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Hydrido–Carbonato, Hydrido–Carbamato, and Carbon Dioxide Complexes of Tungsten Derived from the Carbonyl–Dinitrogen Complex *trans*-$[W(CO)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^1$

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Reaction of *trans*-$[W(CO)(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with excess MeOH or HNR_2 (R = Me, Et, R_2 = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$) under CO_2 afforded a hydrido–carbonato complex $[WH(\eta^1\text{-}OCO_2Me)(CO)(dppe)_2]$ or hydrido–carbamato complexes $[WH(\eta^2\text{-}O_2CNR_2)(CO)(\eta^1\text{-}dppe)(\eta^2\text{-}dppe)]$, respectively. X-ray analyses were performed to disclose the detailed structures of these complexes. The former crystallizes in space group $P2_1/a$ of the monoclinic system with dimensions a = 20.787 (7) Å, b = 22.508 (5) Å, c = 10.402 (3) Å, β = 102.50 (3)°, V = 4751 Å^3, and Z = 4, while the latter (R_2 = $(CH_2)_4$) is monoclinic, space group $P2_1/a$, with a = 38.117 (11) Å, b = 12.060 (3) Å, c = 11.242 (7) Å, β = 98.26 (5)°, V = 5114 Å^3, and Z = 4. This hydrido–carbamato complex was treated with 1 equiv of $AlEt_3$ under CO_2 to give a carbon dioxide complex *trans*-$[W(CO)(CO_2)(dppe)_2]$ containing η^2-CO_2 ligand.

Introduction

Since our initial isolation of *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1b**; dppe = $Ph_2PCH_2CH_2PPh_2$),[2] reactivities of dinitrogen complexes of the type $[M(N_2)_2(P)_4]$ (M = Mo, W; P = tertiary phosphine) have been extensively studied.[3] Efforts have been made to investigate protonation reactions as well as C–N or Si–N bond-forming reactions of the dinitrogen ligand in these complexes, which have provided much useful information relating to biological and chemical N_2 fixation.

Another important feature is that these dinitrogen complexes and carbonyl–dinitrogen complexes *trans*-$[M(CO)(N_2)(dppe)_2]$ (**2a**, M = W;[4] **2b**, M = Mo[5]) derived from **1b** or its W analogue **1a** can serve as versatile precursors to prepare a series of low-valent Mo and W complexes. One or two dinitrogen ligands in these complexes are easily replaced by various ligands including nitriles,[6,7] isonitriles,[8] amides,[5,7,9] olefins,[7] CO,[2b,4,5] and H_2.[2b,4,10] In this context, reactions of CO_2 with this class of dinitrogen complexes have previously been investigated by Chatt and his co-workers. Thus, treatment of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with CO_2 gives a dimolybdenum complex $[Mo(\mu\text{-}CO_3)(CO)(PMe_2Ph)_3]_2$,[11] while **1b** results in the formation of a mononuclear complex not yet well defined but tentatively formulated as $[Mo(CO_2)_2(dppe)_2]$.[12] More recently Carmona et al. isolated the carbon dioxide complex *trans*-$[Mo(\eta^2\text{-}CO_2)_2(PMe_3)_4]$[13] together with $[Mo(CO)(CO_3)(PMe_3)_4]$ and $[Mo(\mu\text{-}CO_3)(CO)(PMe_3)_3]_2$[14] from the reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with CO_2. Direct coordination of CO_2 or reductive disproportionation of CO_2 into CO and CO_3^{2-} is of interest because activation of CO_2 by transition metal complexes or under metal-mediated electrochemical and photochemical conditions is now attracting significant attention.[15]

This paper deals with the reaction of CO_2 with tungsten carbonyl–dinitrogen complex **2a**. Treatment of **2a** with CO_2 in THF did not produce any tractable compounds except for *cis*-$[W(CO)_2(dppe)_2]$, which was isolated in low yield. However, in the presence of excess MeOH or secondary amines (HNR_2), it afforded a hydrido–carbonato complex $[WH(\eta^1\text{-}OCO_2Me)(CO)(dppe)_2]$ (**3**) or hydrido–carbamato complexes $[WH(\eta^2\text{-}O_2CNR_2)(CO)(\eta^1\text{-}dppe)(\eta^2\text{-}dppe)]$ (**4**), respectively. Furthermore, subsequent reaction of **4c** (R_2 = $(CH_2)_4$) with 1 equiv of $AlEt_3$ under CO_2 gave a carbon dioxide complex *trans*-$[W(CO)(\eta^2\text{-}CO_2)(dppe)_2]$ (**5**). Described here are the details of the syntheses and characterization of these complexes. The results of the X-ray analyses of **3** and **4c** are included, as well as the preliminary X-ray structure of **5**.

