Journal of Organometallic Chemistry, *451* (1993) 83–87

JOM 23496

The synthesis and X-ray structure of a phenoxide-bridged heterobimetallic anion, $W(CO)_5OPh(Cr(CO)_3)^-$, and its reactivity with carbon dioxide and carbonyl sulfide *

Donald J. Darensbourg, Brian L. Mueller and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, TX 77843 (USA)

(Received October 12, 1992; in revised form December 11, 1992)

Abstract

The heterobimetallic complex, $[Et_4N][W(CO)_5OPh(Cr(CO)_3)]$ (**1**), was prepared by the reaction of $[Et_4N][W(CO)_5CH_3]$ and $(\eta^6C_6H_5OH)Cr(CO)_3$ in tetrahydrofuran. Complex **1** crystallizes from THF/hexane in the space group $P2_1$ with unit cell dimensions $a = 7.036(2)$ Å, $b = 11.766(4)$ Å, $c = 15.460(4)$ Å, $\beta = 94.83(2)°$, $V = 1275.3(7)$ Å^3, and $D_{calcd} = 1.779$ g cm^{-3}. The structure was refined to $R = 0.084$ and $R_w = 0.091$ for 1136 reflections having $F > 3.0\sigma(F_o)$. Complex **1** was completely inert towards carbon dioxide, even at high pressure (900 psi), but readily reacted with carbonyl sulfide to afford the thiocarbonate derivative, $[Et_4N][W(CO)_5S\text{-}C(O)\text{-}OPh(Cr(CO)_3)]$.

1. Introduction

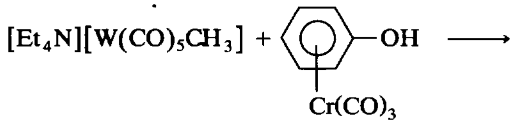
In our efforts to examine the mechanistic aspects of carbon dioxide insertion into transition metal–oxygen bonds several new anionic tungsten carbonyl aryloxide derivatives have been synthesized and their reactivity patterns investigated [1–4]. Indeed the general reaction of carbon dioxide with low-valent transition metal oxygen bonds has received a significant amount of attention in the past, and is currently the subject of renewed interest [5]. In our particular instance the mononuclear group 6 derivatives were found to be prone to loss of carbon monoxide in tetrahydrofuran (THF) solution with concomitant oligomerization [4,6]. For example, the tetranuclear cubane structure, $[W(CO)_3OPh]_4^{-4}$, readily precipitates from THF solution of $W(CO)_5OPh^-$ upon standing at ambient temperature. This clusterification is retarded by CO in solution and by bulky substituents on the phenoxide moiety. Similarly, whereas $W(CO)_5OPh^-$ inserts carbon dioxide to provide the corresponding carbonate reversibly (eqn. (1)), the $W(CO)_5O\text{-}2,6\text{-}Ph_2\text{-}C_6H_3^-$ derivative is completely inert towards reaction with high pressures of CO_2 (> 700 psi) [7]. This difference in reactivity was attributed to a steric interference of the phenyl rings around the metal–oxygen bond.

$$W(CO)_5OPh^- + CO_2 \rightleftharpoons W(CO)_5O_2COPh^- \qquad (1)$$

In this report we wish to present the preparation and characterization of the heterobimetallic anion, $W(CO)_5OPh(Cr(CO)_3)^-$, and the influence of the $-Cr(CO)_3$ unit on the reactivity of the phenoxide ligand toward carbon dioxide and carbonyl sulfide.

2. Results and discussion

When a tetrahydrofuran solution of $[Et_4N][W(CO)_5CH_3]$ was mixed with an equimolar quantity of $(\eta^6\text{-}C_6H_5OH)Cr(CO)_3$, a quantitative reaction occurred to yield complex **1** and methane (eqn. (2)). Complex **1** exhibits two, superimposed IR band patterns in the



$$[Et_4N][W(CO)_5CH_3] + (\eta^6\text{-}C_6H_5OH)Cr(CO)_3 \longrightarrow$$

$$[Et_4N][W(CO)_5OPh(Cr(CO)_3)] + CH_4 \qquad (2)$$

1

Correspondence to: Professor D.J. Darensbourg.

* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

0022-328X/93/$6.00

carbonyl stretching region consistent with the presence of "$Cr(CO)_3$" and "$W(CO)_5$" fragments. The ν(CO) modes of [$Cr(CO)_3$] are displaced to lower frequencies from those of the parent complex (η^6-C_6H_5OH)-$Cr(CO)_3$, appearing at 1946(s) and 1853(s) cm^{-1}. On the other hand the carbonyl vibrational modes of the [$W(CO)_5$] unit are shifted to higher frequencies when compared to the corresponding values in the $W(CO)_5OPh^-$ anion, *i.e.* 2065(w), 1913(s), and ~ 1853(m) cm^{-1} *vs.* 2057(w), 1904(s), and 1851(m) cm^{-1}. This shift to higher frequency is indicative of a strongly electron-withdrawing -$Cr(CO)_3$ group on the phenoxide ligand.

The molecular structure of the yellow crystalline product (**1**) obtained from reaction (2) was further defined by X-ray crystallography. The complex crystallized in the monoclinic space group $P2_1$. The anion with atomic labelling scheme is shown in Fig. 1. Atomic coordinates are provided in Table 1, and selected bond distances and angles are given in Tables 2 and 3, respectively. The structural features relevant to the reactivity of the oxygen lone pairs are the W–O bond length (2.35(3) Å) and the W–O–C bond angle (128(2)°). That is, the W–O bond distance in complex **1** is significantly longer than that seen in $(CO)_5W\text{–}OPh^-$ (2.192(20) Å) [3], $(CO)_5W\text{–}O\text{–}2,6\text{-}Ph_2\text{–}C_6H_3^-$ (2.171(9) Å) [7] and *cis*-$(CO)_4[PPh_2Me]W\text{–}OPh^-$ (2.191(6) Å) [7]. Hence, although variations in substituents on the phenyl ring and on the metal center have a negligible influence on the ligation of the aryloxy moiety, the addition of the electron-withdrawing $Cr(CO)_3$ unit significantly lengthens the W–OPh bond. On the other hand the W–O–C bond angles in all of these derivatives span a narrow range of 128–133°.

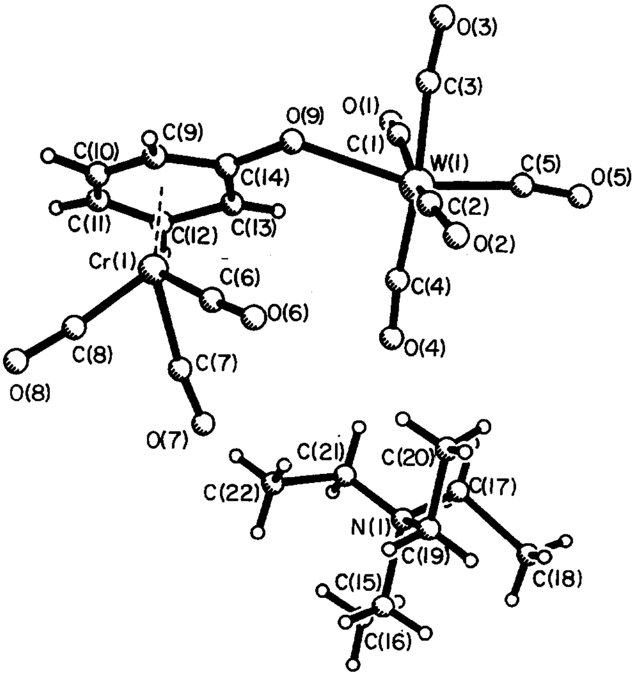


Fig. 1. Ball-and-stick plot of $[Et_4N][W(CO)_5OPh(Cr(CO)_3)]$ (1) with atomic labeling scheme.

