅). Elemental analysis: Found: C, 45.59; H, 4.30. C₁₈H₂₀O₃W calc.: 46.18; H, 4.31.

Spectral data for (2b): MS (EI, ¹⁸⁴W): n/z 436 (M⁺). IR (KBr): ν (W = O) 940 (s); ν (O–O) 856(s); ν (W–O) 562 (s) cm⁻¹. ¹H NMR (300 MHz, d⁶-acetone, 297 K): δ 4.35 (s, 2H), 3.50 (s, 3H), 2.35 (s, 15H). ¹³C NMR (75 MHz, d⁶-acetone, 297 K): δ 121.2 (C_a, $J_{WC} = 203$ Hz), 120.9 (C_5 Me₅), 119.7 (Cp, $J_{WC} = 40$ Hz), 60.7 (CH₂), 57.0 (CH₃), 10.1 (C₅Me₅). Elemental analysis: Found: C_a, 38.32; H, 4.63. C₁₄H₂₀O₄W calc.: C, 38.55; H, 4.62.

Spectral data for (2c): MS (EI, ¹⁸⁴W): m/z 434 (M⁺). IR (KBr): ν (W = O) 940 (s); ν (O–O) 856 (s); ν (W–O) 564 (s) cm⁻¹. ¹H NMR (300 MHz, d⁶-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). ¹³C NMR (75 MHz, d⁶-acetone, 297K): δ 125.2 (C_β, J_{WC} = 41 Hz), 120.6 (C₅Me₅), 116.3 (C_α, J_{WC} = 203 Hz), 22.9 (CH₂), 22.6 (CH₂), 13.3 (CH₃), 10.1 (C₅Me₅). Elemental analysis: Found: C, 41.09; H, 5.03. C₁₅H₂₂O₃W calc.: C, 41.49; H, 5.11.

C₁₅H₂₂O₃W calc.: C, 41.49; H, 5.11. Spectral data for (2d): MS (EI, ¹⁸⁴W): m/z 432 (M⁺). IR (KBr): ν (W = O) 939 (s); ν (O–O) 856 (s); ν (W–O) 563 (s) cm⁻¹. ¹H NMR (400 MHz, d⁶-acetone, 293 K): δ 5.60 (s, 1H), 5.56 (s, 1H), 2.47 (s, 15H), 2.20 (s, 3H). ¹³C NMR (100 MHz, d⁶-acetone, 294K): δ 129.0 (C = CH₂), 126.3 (C_α, J_{WC} = 203 Hz), 125.0 (C_β, J_{WC} = 40 Hz), 122.3 (CH₂), 121.9 (C₅Me₅), 24.0 (CH₃), 11.1 (C₅Me₅). Elemental analysis: Found: C, 40.97; H, 4.67. C₁₅H₂₀O₃W calc.: C, 41.69; H, 4.66.

4.2. Synthesis of $(C_5 Me_5)W(O)_2(CCPh)$

A toluene solution (35 mL) of (2a) (500 mg, 1.07 mmol) and PPh₃ (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 OPPh₃ formed, giving $(C_5Me_5)W(O)_2(CCPh)$ (3a, 464 mg. 1.03 mmol, 96%) as yellow powder on evaporation of the CH₂Cl₂ solvent. Samples of $(C_5Me_5)W(O)_2(CCPh)$ were further purified by recrystallization in acetone solution at $-20^{\circ}C$.

Spectral data for (**3a**): MS (EI, ¹⁸⁴W): m/z 452 (M⁺). IR (KBr): ν (W = O) 934 (s), 893 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 7.43 (d, 2H, $J_{\rm HH} = 7.4$ Hz), 7.29 ~ 7.26 (m, 3H), 2.24 (s, 15H). ¹³C NMR (100 MHz, CDCl₃, 294 K): δ 131.4 (2C, o-C₆H₅), 128.9 (1C, p-C₆H₅), 128.7 (1C, i-C₆H₅), 128.9 (2C, m-C₆H₅), 128.9 (C_{α}, $J_{\rm WC} = 266$ Hz), 122.5 (C_{β}, $J_{\rm WC} = 50$ Hz), 119.7 (C₅Me₅), 10.8 (C₅Me₅). Elemental analysis: Found: C, 47.62; H, 4.45. C₁₈H₂₀O₂W calc.: C, 47.81; H, 4.46.

