Journal of Organometallic Chemistry, 428 (1992) 69–83
Elsevier Sequoia S.A., Lausanne
JOM 22088

Reaction of bis(cyclopentadienyl)hydridophenyltungsten(IV) with carboxylic acids, carbon dioxide, and related compounds *

Takashi Ito, Shuichiro Sugimoto, Tatsuro Ohki, Toshiyuki Nakano
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240 (Japan)

and Kohtaro Osakada
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4219 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

(Received May 17, 1991)

Abstract

Reactions of $Cp_2W(H)Ph$ (**1**) ($Cp = \eta^5$-C_5H_5) with protonic acids were studied and the resulting complexes were characterized spectroscopically. Its reactions with carboxylic acids afforded hydridocarboxylato and dicarboxylato complexes selectively, depending upon the solvent employed. The mononuclear carbonato complex $Cp_2W(\eta^2$-$CO_3)$ was obtained in high yield by the reaction of **1** with carbon dioxide in acetone in the presence of water. The possible paths for these reactions are discussed.

Introduction

Bis(cyclopentadienyl)hydridophenyltungsten(IV) (**1**), one of rare examples of the transition metal complexes which possess both metal–hydrogen and metal–carbon bonds in one molecule, has been synthesized by Green et al. since 1971 by direct intermolecular oxidative addition of the aromatic C–H bond to chemically [1], photochemically [2], or thermally [3] generated tungstenocene. However, little has been studied on the reactivity of **1** since then. As an extension of our study on the preparation of carboxylato complexes of group 6 transition metals [4–6], we investigated the reaction of **1** with carboxylic acids and related compounds under several conditions to establish the new preparative method for tungsten(IV) carboxylates of the type $Cp_2W(OCOR)_2$ (**2**) and $Cp_2WH(OCOR)$ (**3**) ($Cp = \eta^5$-C_5H_5) with a high selectivity. Dicarboxylato complex of the type **2** has so far been

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Correspondence to: Professor T. Ito, Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan.

* Dedicated with admiration and appreciation to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honor of his contributions to organometallic chemistry.

prepared starting from Cp_2WH_2 through its reaction with carboxylic acids in the presence of oxygen [5] or via Cp_2WCl_2 by its reaction with sodium carboxylates NaO_2CR (R = Ph and CF_3) [7]. A fairly intricate method has been employed to prepare carboxylato(hydrido) complex **3** in which the photochemical reaction between Cp_2WH_2 and methyl carboxylate was involved [2b,8].

Also reported in the later part of this paper is the reaction of **1** with carbon dioxide in acetone containing a small amount of water to afford a mononuclear carbonato complex of the type $Cp_2W(\eta^2\text{-}CO_3)$ (**4**). Development of an efficient process for the transformation of carbon dioxide into useful organic compounds utilizing organo-transition metal compounds is becoming very important especially in view of the current global environmental problems [9]. Some of the present results have been briefly communicated elsewhere [10].

Results and discussion

1. Reaction of hydridophenyl complex 1 with carboxylic acids

The reactions of **1** with carboxylic acids (RCO_2H) without solvent afforded two types of products, $Cp_2WH(OCOR)$ and $Cp_2W(OCOR)_2$, depending on the nature of the carboxylic acid employed. Thus, the carboxylic acids with comparatively high acidity such as formic and trifluoroacetic acids give the corresponding dicarboxylates (**2**) in high yields (Table 1, runs 1 and 11) whereas weaker acids such as acetic, propionic and isobutyric acids yield hydrido-carboxylates (**3**) selectively (Table 1, runs 3, 5, and 6). Methacrylic acid afforded both dicarboxylate and hydrido-carboxylate in the ratio of 2:1 (Table 1, run 7). In each case, accompanying formation of a quantitative amount of benzene was observed. Evolution of H_2 was observed in the reaction of formic acid.

$$\underset{(\mathbf{1})}{Cp_2W(H)Ph} + 2RCO_2H \xrightarrow{\text{neat}} \underset{(\mathbf{2})}{Cp_2W(OCOR)_2} + PhH + H_2 \tag{1}$$

(R = H, CF_3, $CH_2{=}CMe$)

$$\underset{(\mathbf{1})}{Cp_2W(H)Ph} + RCO_2H \xrightarrow{\text{neat}} \underset{(\mathbf{3})}{Cp_2WH(OCOR)} + PhH \tag{2}$$

(R = Me, Et, ^iPr, $CH_2{=}CMe$)

It is noteworthy that these substrate-dependent selectivities could be altered by employment of an appropriate solvent. Use of diethyl ether yielded hydrido-carboxylate (**3**) selectively, even in the case of highly acidic acid (Table 1, runs 8, 10, 12, and 13). These reactions did not depend on the ratio of the reactants (Table 1, runs 12 and 13). In contrast, the reaction of **1** with acetic or pivalic acids in acetone selectively afforded dicarboxylate complex (**2**) (Table 1, runs 4 and 9). In this case the accompanying formation of comparable amount of 2-propanol was observed.

$$\underset{(\mathbf{1})}{Cp_2W(H)Ph} + RCO_2H \xrightarrow{\text{in } Et_2O} \underset{(\mathbf{3})}{CP_2WH(OCOR)} + PhH \tag{3}$$

(R = CMe_3, CH_2Cl, and CF_3)

$$\underset{(1)}{Cp_2W(H)Ph} + RCO_2H \xrightarrow{\text{in } Me_2CO} \underset{(2)}{Cp_2W(OCOR)_2} + PhH + (CH_3)_2CHOH \quad (4)$$

$(R = H, Me, CMe_3)$

The reaction of acetato(hydrido) complex $Cp_2WH(OCOMe)$ with excess acetic acid in acetone afforded diacetate $Cp_2W(OCOMe)_2$ quantitatively with accompanying formation of 2-propanol (Table 1, run 14).