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Et_4N][W(CO)_5\text{–}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$

	x	*y*	*z*	U_{eq} [a,b]
W(1)	192(3)	0	1392(1)	62(1)
Cr(1)	−1303(8)	42(18)	4399(4)	48(2)
C(1)	−2289(41)	915(35)	1041(27)	50(5)
O(1)	−3993(33)	1239(26)	825(18)	49(5)
C(2)	2653(39)	−385(29)	1700(23)	35(5)
O(2)	4188(37)	−950(29)	1767(22)	72(5)
C(3)	1065(42)	1352(36)	1050(28)	56(5)
O(3)	1655(32)	2126(26)	777(18)	48(5)
C(4)	−912(40)	−1215(34)	1780(25)	36(5)
O(4)	−1575(36)	−2020(28)	1957(21)	66(5)
C(5)	339(37)	−470(27)	243(22)	19(5)
O(5)	169(32)	−875(25)	−400(18)	41(4)
C(6)	853(46)	−704(37)	4088(30)	59(5)
O(6)	2251(40)	−1147(31)	3857(24)	85(5)
C(7)	−2545(44)	−1478(38)	4338(29)	46(5)
O(7)	−3216(38)	−2381(30)	4208(22)	73(5)
C(8)	−640(38)	−447(28)	5506(23)	19(5)
O(8)	−238(33)	−664(24)	6258(19)	42(5)
O(9)	406(34)	1134(27)	2644(19)	50(5)
C(9)	−152(44)	1547(35)	4118(27)	46(5)
C(10)	−1330(46)	1616(40)	4682(33)	78(5)
C(11)	−3305(46)	1371(39)	4591(31)	67(5)
C(12)	−3863(44)	780(35)	3901(27)	50(5)
C(13)	−2667(42)	679(34)	3147(27)	46(5)
C(14)	−776(42)	1142(36)	3296(27)	44(5)
N(1)	−4870(29)	−4848(40)	2056(16)	26(4)
C(15)	−5176(39)	−6095(34)	2581(26)	24(5)
C(16)	−7240(45)	−6307(40)	2631(32)	79(5)
C(17)	−5776(37)	−4749(37)	1158(20)	33(5)
C(18)	−5057(45)	−6068(37)	657(30)	72(5)
C(19)	−2703(35)	−5005(47)	2070(21)	40(5)
C(20)	−1836(45)	−3887(37)	1695(30)	67(5)
C(21)	−5847(44)	−3917(37)	2457(28)	45(5)
C(22)	−4890(46)	−3642(38)	3453(31)	80(5)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Estimated standard deviations are given in parenthesis.

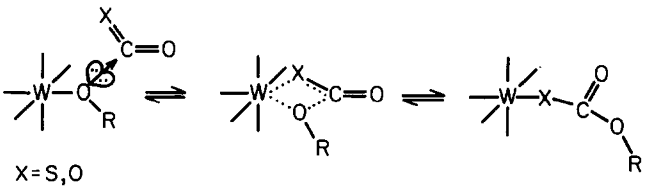
TABLE 2. Selected bond lengths from the anion of the complex $[Et_4N][W(CO)_5\text{–}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (Å)

W–C1	2.083(2)	W–C2	1.815(2)
W–C3	1.801(1)	W–C4	1.757(1)
W–C5	1.871(2)	W–O9	2.35(3)
Cr–C6	1.85(4)	Cr–C7	1.99(5)
Cr–C8	1.83(3)	Cr–C9	2.01(4)
Cr–C10	1.90(5)	Cr–C11	2.14(4)
Cr–C12	2.09(3)	Cr–C13	2.22(4)
Cr–C14	2.20(4)	O9–C14	1.36(5)

TABLE 3. Selected bond angles of the anion in the structure of $[Et_4N][W(CO)_5\text{-}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (°)

C1–W–C2	163.2(1)	C1–W–C3	76.5(1)
C2–W–C3	87.5(1)	C1–W–C4	97.2(1)
C2–W–C4	98.5(1)	C3–W–C4	172.3(1)
C1–W–C5	91.0(1)	C2–W–C5	92.7(1)
C3–W–C5	86.3(1)	C4–W–C5	98.3(1)
C1–W–O9	85.1(6)	C2–W–O9	86.1(6)
C3–W–O9	74.9(8)	C4–W–O9	100.4(7)
C5–W–O9	161.2(7)		
C6–Cr–C7	86(2)		
C6–Cr–C8	87(2)		
C7–Cr–C8	81(2)		