Results

As summarized in Scheme I, treatment of **2a** with excess MeOH or secondary amines in THF under CO_2 gave a hydrido–carbonato complex **3** or hydrido–carbamato complexes **4**, respectively. Structure studies were undertaken for **3** and **4c**, whose results are presented in Tables I and IV as well as Figures 1 and 2. Spectroscopic data for **4** shown in Tables II and III are consistent with the X-ray structure of **4c**, while NMR spectra of **3** have disclosed its fluxional character in solution. Complex **4c** reacted

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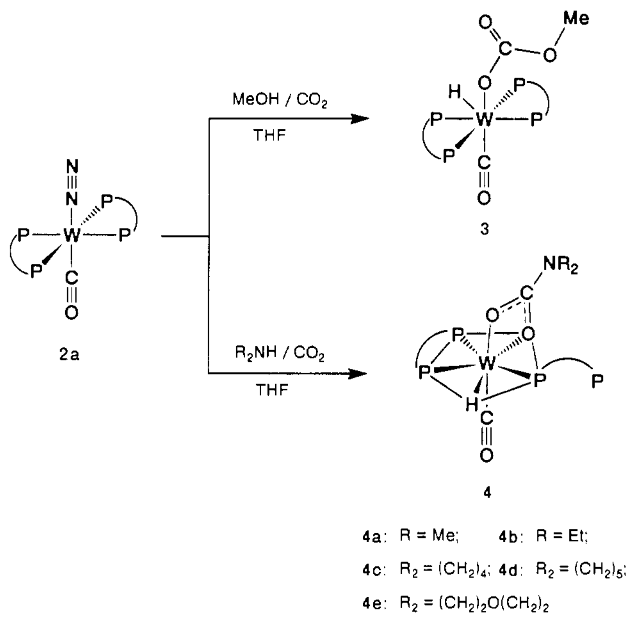
Scheme I



with $AlEt_3$ in THF under CO_2 to give a carbon dioxide complex **5**, which was characterized by its IR spectrum and X-ray diffraction study (Figure 3).

Discussion

Reaction of *trans*-[W(CO)(N₂)(dppe)₂] (2a) with MeOH under CO₂. Treatment of **2a** dissolved in THF with CO_2 in the presence of excess MeOH at room temperature gives a hydrido–carbonato complex **3** as yellow crystals after addition of MeOH to the reaction mixture (Scheme I). Analytically pure **3** was obtained in 58% yield by subsequent recrystallization of the product from THF/hexane. However, the Mo complex **2b** did not afford the analogous hydrido–carbonato complex in a pure form under the same reaction conditions. The IR spectrum of **3** shows a strong $\nu(C\equiv O)$ band at 1790 cm^{-1} assignable to a terminal carbonyl ligand and two characteristic $\nu(OCO_2)$ bands at 1671 and 1293 cm^{-1}. The $\nu(OCO_2)$ values observed here correspond to those of fully characterized methyl carbonato complexes such as $[Zn(Me_4[14]aneN_4)(\eta^1\text{-}OCO_2Me)]ClO_4$ (1676 and 1310 cm^{-1})[16] and $[PtH(\eta^1\text{-}OCO_2Me)\{P(C_6H_{11})_3\}_2]$ (1640 and 1295 cm^{-1}),[17] suggesting the presence of the monodentate carbonato ligand.[18] Although there appeared no bands attributable to $\nu(W\text{–}H)$,[19] the ^1H NMR spectrum of **3** showed a quintet at −3.56 ppm ($J_{P\text{-}H}$ = 40 Hz) due to a hydrido proton. The simple quintet resonance observed for the hydrido proton is diagnostic of the fluxional character of this seven-coordinate complex **3** in solution at room temperature; this was also confirmed by the $^{31}P\{^1H\}$ NMR spectrum of **3**, which showed a singlet at 49.2 ppm ($J_{W\text{-}P}$ = 226 Hz). Since both ^1H and $^{31}P\{^1H\}$ NMR spectra recorded at −80 °C were analogous, **3** remains fluxional even in this low-temperature region.