The resulting dicarboxylato (**2**) and carboxylato(hydrido) (**3**) complexes are characterized by IR and ^1H NMR spectroscopies, the representative data of which are listed in Table 2 including those for reported compounds. All these complexes showed the asymmetric and symmetric ν(OCO) bands at around 1600–1700 and 1230–1400 cm^{-1}, respectively, suggesting the unidentate mode of coordination of the carboxylato ligands [11]. Besides these bands, strong bands were observed for carboxylato(hydrido) complexes (**3**) at 1900–1955 cm^{-1} assignable to ν(W–H). The carboxylates with highly electron withdrawing alkyl groups such as trifluoroacetates showed fairly high frequencies for these three bands.

In the IR spectrum of the complex obtained after stirring hydrido(acetato) complex in a large excess of $MeCO_2D$ under argon at room temperature for 48 h, the original ν(W–H) absorption at 1910 cm^{-1} disappeared and the new band ascribable to ν(W–D) was observed at 1360 cm^{-1} [$\nu(W{-}H)/\nu(W{-}D) = 1.40$] suggesting complete exchange of hydride ligand in **2** with acid.

2. *Mechanistic consideration of the reactions between 1 and carboxylic acids*

Comparison of the results of the reactions between hydridophenyl complex **1** and acetic, propionic, isobutyric, and pivalic acids suggests that the steric bulkiness of the carboxylic acid does not affect the product selectivity (Table 1, runs 3, 5, 6, and 8).

The reaction of **1** with carboxylic acid afforded hydridocarboxylato complex **3** preferentially except for formic and trifluoroacetic acids where dicarboxylato complex **2** was the principal product. Since an 81% aqueous solution was used in the case of formic acid, the existence of water was expected to affect the product selectivity. To clarify this effect, the reaction of **1** with 83% aqueous solution of acetic acid was carried out and the results were compared with run 3 of Table 1. The reaction of acetic acid in the presence of water afforded a small amount of $Cp_2W(OCOMe)_2$ together with 2.6% of H_2. The results suggest that the presence of water, as well as its high acidity, may be responsible for the formation of diformate and H_2 in the reaction of formic acid. Although the role of H_2O is not clarified yet, one possibility is that the acidity of the carboxylic acids may be enhanced by the presence of water. The reaction of **1** with neat carboxylic acid with high acidity such as trifluoroacetic acid may at first give hydridocarboxylate, which may be further protonated to give dicarboxylate with hydrogen elimination (eq. 5). Similar results have been reported for strong acids such as HCl [1].

$$Cp_2WH(OCOR) + RCO_2H \rightleftharpoons [CP_2WH_2(OCOR)]^+RCO_2^- \xrightarrow{-H_2} Cp_2W(OCOR)_2 \quad (5)$$

The role of acetone solvent in runs 2, 4, and 9 may be the promoter of the hydride abstraction from the intermediary hydridocarboxylate as is reported for

Table 1

Reaction of $Cp_2W(H)Ph$ (1) with carboxylic acids RCOOH [a]

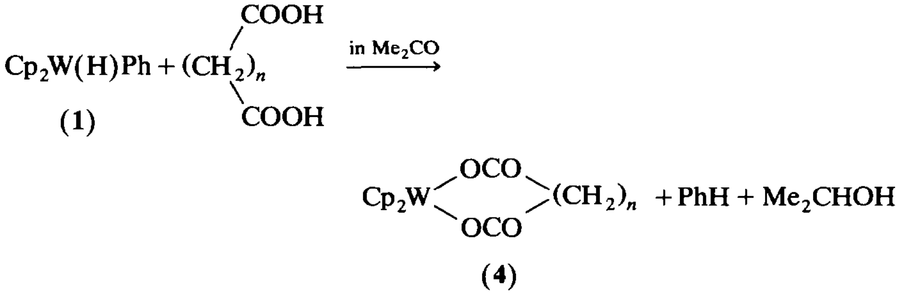
Run	RCOOH		1 (mmol)	Solvent	(ml)	Time (h)	Products (mol% for 1)			
	R	mmol					Complex		PhH	2-PrOH
1	H [b]	133	0.35	None		24	$Cp_2W(OCOH)_2$	97	94 [c]	–
2	H [b]	0.20	0.20	Acetone	5	22	$Cp_2W(OCOH)_2$	44	27	ND [d]
3	Me	87	0.27	None		24	$Cp_2WH(OCOMe)$	94	96	–
4	Me	8.7	0.12	Acetone	5	14	$Cp_2W(OCOMe)_2$	61	65	40
5	Et	67	0.33	None		24	$Cp_2WH(OCOEt)$	85	81	–
6	^iPr	59	0.27	None		24	$Cp_2WH(OCO^iPr)$	84	88	–
7	$CH_2{=}CMe$	48	0.31	None		24	$Cp_2WH(OCOCMe{=}CH_2)$ $Cp_2W(OCOCMe{=}CH_2)_2$	63 32	92	–
8	^tBu	25	0.41	Et_2O	5	48	$Cp_2WH(OCOCMe_3)$	99	82	–
9	^tBu	25	0.41	Acetone	5	48	$Cp_2W(OCOCMe_3)_2$	88	72	49
10	CH_2Cl	0.40	0.39	Et_2O	5	48	$Cp_2WH(OCOCH_2Cl)$	88	77	–
11	CF_3	40	0.28	None		24	$Cp_2W(OCOCF_3)_2$	98	77	–
12	CF_3	0.24	0.24	Et_2O	5	48	$Cp_2WH(OCOCF_3)$	93	85	–
13	CF_3	0.20	0.39	Et_2O	5	48	$Cp_2WH(OCOCF_3)$	82	76	–
14	Me	8.7	0.11 [e]	Acetone	5	48	$Cp_2W(OCOMe)_2$	94 [f]	0	46 [f]

[a] At room temperature. [b] An 81% aqueous solution of formic acid. [c] In addition, H_2 (32%) was evolved. [d] Not measured. [e] $Cp_2WH(OCOMe)$. [f] Yields based on $Cp_2WH(OCOMe)$ used.