Like the sterically encumbered $W(CO)_5O\text{–}2,6\text{-}Ph_2\text{–}C_6H_3^-$ anion, complex **1** is completely inert towards carbon dioxide as indicated by *in situ* high pressure (900 psi) ^{13}C nuclear magnetic resonance (NMR) measurements. However, it readily reacts with COS to provide the thiocarbonate derivative, $[Et_4N][W(CO)_5\text{-}S\text{-}C(O)O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ (ν(CO) in THF: 2061(w), 1946(s), 1918(s), 1869(s)). The lone pairs on the oxygen atom of complex **1** appear on the basis of its solid-state structure to be more accessible than those in the $W(CO)_5O\text{–}2,6\text{-}Ph_2\text{–}C_6H_3^-$ derivative; nevertheless, the phenoxide ligand in complex **1** is much less basic. Reiterating the previously presented Scheme, these observations can be rationalized by a weakening of the interaction of the Lewis acid site carbon of CO_2 with the lone pairs of the aryloxide oxygen atom, for steric and/or electronic reasons, without the benefit of significant W–X interaction [7].



3. Experimental section

3.1. Materials and methods

All reactions were carried out under a dry nitrogen atmosphere on a double-manifold Schlenk vacuum line. Solid transfers were performed under a stream of nitrogen or in an argon-filled glovebox. THF, DME, and hexane were purified by distillation from blue sodium benzophenone ketyl solutions under nitrogen. Solution infrared spectra were taken in 0.1 mm CaF_2 or NaCl cells on an IBM FTIR Model 32 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200E spectrometer. High-pressure NMR experiments were conducted in a specially designed sapphire NMR tube [8].

3.2. Synthesis of $[Et_4N][W(CO)_5CH_3]$

This compound was prepared from $[Et_4N][W(CO)_5Cl]$ and methyllithium by the procedure previously published [9]. $[Et_4N][W(CO)_5Cl]$ (4.46 mmol) was dissolved in 30 ml of THF and titrated with methyllithium (1.25 M in Et_2O) in 0.5 ml aliquots. The progress of the reaction was monitored by the disappearance of the strong ν(CO) band of the starting metal carbonyl chloride at 1912 cm^{-1}. Upon complete conversion to the methyl compound, excess alkyl lithium reagent was quenched by the addition of 10 ml of aqueous NaOH. THF was removed under reduced pressure and the crude product was washed with three 30 ml aliquots of degassed, distilled water to eliminate alkali metal salts. After vacuum drying for 2 h the product was recrystallized from THF/hexane to afford a yellow solid. IR, ν(CO) in THF, 2028(w), 1883(s), and 1834(m) cm^{-1}.

3.3. Synthesis of $(\eta^6\text{-}C_6H_5OH)Cr(CO)_3$

This arene–chromium tricarbonyl derivative was prepared by a modified version of a previously reported procedure [10]. Gold labeled phenol (2.1 g, 22.7 mmol) and $Cr(CO)_6$ (5.0 g, 22.8 mmol) were dissolved in DME in a Schlenk flask. The reaction mixture was covered with aluminum foil to exclude light and refluxed for three days to give a yellowish-green solution. The solution was cooled and filtered. The solvent and excess $Cr(CO)_6$ were removed under reduced pressure. The solid was dissolved in warm hexane and filtered through Celite to remove the green coloration. The solvent was removed at reduced pressure to yield a yellow solid in good yield. IR, ν(CO) in THF, 1962.5(s), and 1880.5(s) cm^{-1}.

3.4. $[Et_4N][W(CO)_5\text{-}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$

$[Et_4N][W(CO)_5CH_3]$ (100 mg, 0.11 mmoles) was placed in a Schlenk tube along with excess $[\eta^6\text{-}(HO)C_6H_5]Cr(CO)_3$ and 10 ml of THF added. The solution turned orange immediately, and the reaction was monitored by infrared spectroscopy which showed quantitative conversion of the $W(CO)_5Me^-$ to the desired aryloxide. The resultant complex was isolated in near quantitative yield as an oil by the addition of hexane to the THF solution followed by washing with several 10 ml aliquots of hexane. Crystals were obtained by slow layering of hexane over a THF solution of the complex at −11°C. IR (THF, cm^{-1}) 2065(w), 1946(s), 1913(s), 1853(s). Anal. Calcd. for $C_{22}H_{10}NO_9CrW$: C, 39.55; H, 1.51. Found: C, 40.01; H, 1.63. ^{13}C NMR(CD_3CN) carbonyls (enriched in ^{13}CO by placing an atmosphere of ^{13}CO over a THF solution of the complex) δ 238.0(Cr–CO, 3CO), cis δ 200.0(W–CO, 4CO), trans δ 204.5(W–CO, 1CO), C_6H_4 δ 161.8, 100.8, 86.4, 68.2.