To clarify the solid-state structure of **3**, X-ray crystallography was performed. The ORTEP diagram obtained is shown in Figure 1, and selected bond distances and angles appear in Table I. These clearly demonstrate that **3** has the W center octahedrally coordinated by CO, OCO_2Me, and two chelating dppe ligands; the hydride was not located. The most plausible seven-coordinate structure for **3** is monocapped octahedral as reported, for example, in $[TaH(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$,[20] although the position capped by the hydrido ligand in **3** is not clear.

The five non-hydrogen atoms in the methyl carbonato ligand and the W atom are almost in the same plane, with the deviations

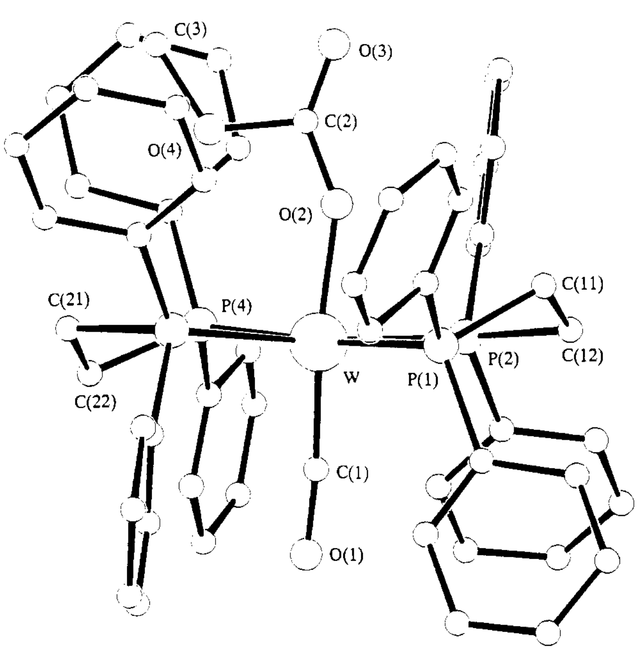


Figure 1. Molecular structure of $[WH(\eta^1\text{-}OCO_2Me)(CO)(dppe)_2]$ (**3**).

Table I. Selected Bond Distances and Angles in Complexes **3** and **4c**

$[WH(\eta^1\text{-}OCO_2Me)(CO)(dppe)_2]$ (**3**)

(a) Bond Distances (Å)

W–P(1)	2.478 (4)	W–P(2)	2.493 (4)
W–P(3)	2.491 (4)	W–P(4)	2.504 (4)
W–C(1)	1.87 (1)	W–O(2)	2.00 (2)
C(1)–O(1)	1.25 (1)	O(2)–C(2)	1.28 (2)
C(2)–O(3)	1.19 (3)	C(2)–O(4)	1.38 (2)
O(4)–C(3)	1.44 (3)		

(b) Bond Angles (deg)

P(1)–W–P(2)	78.4 (1)	P(1)–W–P(3)	102.4 (1)
P(1)–W–P(4)	175.2 (2)	P(1)–W–C(1)	101.2 (3)
P(1)–W–O(2)	81.6 (4)	P(2)–W–P(3)	174.4 (2)
P(2)–W–P(4)	99.9 (1)	P(2)–W–C(1)	84.1 (3)
P(2)–W–O(2)	84.9 (4)	P(3)–W–P(4)	78.9 (1)
P(3)–W–C(1)	101.1 (3)	P(3)–W–O(2)	89.7 (4)
P(4)–W–C(1)	83.0 (3)	P(4)–W–O(2)	93.9 (4)
C(1)–W–O(2)	167.8 (5)	W–C(1)–O(1)	172.6 (9)
W–O(2)–C(2)	151.8 (13)	O(2)–C(2)–O(3)	139.0 (19)
O(2)–C(2)–O(4)	105.1 (17)	O(3)–C(2)–O(4)	115.9 (17)
C(2)–O(4)–C(3)	116.5 (20)		

$[WH\{\eta^2\text{-}O_2C\overline{N(CH_2)_3CH_2}\}(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$ (**4c**)

(a) Bond Distances (Å)

W–P(1)	2.522 (6)	W–P(2)	2.399 (6)
W–P(3)	2.471 (6)	W–O(2)	2.19 (1)
W–O(3)	2.27 (2)	W–C(1)	1.91 (2)
O(2)–C(2)	1.31 (3)	O(3)–C(2)	1.29 (3)
C(2)–N	1.33 (3)	C(1)–O(1)	1.19 (3)