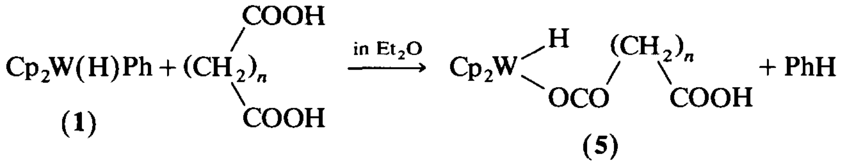
the reaction of molybdenum dihydride with acid in the presence of acetone [12]. The pathway is supported by the results of the reaction between hydridocarboxylate **3** and acetic acid to give **2** (Table 1, run 14). The absence of hydridoformate in the reaction product between **1** and an equimolar amount of formic acid in acetone which gives diformate suggests that the second stage of the reaction is very rapid and the first stage of formation of hydridoformate may be rate determining.

3. Reactions of 1 with dicarboxylic acids

From the findings described above that the reaction of **1** with carboxylic acid proceeds selectively depending on the solvent used, the study was extended to its reaction with dicarboxylic acid. As is shown in Table 3, the reactions of oxalic acid in ethanol and malonic acid in acetone afforded metallacyclic dicarboxylate type products **4** (eq. 6), whereas those reactions in Et_2O yielded hydridocarboxylates **5**, which are unstable owing to the presence of free carboxyl group in the ligand (eq. 7). Complex **1** did not react with succinic acid in Et_2O probably because of low acidity of the latter (compare pK_1 value of 4.21 with those of 1.27 and 2.86 for oxalic and malonic acids, respectively). The reaction of **1** with succinic acid in acetone yielded a poorly soluble reddish brown solid which was tentatively assigned as a succinate-bridged dinuclear complex $\{Cp_2W(OCOCH_2CH_2CO_2H)\}_2\{\mu\text{-}(CH_2COO)_2\}$ on the basis of its IR spectrum (Table 4). Failure in obtaining cyclic complex **4** in the case of succinic acid may be ascribed to the difficulty in its forming a 7-membered ring as compared with 5- and 6-membered rings with oxalic and malonic acids, respectively. The similar reaction with succinic acid in ethanol gave a reddish brown solid which was characterized as type **5** complex from its IR spectrum.



$$\underset{(1)}{Cp_2W(H)Ph} + (CH_2)_n(COOH)_2 \xrightarrow{\text{in } Me_2CO} \underset{(4)}{Cp_2W{<}^{OCO}_{OCO}{>}(CH_2)_n} + PhH + Me_2CHOH \qquad (6)$$



$$\underset{(1)}{Cp_2W(H)Ph} + (CH_2)_n(COOH)_2 \xrightarrow{\text{in } Et_2O} \underset{(5)}{Cp_2W{<}^{H}_{OCO(CH_2)_nCOOH}} + PhH \qquad (7)$$

4. Preparation of carbonatobis(cyclopentadienyl)tungsten(IV)

During the effort to find out any conditions to promote the reaction of **1** with carbon dioxide, we found that new compound which has IR absorption at 1690, 1640 and 1210 cm^{-1} is obtainable when the reaction was carried out in wet acetone. Although the yield of the product was not high enough when the unpurified acetone was employed as solvent, later investigation showed that the

Table 2

IR and ^1H NMR data for complexes **2** and **3**

Complex	IR[a] (cm^{-1})			^1H NMR (δ, ppm)[b]				
	ν(W–H)	$\nu(OCO)_a$	$\nu(OCO)_s$	Solvent	Cp	Carboxylates	W–H	Ref.
$Cp_2W(OCOH)_2$	–	1640vs	1260vs	D_2O	5.80 5.88	7.57(1H, CHO)	–	[5b]
$Cp_2W(OCOMe)_2$	–	1640vs	1275vs	C_6D_6	5.06	2.06(3H, Me)	–	[5b]
$Cp_2W(OCOCMe_3)_2$	–	1625vs	1315vs	CD_3OD	5.60	1.05(18H, Me)	–	
$Cp_2W(OCOCF_3)_2$	–	1700vs	1400vs	$(CD_3)_2CO$	5.95	–	–	
$Cp_2WH(OCOMe)$	1910s	1640vs	1290vs	C_6D_6	4.52	1.88(3H, Me)	−11.35	
$Cp_2WH(OCOEt)$	1900s	1635vs	1290s	C_6D_6	4.46	2.16(q, 2H, CH_2) 1.10(t, 3H, Me)	−11.23	
$CP_2WH(OCOCHMe_2)$	1905s	1655vs	1295vs	C_6D_6	4.40	2.33(m, 1H, CH) 1.06(d, 6H, Me)	−11.23	
$CP_2WH(OCOCMe_3)$	1910s	1610vs	1330vs	C_6D_6	4.45	1.15(s, 9H, Me)	−11.20	
$Cp_2WH(OCOCH_2Cl)$	1900s	1650vs	1320vs	CD_3OD	5.06	3.70(s, 2H, CH_2)	−12.05	
$Cp_2WH(OCOCF_3)$	1955s	1690vs	1320vs	CD_3OD	5.00	–	−12.08	

[a] KBr disc. [b] Signals are all singlets unless otherwise stated.

yield of the product increased when a certain amount of water was added to the system.

$$\underset{(\mathbf{1})}{Cp_2W(H)Ph} + CO_2 + H_2O + Me_2CO \longrightarrow \underset{(\mathbf{6})}{Cp_2W(\eta^2\text{-}CO_3)} + Me_2CHOH \qquad (8)$$

No reaction took place between carbon dioxide and **1** dissolved in dry acetone which was distilled over Drierite. In contrast, stirring a brownish yellow solution of **1** in acetone containing H_2O (6 : 1, v/v) under CO_2 atmosphere at room temperature for 36 h resulted in a reddish violet heterogeneous system, from which violet prisms of carbonato complex **6** were isolated in yield of 96%. The accompanying formation of benzene and 2-propanol in yields of 63 and 55%, respectively, was observed. When tetrahydrofuran was used instead of acetone, the yield of **6** was minimal even in the presence of water.