3.5. *High-pressure NMR experiments*

In a typical experiment 40–50 mg of the compound to be studied was dissolved in deuterated acetone, and the solution was transferred via syringe to the high-pressure NMR tube under N_2 purge. The tube was then charged with the desired pressure of $^{13}CO_2$ up to 200 psi. If higher pressures were required, the NMR tube was connected to a single-stage regulator and brought up to pressure with natural isotopic abundance 99.99% pure CO_2. The NMR tube was then carried to the instrument in a Plexiglass carrier to protect the researcher in case of tube rupture. The NMR tube was loaded and the experiment run with no modifications to the NMR instrument.

3.6. $[Et_4N][W(CO)_5\text{-}SC(O)O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$

$[Et_4N][W(CO)_5\text{-}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ was dissolved in THF under a nitrogen atmosphere. Upon evacuation of the nitrogen atmosphere and the addition of an atmosphere of COS, an immediate darkening of the solution was observed. The infrared spectrum in the ν(CO) region exhibited the same four band pattern of the starting material with an expected shift to slightly higher frequencies (IR, ν(CO) in THF, 2061(W), 1946(S), 1918(S), and 1869(M) cm^{-1}). The solution was filtered through Celite, and upon layering the THF solution with hexane and storing for 12 h at −11°C, crystals were isolated. Anal. Calc. for $[Et_4N][W(CO)_5\text{-}SC(O)O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$: C, 37.16; H, 3.39. Found: C, 36.97; H, 3.27%.

TABLE 4. Crystallographic data for the compound $[Et_4N][W(CO)_5\text{-}O(\eta^6\text{-}C_6H_5)Cr(CO)_3]$

(a) Crystal data	
Formula	$C_{22}H_{10}NO_9CrW$
Formula wt.	683.3 amu
Cryst syst.	Monoclinic
Space grp	$P2_1$(No. 3)
a (Å)	7.036(2)
b (Å)	11.766(4)
c (Å)	15.460(4)
β (°)	94.83(2)
V (Å^3)	1275.3(7)
Z	2
D(calc) (g/ml)	1.779
Temp (K)	191
Cryst dimen (mm)	0.05 × 0.16 × 0.64
μ(Mo Kα) (mm^{-1})	5.067
(b) Data collection	
Radiation	Mo Kα
Wavelength (Å)	0.71073
Scan limits (°)	$4.0 < 2\theta < 50.0$
Scan method	θ–2θ
Rflns collected	2481
Max h, k, l	8, 14, 18
Min h, k, l	−8, 0, 0
Indpdt. obs. rflns.	1136 [$3\sigma(F_o)$]
(c) Refinement	
R [a]	0.084
wR [a]	0.091
N_0/N_v	10.6
S [a]	2.92
g [a]	0.0003

[a] $R = (\Sigma|F_o - F_c|/\Sigma F_o)$; $wR = (\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2)^{1/2}$; $w^{-1} = \sigma^2 F + gF^2$; $S = (\Sigma w(F_o - F_c)^2/N_{data} - N_{params})^{1/2}$.

3.7. *X-ray structure determination of* $[Et_4N][W(CO)_5\text{-}O(\eta^6\text{-}C_6H_5)Cr(CO)_3)]$

A bright yellow needle was mounted on a glass fiber with epoxy cement, at room temperature and cooled to 191 K in a N_2 stream. Preliminary examination and data collection was performed on a Nicolet $R3m/V$ X-ray diffractometer. Scan range for data collection was 1.20° plus Kα separation, with a variable scan rate of 1.50 to 15.00° min^{-1}. Three control reflections, collected every 97 reflections, showed no significant trends. Background measurement was by stationary crystal and stationary counter technique at the beginning and end of each scan for one-half of the total scan time. Lorentz and polarization corrections were applied to 2411 reflections. The structure was solved by Direct Methods [11]. Careful examination of the crystallographic data afforded considerable evidence of possible twinning. Painstaking attempts to correct and isolate data for one individual twin failed. Finally the structure was constrained to idealized atomic distances (excluding the $Cr(C_6H_5)(CO)_3$ fragment and the W1–O9 distances) and refined to convergence. Full-matrix least-squares isotropic refinement for all non-hydrogen atoms yielded $R = 0.084$, $wR = 0.091$ and $S = 2.92$ at convergence (for 1136 reflections $I > 36(I)$ and 107 parameters). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral atom scattering factors were taken from ref. 11a. Crystallographic data and experimental conditions are provided in Table 4.