(b) Bond Angles (deg)

P(1)–W–P(2)	78.4 (2)	P(1)–W–P(3)	158.3 (2)
P(1)–W–O(2)	79.6 (4)	P(1)–W–O(3)	88.2 (4)
P(1)–W–C(1)	89.6 (7)	P(2)–W–P(3)	123.0 (2)
P(2)–W–O(3)	109.7 (4)	P(2)–W–C(1)	81.1 (7)
P(3)–W–O(2)	80.1 (4)	P(3)–W–O(3)	87.4 (4)
O(2)–W–O(3)	59.2 (6)	O(2)–W–C(1)	109.1 (8)
O(3)–W–C(1)	168.3 (8)	W–C(1)–O(1)	178.6 (19)

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Table II. IR and ^{1}H NMR Data for Complexes **4**

	IR^a			^{1}H NMR^b			
					J(P–H)		
complex	ν(W–H)	ν(C≡O)	ν(O_2CN)	δ(WH)	P(1)	P(2)	P(3)
4a	1811	1732	1555	−2.75	15	89	68
4b	1800	1747	1539	−2.65	16	90	70
4c	1805	1750	1546	−2.70	15	90	70
4d	1808	1730	1538	−2.63	16	90	68
4e	1810	1732	1532	−2.72	15	89	67

^{a} KBr disk, cm^{-1}. ^{b} Doublet of doublets of doublets, C_6D_6 solution, δ in ppm and J in Hz.

of these atoms from their least-square plane being less than 0.1 Å. This least-square plane is nearly perpendicular to the basal plane consisting of four P atoms and the W atom (dihedral angle: 93°). The angle of the W–O(2)–C(2) linkage (152 (1)°) is significantly larger than those in the other monodentate carbonato complexes of Zn (132.4 (3)°) and Pt (122.2 (7)°) cited above and monodentate bicarbonato complexes such as [Rh(CO)(η^1-OCO_2H)(PPh_3)$_2$] (118.6 (2)°)[21] and [PdMe(η^1-OCO_2H)(PEt_3)$_2$] (131 (1)°).[22] The O(2)–C(2)–O(3) angle is also much wider (139 (2)°) than the value expected for the sp^2 C(2) atom, whereas O(2)–C(2)–O(4) is 105 (2)°. These probably result from the steric repulsion of the methyl carbonato ligand toward the dppe ligands. The CO ligand occupies the site trans to the methyl carbonato ligand, and the W–C(1)–O(1) linkage is essentially linear (172.6 (9)°).

Although a significant number of well-defined carbonato complexes are known, those having both a hydrido ligand and a carbonato ligand are still rare. Other hydrido–carbonato complexes reported to date are the seven-coordinate Mo complex [MoH(η^2-O_2COR)(dppe)$_2$] with pentagonal bipyramidal structure prepared from the reaction of [MoH_4(dppe)$_2$] with $CH_2{=}CHCH_2OCO_2R$[18] and the Pt complex [PtH(η^1-OCO_2-Me){P(C_6H_{11})$_3$}$_2$] obtained from [PtH_2{P(C_6H_{11})$_3$}$_2$] in MeOH under CO_2.[17]

Reactions of 2a with Secondary Amines under CO_2. When treated with excess secondary amine in THF under CO_2, **2a** affords the hydrido–carbamato complexes [WH(η^2-O_2CNR_2)(CO)(η^1-dppe)(η^2-dppe)] (**4**) in moderate yields as orange crystals (Scheme I). As summarized in Table II, complexes **4** show three characteristic IR bands assignable to ν(W–H),[23] ν(C≡O), and ν(O_2CN), respectively. The quite low values of the ν(O_2CN) bands (1532–1555 cm^{-1}) are indicative of the η^2 coordination of the carbamato ligands in **4**, presenting a sharp contrast to the η^1 coordination of the methyl carbonato ligand in **3**. In the ^{1}H NMR spectra the hydrido resonances appear at −2.6 to −2.8 ppm as a doublet of doublets of doublets together with signals due to the carbamato and dppe ligands, indicating the presence of coupling between the hydrido protons and only three P atoms (Table II). The results of the ^{31}P{^{1}H} NMR spectra of **4** are consistent with this feature. Thus, the spectra show the existence of four nonequivalent P atoms and the chemical shifts of three signals (P(1)–P(3)) are diagnostic of the coordinated P atoms, whereas those denoted as P(4) are observed at much higher field than the other three resonances (Table III). Since free dppe exhibits the peak at −13.2 ppm under the same conditions, these high-field resonances are assigned to uncomplexed P atoms. Appearance of a signal for an uncomplexed P atom at higher field than that for the coordinated P atom in η^1-diphosphine ligands has been reported for some complexes.[24] The coupling constants between the P atoms are also summarized in Table III, which clearly indicate that the P(3) atom belongs to the monodentate dppe ligand, since the uncomplexed P(4) atom shows distinctive coupling to the P(3) atom among the three coordinated P atoms. The P(1) and P(2) atoms are accordingly assigned to the chelating dppe ligand.