As to the interaction of carbon dioxide with the tungsten complex, its insertion into tungsten–oxygen [13], –nitrogen [14], and –hydrogen bonds [15], its reduction with $[Cp_2W(H)Li]_4$ to give carbonyl complex [16], and its attack in the wet state to zerovalent tungsten complex to give hydrido(hydrogencarbonato) complex [17] have so far been reported.

In the present reaction system, carbon dioxide may react with **1** as carbonic acid since no reaction takes place in the absence of water. Protonolysis of **1** with carbonic acid may give benzene and (hydrido)hydrogencarbonato intermediate **A** (Path I in Scheme 1). Nucleophilic attack of the central tungsten of **A** to acetone which is activated by protonation with excess carbonic acid may give cationic tungsten(VI) intermediate **B**, which may release 2-propanol via the neutral intermediate **C** to give final product **6**. The alternate pathway in which intramolecular activation of acetone is taken account (path II in Scheme 1) cannot be ruled out. Reduction of acetone by a similar system consisting of Cp_2MoH_2 and carboxylic acid has been reported [12].

Table 3

Reaction of $Cp_2W(H)Ph$ (**1**) with dicarboxylic acids $HOOC(CH_2)_nCOOH$ at room temperature

Run	$HOOC(CH_2)_nCOOH$		**1** (mmol)	Solvent	(ml)	Time (h)	Products (mol% for **1**)			
	n	(mmol)					Complex		PhH	2-PrOH
15	0	0.26	0.26	Et_2O	5	48	$Cp_2WH(OCOCOOH)$	77	50	
16	0	0.56	0.27	EtOH	5	24	$Cp_2W\{(OCO)_2\}$	65	52	
17	1	0.32	0.15	Et_2O	5	48	$Cp_2WH(OCOCH_2COOH)$	86	76	
18	1	0.65	0.32	Acetone	5	48	$Cp_2W\{(OCO)_2CH_2\}$	82	81	80
19	2	0.38	0.37	Et_2O	5	48	No reaction			
20	2	0.63	0.31	EtOH	5	48	$Cp_2WH(OCOCH_2CH_2COOH)$	78	79	
21	2	0.25	0.24	Acetone	5	24	$\{Cp_2W(OCOCH_2CH_2COOH)\}_2\text{-}\{\mu\text{-}(OCOCH_2)_2\}$	65	62	40

Table 4

IR and ^1H NMR data for complexes obtained by reaction between 1 and dicarboxylic acids

Complex	IR [a] (cm^{-1})				^1H NMR (δ, ppm) [b]		
	ν(W–H)	ν(COOH)	$\nu(OCO)_a$	$\nu(OCO)_s$	Solvent	Cp	Others
$Cp_2W\{(OCO)_2\}$	–	–	1710vs	1430s	D_2O	5.98	
$Cp_2W\{(OCO)_2CH_2\}$	–	–	1625vs	1360vs	D_2O	5.88	3.38(CH_2)
$\{Cp_2W(OCOCH_2CH_2COOH)\}_2$-$\{\mu$-$(OCOCH_2)_2\}$	–	3200–2300br	1710s 1620vs	1360vs			
$Cp_2WH(OCOCOOH)$	1920s	3200–2300br	1700vs 1620vs	1350s			
$Cp_2WH(OCOCH_2COOH)$	1895s	3000–2100br	1730vs 1590vs	1360vs	CD_3OD	5.02 [c]	
$Cp_2WH(OCOCH_2CH_2COOH)$	1920br	3600–2300br	1720vs 1640s	1360vs			
$Cp_2W(\eta^2$-$CO_3)$ (6) [d]	–	–	1690vs 1640vs	1210s	CD_3OD	5.84	

[a] KBr disc. [b] Signals are all singlets. [c] The other signals were not discernible owing to poor solubility of the complex. [d] ^{13}C NMR in CD_3OD: δ 97.5 (s, Cp); δ 179.7 ppm (s, CO_3).