4. Supplementary material available

Tables of anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters, complete bond lengths and bond angles, unit cell packing diagram, and structure factor tables for $[Et_4N][W(CO)_5OPh(Cr(CO)_3)]$, are available upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments

The support of this research by the National Science Foundation (Grant CHE 91-19737) and the Robert A. Welch Foundation is gratefully acknowledged.

References

1 D. J. Darensbourg, K. M. Sanchez and A. L. Rheingold, *J. Am. Chem. Soc., 109* (1987) 290.

2 D. J. Darensbourg, K. M. Sanchez and J. H. Reibenspies, *Inorg. Chem., 27* (1988) 3269.

3 D. J. Darensbourg, K. M. Sanchez, J. H. Reibenspies and A. L. Rheingold, *J. Am. Chem. Soc., 111* (1989) 7094.

4 D. J. Darensbourg, B. L. Mueller, C. J. Bischoff, C. C. Johnson, K. M. Sanchez and J. H. Reibenspies, *Isr. J. Chem., 30* (1990) 369.

5 (a) D. A. Palmer and R. van Eldick, *Chem. Rev., 83* (1983) 651; (b) R. Eisenberg and D. E. Hendricksen, *Adv. Catal., 28* (1979) 79; (c) B. R. Flynn and L. Vaska, *J. Am. Chem. Soc., 95* (1973) 5081; (d) B. R. Flynn and L. Vaska, *J. Chem. Soc. Chem. Commun.* (1974) 703; (e) T. Yoishida, D. L. Thorn, T. Okano, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc., 101* (1979) 4212; (f) D. A. Palmer, R. van Eldik, H. Kelm and G. M. Harris, *Inorg. Chem., 19* (1980) 1009; (g) D. A. Palmer, R. van Eldik, H. Kelm and G. M. Harris, *Inorg. Chem., 19* (1980) 3679; (h) D. A. Palmer, R. van Eldik and G. M. Harris, *Inorg. Chem., 19* (1980) 3673; (i) E. Chaffee, T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc., 95* (1973) 4169; (j) E. G. Lundquist, K. Folting, J. C. Huffman and K. G. Caulton, *Inorg. Chem., 26* (1987) 205; (k) J. F. Hartwig, R. G. Bergmann and R. A. Anderson, *J. Am. Chem. Soc., 113* (1991) 6499.

6 (a) T. J. McNeese, M. B. Cohen and B. M. Foxman, *Organometallics 552* (1984) 3; (b) T. J. McNeese, T. E. Mueller, D. A. Wierda, D. J. Darensbourg, T. J. Delord, *Inorg. Chem., 24* (1985) 3465.

7 D. J. Darensbourg, B. L. Mueller, C. J. Bischoff, S. S. Chojnacki and J. H. Reibenspies, *Inorg. Chem., 30* (1991) 2418.

8 (a) D. C. Roe, *ACS Symp. Ser.* (357) (1985) 204; (b) D. J. Darensbourg, P. Wiegreffe and C. G. Riordan, *J. Am. Chem. Soc., 112* (1990) 5759.

9 C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc., 100* (1978) 7565.

10 J. A. Heppert, T. J. Boyle and F. Takusagawa, *Organometallics 8* (1989) 461.

11 (a) D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, UK, 1974, pp. 55, 99; (b) G. M. Sheldrick, SHELXTL-PLUS, revision 3.4, Nicolet Instrument Corp. Madison, WI, 1988, (c) R. Diamond, *Acta Crystallogr., A25* (1969) 43; (d) A. C. T. North, D. Phillips and F. S. Mathews, *Acta Crystallogr., A24* (1968) 351.