To clarify this unexpected structural feature of **4**, X-ray analysis was undertaken with a single crystal of **4c**. The ORTEP drawing of **4c** is shown in Figure 2, and selected bond distances and angles are listed in Table I. As suggested by the ^{31}P{^{1}H} NMR spectra of **4**, Figure 2 shows the existence of both chelating and monodentate dppe ligands together with η^2-carbamato and terminal CO ligands. The position of the hydrido ligand could not be determined by the X-ray analysis, but it may be present between the P(2) and P(3) atoms because the P(2)–W–P(3) angle of 123.0 (2)° is significantly larger than any other angles between two adjacent atoms ligating to the W atom. Thus, the structure of **4c** can be approximated as a distorted pentagonal bipyramid with the O(3) atom of the η^2-carbamato ligand and the C(1) atom of the CO ligand in two axial sites (O(3)–W–C(1) = 168.3 (8)°). However, unequivocal assignment of the two ^{31}P NMR resonances of the chelating dppe ligand was not possible on the basis of the X-ray structure obtained here. The tentative assignment of the resonance with the smaller chemical shift to the P(1) atom mainly arises from the $J_{\mathrm{P-H}}$ values determined by the ^{1}H NMR spectra of **4c** recorded in the selective ^{31}P decoupling mode. The P atom having the $J_{\mathrm{P-H}}$ value close to that of the P(3) atom was assigned to the P(2) atom adjacent to the hydrido ligand like the P(3) atom. The much larger coupling constant observed between the P(1) and P(3) atoms is consistent with the P(1)–W–P(3) angle of 158.3 (2)°.

An interesting feature of **4** is the presence of the hydrido ligand together with the carbamato ligand. To our knowledge, few well-defined hydrido–carbamato complexes have been reported to date,[25] although their reactivities are of much interest as the possible intermediate stages of the catalytic reactions using CO_2 and amines promoted by transition metal complexes. Investigation of the reactivity of these hydrido–carbamato complexes **4** is now in progress.

Reaction of 4c with $AlEt_3$. Treatment of **4c** with 1 equiv of $AlEt_3$ in THF under CO_2 afforded a carbonyl–carbon dioxide complex *trans*-[W(CO)(η^2-CO_2)(dppe)$_2$] (**5**) as orange crystals (eq 1). The IR spectrum of **5** shows three characteristic bands

$$[\mathrm{WH}\{\eta^2\text{-}\mathrm{O_2C}\overline{\mathrm{N(CH_2)_3CH_2}}\}(\eta^1\text{-dppe})(\eta^2\text{-dppe})] + \mathrm{AlEt_3} \xrightarrow{\mathrm{CO_2}} trans\text{-}[\mathrm{W(CO)}(\eta^2\text{-}\mathrm{CO_2})(\mathrm{dppe})_2] \quad (1)$$

at 1677, 1187, and 1120 cm^{-1}, which correspond to the appearance of three bands at 1670, 1155, and 1100 cm^{-1} associated with the η^2-CO_2 ligand in *trans*-[Mo(CO_2)$_2$(PMe_3)$_4$].[13] Another strong band observed at 1788 cm^{-1} can be attributed to the terminal CO ligand in **5**. Although this spectral feature of **5** is diagnostic of the assignment of **5** as the carbonyl–carbon dioxide complex, the X-ray analysis was undertaken to confirm its structure, since the unambiguous characterization of CO_2 complexes is now possible only by the X-ray crystallography.

Unfortunately the intensities of the standard reflections significantly decayed during data collection due to the instability of **5**. Thus, structure refinement by using reflection data obtained from two crystals resulted in the poor convergence of the R values

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(22) Crutchley, R. J.; Powell, H.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15.