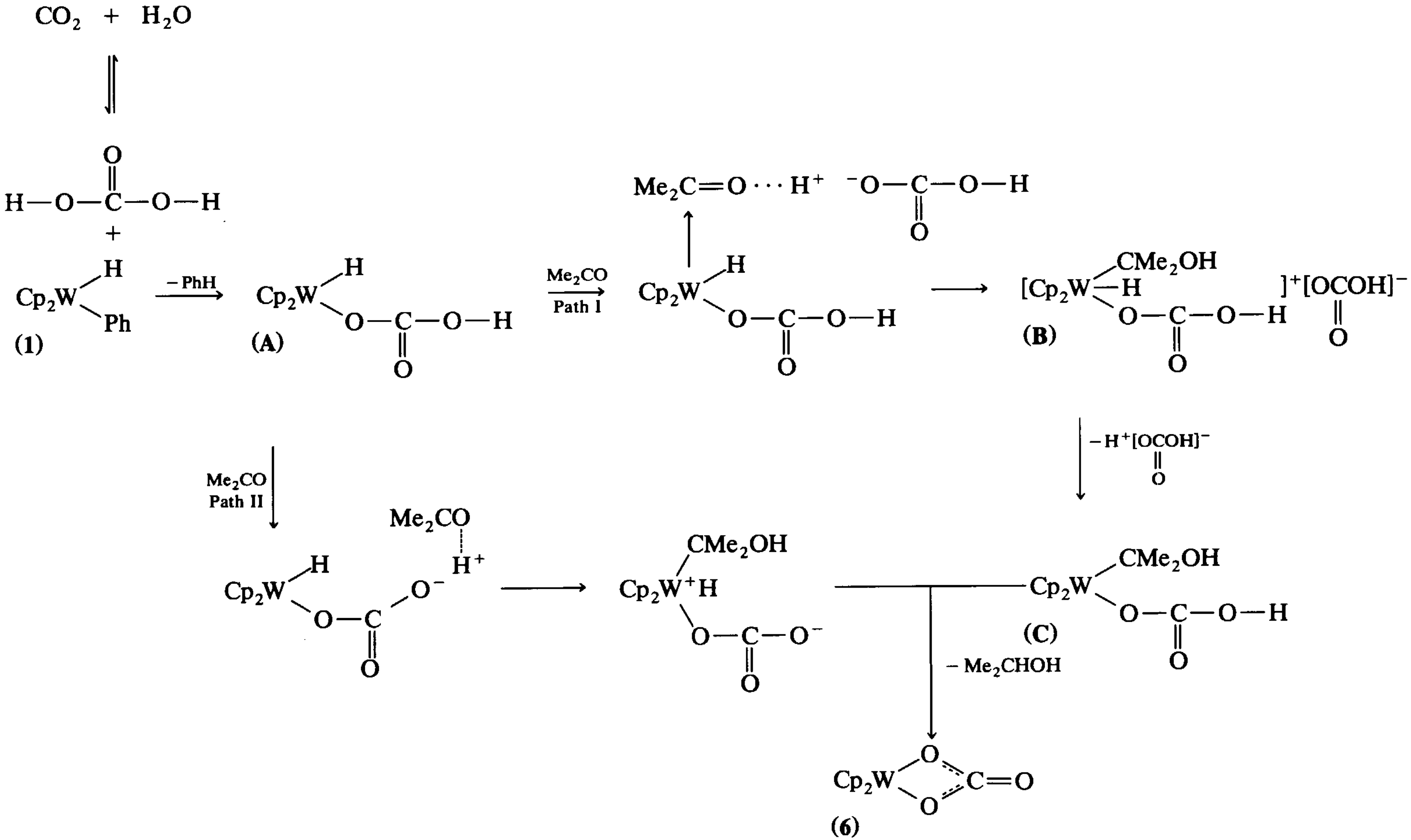
The resulting carbonato complex **6** was characterized by means of IR, ^1H NMR and ^{13}C NMR spectroscopies, some of which are included in Table 4. Similar carbonato bands have been reported for the related carbonato complexes of palladium, $Pd(PPh_3)_2CO_3$ [18] and the molybdenum analogue of **6**, $Cp_2Mo(CO_3)$ [19]. Although these spectral as well as elemental analytical results (see Experimental section) clearly support the formulation of $Cp_2W(\eta^2$-$CO_3)$ for **6**, there still exists the possibility that it may have the dimeric structure, i.e., $\{Cp_2W\}_2(\mu$-$CO_3)_2$. In order to clarify this, we attempted to establish its structure by X-ray diffraction. Violet prisms of **6** were obtained by recrystallization from methanol/diethyl ether. Crystallographic data are collected in Table 5. Figure 1 shows the structure of one of the two crystallographically independent molecules that have similar structures to each other. The results ambiguously indicate a monomeric structure for **6** although the bond distances and angles are not determined precisely owing to the insufficient convergence of the structure refinement (see Experimental). A similar

Table 5

Crystallographic data and details of structure determination of $Cp_2W(\eta^2$-$CO_3)$ (**6**)

Mw	374.05	$F(000)$	1392
Crystal size (mm)	0.2×0.2×0.5	μ (cm^{-1})	106.61
Crystal system	monoclinic	2θ range (°)	3.0–40.0
Space group	$P2_1/a$	h, k, l range	$-13 \leq h \leq 14$
a (Å)	14.178(3)		$0 \leq k \leq 14$
b (Å)	11.429(4)		$0 \leq l \leq 12$
c (Å)	14.302(5)	No. of unique reflections	1999
β (°)	107.49(2)	No. of reflections used	1549 [$F_o > 3\sigma(F_o)$]
V (Å^3)	2210.4	R	0.082
Z	8	R_w	0.086
d_{calc} ($g\ cm^{-3}$)	2.249	Weighting scheme [a]	0.068

[a] Parameter q in $[\sigma(F_o)^2 + q^2(F_o)^2]^{-1}$.



Scheme 1

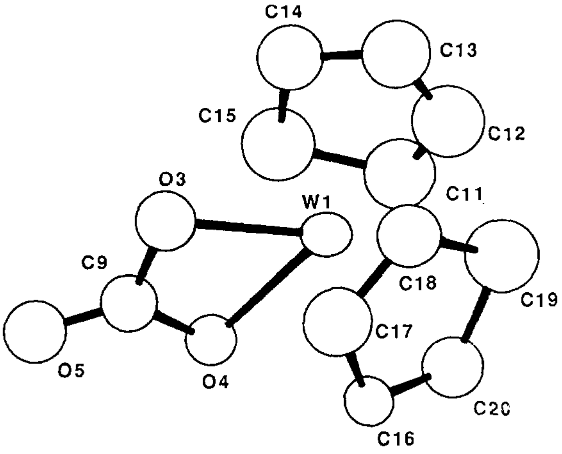


Fig. 1. Molecular diagram of $Cp_2W(\eta^2\text{-}CO_3)$ (**6**).

structure has been reported for the analogous complex of molybdenum $Cp_2Mo(\eta^2\text{-}CO_3)$ which was obtained by the photochemical reaction of Cp_2MoH_2 with carbon dioxide [19].