Spectral data for (3b): MS (EI, ¹⁸⁴W): m/z 420 (M⁺). IR (KBr): ν (W = O) 933 (s), 897 (s) cm⁻¹. ¹H NMR (300 MHz, d⁶-acetone, 297 K): δ 4.30 (s, 2H), 3.47 (s, 3H), 2.35 (s, 15H). ¹³C NMR (75 MHz, d⁶-acetone, 297 K): δ 125.6 (C_{β}, J_{WC} = 50Hz), 119.7 (C₅Me₅), 118.2 (C_{α}, J_{WC} = 266 Hz), 60.5 (CH₂), 57.1 (CH₃), 10.5 (C₅Me₅). Elemental analysis: Found: C, 40.41; H, 4.78. C₁₄H₂₀O₃W calc.: 30.02; H, 4.8.

Spectral data for (3c): MS (EI, ¹⁸⁴W): m/z 418 (M⁺). IR (KBg): ν (W = O) 934 (s), 897 (s) cm⁻¹. ¹H NMR (300 MHz, d⁶-acetone, 297 K): δ 2.45 (t, 2H, $J_{\rm HH} = 7.2$ Hz), 2.33 (s, 15H), 1.71 (m, 2H, $J_{\rm HH} = 7.2$ Hz), 1.13 (t, 3H, $J_{\rm HH} = 7.2$ Hz). ¹³C NMR (75 MHz, d⁶-acetone, 297 K): δ 131.4 (C_{β}, $J_{\rm WC} = 51$ Hz), 119.2 (C₅Me₅), 113.6 (C_{α}, $J_{\rm WC} = 264$ Hz), 22.8 (CH₂), 22.2 (CH₂), 13.2 (CH₃), 10.5 (C₅Me₅). Elemental analysis: Found: C, 43.11; H, 5.36. C₁₅H₂₂O₂W calc.: C, 43.08; H, 5.3.

Spectral data for (3d): MS (EI, ¹⁸⁴W): m/z 416 (M⁺). IR(KBr): ν (W = O) 937 (s), 898 (s) cm⁻¹. ¹H NMR (400 MHz, d⁶-acetone, 293K): δ 5.68 (s, 1H), 5.66 (s, 1H), 2.50 (s, 15H), 2.20 (s, 3H). ¹³C NMR (100 MHz, d⁶-acetone, 294K): δ 130.0 (C_β, J_{WC} = 52 Hz), 128.2 (C_α, J_{WC} = 266 Hz), 124.1 (CH₂), 123.1 (C = CH₂), 120.8 (C₅Me₅), 23.6 (CH₃), 11.5 (C₅Me₅). Elemental analysis: Found: C, 42.99; H, 4.80. C₁₅H₂₀O₂W 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 $22.0-39.0^{\circ}$. Three standard reflections (6, 0, 0; 0, 12, 0; 0, 0, 7) were monitored every 3600 s. No significant change in intensities ($\leq 1\%$) 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)

· · · · · · · · · · · · · · · · · · ·	
$Formula = C_{18} H_{20} O_2 W$	mol. wt. = 452.20
Crystal system, Space group	monoclinic, P 2
a = 7.8004(8) Å	b = 13.417(2) Å
c = 8.216(1) Å	$\beta = 103.64(1)^{\circ}$
Vol. = $835.6(2)$ Å ³	Z = 2
$D_{\rm c} = 1.797 \ {\rm g/cm^3}$	F(000) = 434
2θ (max)	60°
h, k, l ranges	- 10 10, 0 18, 0 11
Crystal size, mm.	0.12×0.40×0.45
μ (Mo-K _a) 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
$R_{\rm F}; R_{\rm W}$	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 $U_{\rm H} = U_{\rm C} + 0.1$. 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 com-
plex (3a); e.s.ds. re:	fer to the last	digit printed		

	x	у	Ζ	B _{eq}
W	0.32991(4)	0.50000	0.07975(4)	2.788(22)
01	0.3332(10)	0.5668(7)	- 0.0983(10)	4.6(4)
02	0.1512(11)	0.4204(7)	0.0379(11)	4.5(4)
Cl	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)
C 10	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)

Acknowledgements

We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 86-2113-M007-003).

References

- (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. Biown, 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. Xuehn, 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 na2₁, a = 18.078(4), b = 12.485(3), c = 6.464(3) Å, V = 1459.0(8) Å³, Z = 4, $\rho_{calcd} = 1.968$ gcm⁻³, F(000) = 828, $\lambda(Mo K_{\alpha}) = 0.7107$ Å, T = 298 K, $\mu = 80.79$ 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.