(23) A medium band at 1805 cm^{-1} observed for **4c** shifted to 1292 cm^{-1} in [WD{η^2-$\mathrm{O_2C}\overline{\mathrm{N(CH_2)_3CH_2}}$}(CO)($\eta^1$-dppe)($\eta^2$-dppe)], which corresponds well to the calculated value of 1278 cm^{-1}.

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Table III. ^{31}P NMR Data for Complexes **4**[a]

complex	chem shift (δ)				coupling constant (*J*)[f]			
	P(1)[b]	P(2)[c]	P(3)[d]	P(4)[e]	P(1)–P(2)	P(1)–P(3)	P(2)–P(3)	P(3)–P(4)
4a	54.5	72.6	41.1	−12.3	22	143	22	39
4b	51.9	71.8	40.5	−12.6	21	145	21	39
4c	54.3	72.4	40.9	−12.6	22	143	22	39
4d	53.7	72.0	40.7	−12.4	20	143	20	37
4e	54.7	72.5	41.2	−12.5	20	141	20	38

[a] C_6D_6/C_6H_6 solution, δ in ppm and *J* in Hz. [b] Doublet of doublets. [c] Triplet. [d] Doublet of doublets of doublets. [e] Doublet. [f] No coupling was resolved for P(1)–P(4) and P(2)–P(4).

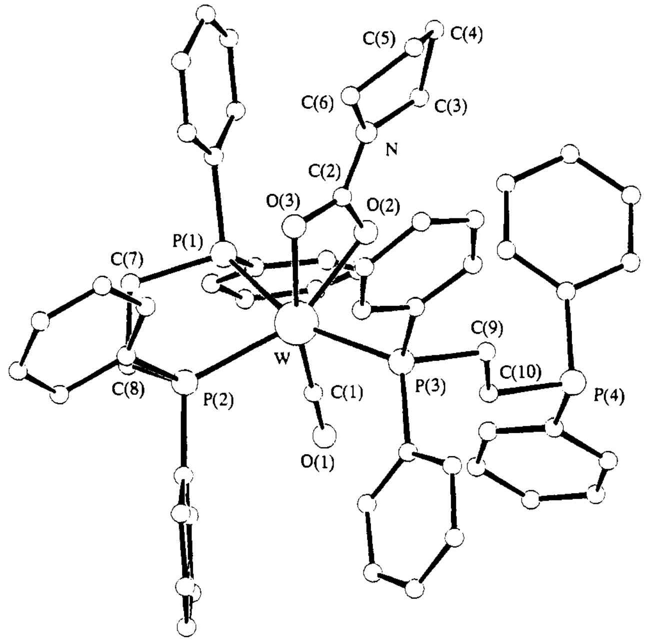

Figure 2. Molecular structure of $[WH\{\eta^2\text{-}O_2C\overline{N(CH_2)_3CH_2}\}(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$ (**4c**).

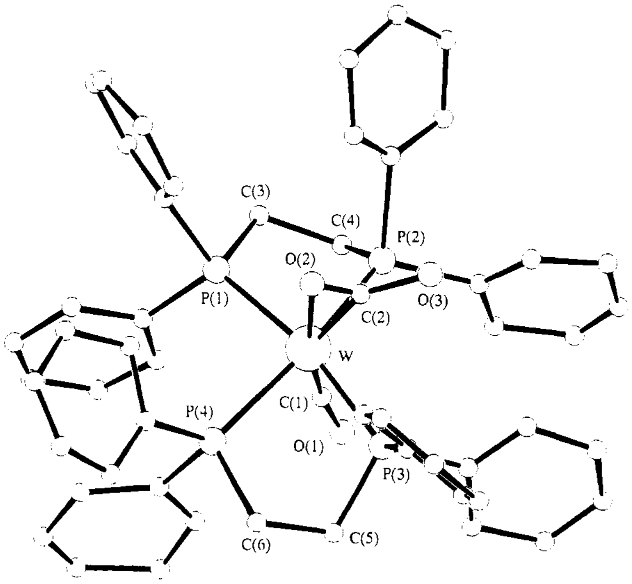

Figure 3. Molecular structure of *trans*-$[W(CO)(\eta^2\text{-}CO_2)(dppe)_2]$ (**5**).