The carbonato complex **6** was also obtained by similar treatment of $Cp_2WH(OEt)$ [10] or $Cp_2WH(OCOH)_2$ (yield 98%) with carbon dioxide. Furthermore the reaction of Cp_2WX_2 ($X = Cl$ or I) [20] with $NaHCO_3$ in $EtOH/H_2O$ (6:1) afforded **6** (yield 43% for X = Cl and 97% for X = I) (eq. 9).

$$Cp_2WX_2 + NaHCO_3 \xrightarrow{EtOH/H_2O} Cp_2W(\eta^2\text{-}CO_3) \qquad (9)$$

The reaction of carbonato complex **6** with gaseous hydrogen chloride in ethanol gave Cp_2WCl_2 in yield of 73% together with carbon dioxide (68%) and water (eq. 10).

$$Cp_2W(\eta^2\text{-}CO_3) + 2HCl \xrightarrow{EtOH} Cp_2WCl_2 + CO_2 + H_2O \qquad (10)$$

Experimental

Most manipulations were carried out either under dry, oxygen-free nitrogen or argon or *in vacuo* with Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. Infrared spectra were recorded on a JASCO A-202 spectrometer using KBr discs prepared under an inert atmosphere. NMR spectra were measured on a JEOL JNM-PMX-60 (^1H NMR) and FX-90Q (^{13}C NMR) spectrometers. GLC was performed on a Shimadzu GC-7APTF or GC-3BT gas chromatograph. Gas evolved during the reaction was measured by a Toepler pump and analyzed by GLC using molecular sieve 5A and Unibeads-1S columns.

Guaranteed grade commercial formic acid (90% aqueous solution) and other liquid carboxylic acids were degassed prior to use and introduced into the reaction flask by a trap-to-trap method. Guaranteed grade pivalic, chloroacetic, succinic, and malonic acids and oxalic acid dihydrate were used without further purification. The complex $Cp_2W(H)Ph$ (**1**) was prepared by photoirradiation of Cp_2WH_2 [21] in benzene with a Riko 100-W high-pressure mercury lamp through Pyrex glass according to the reported method [2].

Reaction of bis(cyclopentadienyl)hydridophenyltungsten(IV) (1) with carboxylic acids

Since the procedure for these reactions were general to some extent, typical examples are described below.

(a) Reaction of 1 with neat isobutyric acid. The yellow mixture of complex **1** (0.12 g, 0.31 mmol) and isobutyric acid (5.0 ml, 59 mmol) was stirred *in vacuo* at room temperature for 48 h to give a reddish brown solution. The volatile part was removed from the reaction mixture by a trap-to-trap method, from which benzene (88% on the basis of **1**) was detected. To the resulting solid, was added a small amount of toluene and the solvent was evaporated off from the solution to remove a trace amount of contaminated isobutyric acid. The brown residue was crystallized from acetone to give reddish brown crystals of $Cp_2WH(OCOCHMe_2)$ (yield, 84%). Anal. Found: C, 42.1; H, 4.2. $C_{14}H_{18}O_2W$ calc.: C, 41.8; H, 4.5%.

(b) Reaction of 1 with pivalic acid in acetone. To the flask containing complex **1** (0.16 g, 0.41 mmol) and pivalic acid (2.5 g, 24 mmol) was added 5.0 ml of acetone by a trap-to-trap method. On stirring the solution at room temperature for 48 h, a reddish brown solution resulted from which volatile liquid was removed by evaporation *in vacuo*. Benzene (72%) and 2-propanol (49%) was detected in the liquid thus recovered. The residual solid was washed with Et_2O and crystallized from acetone to give reddish brown crystals of $Cp_2W(OCOCMe_3)_2$ (yield 88%). Anal. Found: C, 45.7; H, 5.2. $C_{20}H_{28}O_4W$ calc.: C, 46.5; H, 5.5%.

(c) Reaction of 1 with chloroacetic acid in diethyl ether. To the flask containing complex **1** (0.15 g, 0.39 mmol) and chloroacetic acid (0.38 g, 0.40 mmol), Et_2O (5.0 ml) was added by a trap-to-trap method. The mixture was stirred at room temperature for 48 h and the reddish brown precipitate was formed in the flask. After filtration, benzene (82%) was detected in the filtrate and the work up of the residual solid as above gave reddish brown crystals of $Cp_2WH(OCOCH_2Cl)$ (yield 88%). Anal. Found: C, 35.1; H, 3.0; Cl, 8.0. $C_{12}H_{13}O_2ClW$ calc.: C, 35.3; H, 3.2; Cl, 8.7%.

Reaction of bis(cyclopentadienyl)hydridophenyltungsten(IV) (1) with dicarboxylic acids

Since the procedure for these reactions were general, typical examples are described below.

(a) Reaction of 1 with oxalic acid in ethanol. To the flask containing complex **1** (0.11 g, 0.27 mmol) and oxalic acid hydrate $(COOH)_2 \cdot 2H_2O$ (0.071 g, 0.56 mmol), ethanol (5.0 ml) was added by a trap-to-trap method. On stirring the yellow suspension *in vacuo* at room temperature for 1 day, a brown precipitate in reddish brown solution resulted. In the solution, benzene (52%) was detected. After evaporating off the solvent from the system, the residue was washed with diethyl ether and ethanol, then crystallized from water to give reddish brown microcrystals of $Cp_2W\{(OCO)_2\}$ (yield 65%). Anal. Found: C, 35.5; H, 2.4. $C_{12}H_{10}O_4W$ calc.: C, 35.9; H, 2.5%.

(b) Reaction of 1 with oxalic acid in diethyl ether. The reaction of **1** (0.10 g, 0.26 mmol) and oxalic acid hydrate (0.033 g, 0.26 mmol) in Et_2O (5.0 ml) was carried out similarly to afford, after stirring for 2 days, a brown precipitate and a yellow

supernatant solution. In the solution, benzene (50%) was detected. Evaporating off the solvent from the system left a brown solid, which was washed 5 times with hexane (5 ml), extracted with ethanol, and the resulting brown powder was washed 3 times with Et_2O (5 ml). The product, which was characterized as $Cp_2WH(OCOCOH)$ on the basis of IR (yield 77%), was found to be difficult to purify enough, owing to its instability in ethanol converting itself to the dicarboxylato type complex $Cp_2W\{(OCO)_2\}$.