and clarification of detailed bond distances and angles in **5** must await further trials to get more excellent diffraction data. Nevertheless, the preliminary result shown in Figure 3 demonstrates the η^2 coordination of CO_2 ligand by both the C(2) and O(2) atoms in the trans position to the terminal CO ligand. Complex **5** is one of the still rare examples of the CO_2 complexes with a mononuclear metal center[13,26] and the first one of a W complex with a CO_2 ligand.[27] The $\nu(C{\equiv}O)$ value observed for **5** at 1788 cm^{-1} is much higher than those of a five-coordinate complex $[W(CO)(dppe)_2]$ (**6a**)[4] (1716 cm^{-1}) and *trans*-$[W(CO)(DMF)(dppe)_2]$ (1680 cm^{-1}) and slightly lower than those of **2a** (1817 and 1795 cm^{-1}; split by a crystal effect).[4] This result suggests some electron-withdrawing ability of this CO_2 ligand, which is almost comparable to the N_2 ligand. Since the reaction of **4c** with 1 equiv of $AlEt_3$ under Ar produces the five-coordinate complex **6a** in moderate yield, the role of $AlEt_3$ in this reaction appears to be the removal of pyrrolidine or carbamic acid from **4c**. However, **5** could not be isolated directly by treatment of **6a** with CO_2 in THF or benzene. When redissolved in solvents such as THF or benzene even under CO_2, **5** decomposed rapidly, and this has precluded further study of the reactivity of the coordinated CO_2 in **5**.

Experimental Section

Manipulations were carried out under a CO_2 or Ar atmosphere as appropriate, using Schlenk tube techniques. Solvents were purified according to common methods and were stored under an inert atmosphere. Carbonyl complexes **2** and **6a** were prepared as previously reported.[4,5] NMR spectra were recorded on a JEOL JMN-GX-400 spectrometer at 400 MHz for ^1H or 162 MHz for ^{31}P nuclei, and chemical shifts were referred to the C_6D_5H impurity at 7.20 ppm in C_6D_6 or to external 85% H_3PO_4, respectively. IR spectra were measured by a Shimadzu IR-408 spectrometer. Elemental analyses were performed at The Elemental Analysis Laboratory, Department of Chemistry, The University of Tokyo.

Preparation of $[WH(\eta^1\text{-}OCO_2Me)(CO)(dppe)_2]$ (3). Methanol (1 mL) was added to a solution of **2a** (100 mg, 0.099 mmol) in THF (4 mL) under CO_2, and the mixture was stirred for 1 h at room temperature. Addition of MeOH (8 mL) to the resultant product solution deposited yellow crystals, which were collected and recrystallized from THF/hexane, affording 62 mg of analytically pure **3** (58%). IR (Nujol mull, cm^{-1}): 1790 (CO), 1671 and 1293 (OCO_2). ^1H NMR (C_6D_6, ppm): 3.13 (s, 3 H, CH_3O), −3.56 (quintet, J_{P-H} = 40 Hz, 1 H, W*H*), 2.6 and 3.1 (br s, 4 H each, PCH_2), 6.6–8.5 (m, 40 H, P*Ph*). ^{31}P NMR ($CD_3C_6D_5$/THF, ppm) 49.2 (s, J_{W-P} = 226 Hz). Anal. Calcd for $C_{55}H_{51}O_4P_4W$: C, 60.89; H, 4.84. Found: C, 60.37; H, 4.84.

Preparations of $[WH(\eta^2\text{-}O_2CNR_2)(CO)(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$ (4). The general procedure to prepare **4** follows. About 10 equiv of R_2NH was added to a solution of **2a** (100 mg, 0.099 mmol) in THF (3 mL), and the mixture was stirred for 1 h at room temperature under CO_2. By addition of hexane (6 mL) to the resultant solution, orange crystals were obtained, which were washed with hexane and dried in vacuo. Spectroscopic data are shown in Tables II and III.

4a. This compound was recrystallized from C_6H_6/hexane. Yield: 60%. Anal. Calcd for $C_{56}H_{55}NO_3P_4W{\cdot}C_6H_6$: C, 63.32; H, 5.24; N, 1.19. Found: C, 63.16; H, 5.19; N, 1.28.

4b. Yield: 64%. Anal. Calcd for $C_{58}H_{59}NO_3P_4W$: C, 61.87; H, 5.29; N, 1.24. Found: C, 61.96; H, 5.34; N, 1.40.

4c. Yield: 76%. Anal. Calcd for $C_{58}H_{57}NO_3P_4W$: C, 61.98; H, 5.12; N, 1.25. Found: C, 62.13; H, 5.51; N, 1.07.

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4d. Yield: 61%. Anal. Calcd for $C_{59}H_{59}NO_3P_4W$: C, 62.27; H, 5.24; N, 1.23. Found: C, 62.46; H, 5.56; N, 1.30.

4e. Yield: 76%. Anal. Calcd for $C_{58}H_{57}NO_4P_4W$: C, 61.11; H, 5.05; N, 1.23. Found: C, 60.85; H, 5.35; N, 1.30.

Preparation of *trans*-[W(CO)(η^2-CO_2)(dppe)$_2$] (5). A hexane solution of $AlEt_3$ (0.92 M, 96 μL) was added to a solution of **4c** (100 mg, 0.089 mmol) in THF (3 mL) under CO_2, and the mixture was stirred for 1 h at 50 °C. The color of the solution changed from orange to dark green and then into orange. Addition of hexane to the product solution precipitated orange crystals, which were separated, washed with hexane, and dried in vacuo. Yield: 47 mg (49%). IR (KBr, cm^{-1}): 1788 (CO), 1677, 1187, and 1120 (CO_2). Anal. Calcd for $C_{54}H_{48}O_3P_4W$: C, 61.60; H, 4.61. Found: C, 61.46; H, 4.88. Complex **5** can also be prepared in moderate yields from the reactions undertaken at 0 and −78 °C.

X-ray Diffraction Study for Complexes 3 and 4c. The crystals sealed in glass capillaries under CO_2 were mounted on a Rigaku AFC-6A four-circle diffractometer equipped with a graphite monochromator. The orientation matrices and unit cell parameters were derived from a least-squares fit of 25 machine-centered reflections with 2θ values between 20 and 25°. Data collection was performed at room temperature. Intensity data were corrected for the Lorentz–polarization effect, and absorption corrections were performed. Selected crystallographic data are shown in Table IV.

Structure solution and refinement were carried out by using the UNIX-III program at The Computer Center, The University of Tokyo.[28] The positions of the W atoms were found by the direct methods program MULTAN. Subsequent cycles of block-diagonal least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms. All of these atoms were refined by using anisotropic temperature factors[29] for **3**. For **4c**, anisotropic refinement was undertaken only for the W and P atoms. Hydrogen atoms in **3** were placed at the calculated positions and refined isotropically. Further trials to improve the R values for both complexes were not successful.

Table IV. X-ray Crystallographic Data for **3** and **4c**

	3	**4c**
chem formula	$C_{55}H_{52}O_4P_4W$	$C_{58}H_{57}NO_3P_4W$
fw	1084.7	1123.8
a, Å	20.787 (7)	38.117 (11)
b, Å	22.508 (5)	12.060 (3)
c, Å	10.402 (3)	11.242 (7)
β, deg	102.50 (3)	98.26 (5)
V, Å^3	4751	5114
Z	4	4
space group	$P2_1/a$	$P2_1/a$
T	rt	rt
λ, Å	0.7107	0.7107
ρ_{calcd}, g cm^{-3}	1.52	1.46
μ_{calcd}, cm^{-1}	26.60	24.73
transm coeff	0.513–0.766	0.525–0.631
R ($\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$)	0.094	0.076

X-ray Diffraction Study for 5. Data collection was performed on a Rigaku AFC-5R diffractometer by using two crystals. Lattice constants obtained for both crystals were essentially the same: monoclinic, space group $P2_1/c$, a = 19.488 (12) Å, b = 12.014 (7) Å, c = 20.983 (9) Å, β = 94.54 (5)°, V = 4897 Å^3, and Z = 4. One crystal was used for reflections with 2θ values between 3 and 40°, while the other was for those between 40 and 50°. These crystals showed the significant decay in intensities of three standard reflections during data collection (20–25% weakening at the final stages). Structure solution and refinement were carried out as described above. Only W and P atoms were refined anisotropically. The R and R_w values for 3196 reflections with $|F_o| > 5\sigma(F_o)$ converged only to 0.10 and 0.13, respectively.

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Supplementary Material Available: Tables listing details of X-ray crystallography, atomic parameters and temperature factors of non-hydrogen atoms, extensive bond lengths and angles for **3**, **4c**, and **5**, and atomic parameters of hydrogen atoms in **3** and figures showing full atom-numbering schemes for **3**, **4c**, and **5** (20 pages). Ordering information is given on any current masthead page.

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