(c) Reaction of 1 with malonic acid in acetone. To the flask containing complex **1** (0.13 g, 0.32 mmol) and malonic acid (0.068 g, 0.65 mmol) was added acetone (5.0 ml) by a trap-to-trap method. Stirring the yellow suspension at room temperature for 2 days afforded a reddish brown heterogeneous solution. In the system benzene (81%) and 2-propanol (80%) was detected by GLC. The solvent was evaporated off *in vacuo* to leave a reddish brown solid which was washed with acetone and crystallized from methanol to give the product $Cp_2W\{(OCO)_2CH_2\}$ (yield 82%). Anal. Found: C, 37.1; H, 2.8. $C_{13}H_{12}O_4W$ calc.: C, 37.5; H, 2.9%.

Reaction of bis(cyclopentadienyl)hydridophenyltungsten(IV) (1) with carbon dioxide in the presence of water

To the solution of complex **1** (0.14 g, 0.37 mmol) in a solvent composed of acetone (6 ml) and water (1 ml), a flake of dry ice (gaseous carbon dioxide from the cylinder can be used in place of dry ice) was added and the mixture was stirred at room temperature for 36 h. During the period the original reddish brown solution turned to a brown heterogeneous one from which solvent was removed *in vacuo*. In the liquid phase, benzene (63%) and 2-propanol (55%) was detected by GLC. The residue was washed with hexane and diethyl ether and crystallized from ethanol to give reddish brown crystals of $Cp_2W(\eta^2\text{-}CO_3)$ (**6**) (yield 96%). Anal. Found. C, 35.2; H, 2.7. $C_{11}H_{10}O_3W$ calc.: C, 35.3; H, 2.7%.

Reaction of bis(cyclopentadienyl)diiodotungsuten(IV) with sodium hydrogencarbonate

Stirring the mixture containing Cp_2WI_2 [20] (0.22 g, 0.39 mmol), $NaHCO_3$ (0.049 g, 0.58 mmol), ethanol (6 ml) and water (1 ml) for 42 h afforded a reddish brown solution with a green precipitate of the starting Cp_2WI_2. From the supernatant solution, solvent was evaporated off and the residue was washed with hexane and diethyl ether and crystallized from methanol/diethyl ether to give pale violet powdery $Cp_2W(\eta^2\text{-}CO_3)$ (yield 97%).

Reaction of bis(cyclopentadienyl)(carbonato-O,O')tungsten(IV) (6) with hydrogen chloride

Into a solution of complex **6** (71 mg, 0.19 mmol) in ethanol (7 ml), dry hydrogen chloride prepared *in situ* from NaCl (0.12 g, 2.1 mmol) and conc. sulfuric acid (1 ml) was introduced by a trap-to-trap method *in vacuo*. Stirring the mixture at room temperature for 12 h yielded a green heterogeneous system from which green powdery Cp_2WCl_2 (73%) was isolated by filtration followed by washing with hexane, methanol, and diethyl ether. Accompanying formation of carbon dioxide (68%) and water (only qualitatively) was confirmed by GLC.

X-ray crystallographic study of 6

Crystals of complex **6** suitable for X-ray crystallography were grown in methanol/diethyl ether (1:1, v/v) at −20 °C and the violet prism thus obtained

Table 6

Fractional coordinates and equivalent or isotropic temperature factors

Atom	x	y	z	B_{eq} (or B_{iso}) [a]
W1	0.7336(1)	0.3695(1)	0.3860(1)	3.05
W2	0.3992(1)	0.7896(1)	0.0512(1)	2.96
O3	0.711(2)	0.542(2)	0.424(2)	4.5
O4	0.703(2)	0.494(2)	0.272(2)	3.2
O5	0.679(2)	0.682(2)	0.305(2)	4.8
O6	0.324(2)	0.861(2)	−0.080(2)	4.0
O7	0.245(2)	0.762(2)	−0.005(2)	3.9
O8	0.156(2)	0.839(2)	−0.148(2)	4.5
C9	0.692(3)	0.582(4)	0.331(3)	3.9
C10	0.232(35)	0.820(3)	−0.086(3)	3.5
C11	0.872(4)	0.290(4)	0.354(4)	6.2
C12	0.863(4)	0.238(5)	0.430(4)	6.5
C13	0.878(4)	0.293(4)	0.509(4)	5.8
C14	0.890(3)	0.406(4)	0.496(3)	5.4
C15	0.886(4)	0.420(5)	0.383(4)	6.7
C16	0.565(3)	0.325(3)	0.301(3)	2.9
C17	0.572(4)	0.358(4)	0.400(4)	5.8
C18	0.634(3)	0.281(4)	0.464(3)	5.0
C19	0.672(4)	0.183(4)	0.405(4)	6.7
C20	0.622(3)	0.235(4)	0.298(3)	4.6
C21	0.504(3)	0.851(3)	0.197(3)	4.2
C22	0.403(3)	0.836(4)	0.209(3)	4.8
C23	0.336(4)	0.922(4)	0.144(4)	5.8
C24	0.398(3)	0.986(3)	0.093(3)	3.4
C25	0.494(3)	0.960(4)	0.123(3)	5.0
C26	0.499(3)	0.623(4)	0.119(3)	4.8
C27	0.550(4)	0.689(4)	0.077(4)	5.9
C28	0.499(3)	0.706(4)	−0.030(3)	4.7
C29	0.402(3)	0.640(3)	−0.052(3)	4.3
C30	0.401(3)	0.584(4)	0.043(3)	4.7

[a] B_{eq} for W atoms, and B_{iso} for the other atoms.

was mounted in glass capillary tubes under argon. The unit-cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with $19° \leq 2\theta \leq 22°$. Two crystallographically independent molecules were found to be present in a unit cell. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer by using Mo-K_α radiation ($\lambda = 0.71068$ Å).

Calculations were carried out with the program systems SAPI85 [22] on a FACOM A-70 computer. The structure was solved by common Fourier methods. A full-matrix least-squares refinement procedure was used with anisotropic thermal parameters for the tungsten atoms and with isotropic thermal parameters for the other non-hydrogen atoms. Further precise structure refinement using anisotropic thermal factors for all the non-hydrogen atoms was not feasible owing to gradual deterioration of the crystal caused by X-ray exposure and owing to serious influence of the absorption on the intensity (the large μ value and the rod-like shape of the crystals). Empirical absorption correction [23] was applied after all the atoms were located. Final results are summarized in Tables 5, 6, and 7.

Table 7

Selected bond distances (Å) and angles (°)[a]

Distance			
W1-O3	2.09(3)	W2-O6	2.03(2)
W1-O4	2.11(2)	W2-O7	2.11(2)
W1-C11	2.33(6)	W2-C21	2.28(4)
W1-C12	2.31(5)	W2-C22	2.30(5)
W1-C13	2.43(5)	W2-C23	2.36(6)
W1-C14	2.34(4)	W2-C24	2.33(4)
W1-C15	2.25(6)	W2-C25	2.41(4)
W1-C16	2.39(3)	W2-C26	2.39(4)
W1-C17	2.37(6)	W2-C27	2.36(5)
W1-C18	2.28(5)	W2-C28	2.29(5)
W1-C19	2.35(6)	W2-C29	2.27(4)
W1-C20	2.29(4)	W2-C30	2.35(4)
C9-O3	1.36(5)	C10-O6	1.36(5)
C9-O4	1.36(5)	C10-O7	1.30(5)
C9-O5	1.20(5)	C10-O8	1.19(4)
Angle			
O3-W1-O4	64(1)	O6-W2-O7	61(1)
W1-O3-C9	94(2)	W2-O6-C10	98(2)
W1-O4-C9	94(2)	W2-O7-C10	97(2)
O3-C9-O4	109(3)	O6-C10-O7	104(3)
O4-C9-O5	123(4)	O7-C10-O8	127(4)
O3-C9-O5	127(4)	O6-C10-O8	129(4)

[a] Standarad deviations are in parentheses. Distances and angles in the left two columns are those of the molecule in Fig. 1. Distances and angles in the right two columns are those of the other crystallographically independent molecule.

Tables for anisotropic thermal factors and structures factors are available from the author (T.I.).

Acknowledgment

We thank the Ministry of Education, Science and Culture, Japan for support by a Grant-in Aid for Scientific Research (No. 63550640). T.I. thanks the General Sekiyu Research & Development Encouragement & Assistance Foundation and the Iwatani Foundations for financial support. The authors thank Dr. M. Tanaka of Tokyo Institute of Technology for the elemental analysis.

References

1 M.L.H. Green and P.J. Knowles, J. Chem. Soc. A, (1971) 1508.
2 (a) M.L.H. Green, Pure Appl. Chem., 50 (1978) 27; (b) M. Berry, K. Elmitt and M.L.H. Green, J. Chem. Soc., Dalton Trans., (1979) 1950.
3 N.J. Cooper, M.L.H. Green and R. Matahtab, J. Chem. Soc., Dalton Trans., (1979) 1557.
4 T. Ito, A. Takahashi and S. Tamura, Bull. Chem. Soc. Jpn., 59 (1986) 3489.
5 (a) T. Ito and T. Nakano, J. Chem. Soc., Chem. Commun., (1984) 98; (b) J. Chem. Soc., Dalton Trans., (1987) 1857.
6 T. Ito, T. Matsubara and Y. Yamashita, J. Chem. Soc., Dalton Trans., (1990) 2407.
7 M.G. Harris, M.L.H. Green and W.E. Lindsell, J. Chem. Soc. A, (1969) 1453.
8 M.L.H. Green, M. Berry, C. Cloudwell and K. Prout, Nouv. J. Chim., 1 (1977) 187.

9 For example: (a) T. Ito and A. Yamamoto, in S. Inoue and N. Yamazaki (Eds.), Organic and Bioorganic Chemistry of Carbon Dioxide, Halsted Press, New York, 1982, Chap. 3; (b) A. Behr, Angew. Chem. Int. Ed. Engl., 27 (1988) 661; (c) R.P.A. Sneeden, in G. Wilkinson (Ed.) Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, Oxford, 1982, pp. 225–283.
10 T. Ito, T. Ohki and T. Nakano, Synth. React. Inorg. Met. -Org. Chem., 16 (1986) 169.
11 G.B. Deacon and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.
12 T. Ito, M. Koga, S. Kurishima, M. Natori, N. Sekizuka and K. Yoshioka, J. Chem. Soc., Chem. Commun., (1990) 988.
13 M.H. Chisholm. F.A. Cotton, M.W. Extine and W.W. Reichert, J. Am. Chem. Soc., 100 (1978) 1727.
14 M.H. Chisholm and M.W. Extine, J. Am. Chem. Soc., 97 (1975) 5625; ibid., 99 (1977) 792.
15 D.J. Darensbourg, A. Rokickl and M.Y. Darensbourg, J. Am. Chem. Soc., 103 (1981) 3223.
16 B.R. Francis, M.L.H. Green, T. Luong-thi and G.A. Moser, J. Chem. Soc., Dalton Trans., (1976) 1339.
17 M.G. Mason and J.A. Ibers, J. Am. Chem. Soc., 104 (1982) 5153.
18 P.J. Hayward, D.M. Blake, G. Wilkinson and C.J. Nyman, J. Am. Chem. Soc., 92 (1970) 5873.
19 K.A. Belmore, R.A. Vanderpool, J.-C. Tsai, M.A. Khan and K.M. Nicholas, J. Am. Chem. Soc., 110 (1988) 2004.
20 R.L. Cooper and M.L.H. Green, J. Chem. Soc. A, (1967) 1155.
21 M.L.H. Green and P.J. Knowles, J. Chem. Soc., Perkin Trans. 1, (1973) 989.
22 F. Fan, SAPI85, Chinese Academy of Science, Beijing, China, 1985.
23 C. Katayama, Acta Crystallogr., Sect. A, 42 (1986) 19.