

## Investigations into the Steric Influences on the Reaction Mechanism of CO<sub>2</sub> Insertion into Metal–Oxygen Bonds. COS Activation as a Model for CO<sub>2</sub>

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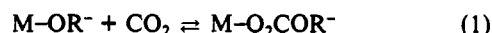
Steric influences on the insertion of CO<sub>2</sub> into metal–oxygen bonds have been investigated. The compounds [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1) and [Et<sub>4</sub>N][W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)OPh] (2) have been synthesized and their reactivities toward CO<sub>2</sub> studied. Complex 1 showed no reactivity toward CO<sub>2</sub> even at elevated pressures (900 psi). The anion of 2 demonstrated a retarded rate of reaction with CO<sub>2</sub> as compared to the parent complex, [Et<sub>4</sub>N][W(CO)<sub>5</sub>OPh], a result ascribed to the steric bulk of the *cis* phosphine ligand. In general, it was found that the reactivity of metal–oxygen bonds toward CO<sub>2</sub> was adversely affected by the increased steric demands of substituents on either the metal center or the aryl group of the ligated aryloxy. Complexes 1 and 2 were characterized in the solid state by X-ray crystallography. Complex 1 crystallized in the space group *P2<sub>1</sub>/c* with cell dimensions *a* = 12.658 (3) Å, *b* = 15.136 (3) Å, *c* = 33.471 (6) Å,  $\beta$  = 95.388 (15)°, *V* = 0.6385 (2) Å<sup>3</sup>, *Z* = 8, and *R<sub>F</sub>* = 6.4%. Complex 2 crystallized in the space group *P2<sub>1</sub>/n* with cell dimensions *a* = 11.309 (7) Å, *b* = 16.9389 (8) Å, *c* = 16.888 (13) Å,  $\beta$  = 102.39 (5)°, *V* = 3160 (3) Å<sup>3</sup>, *Z* = 4, and *R<sub>F</sub>* = 4.3%. These compounds were also reacted with COS as a model for CO<sub>2</sub>. [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] reacted cleanly under 1 atm of COS and at ambient temperature to afford the product of COS insertion into a metal–oxygen bond, [Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3). The enhanced reactivity of 1 toward COS as compared to CO<sub>2</sub> is proposed to be in part due to W...S bond formation in the transition state. Complex 3 was subjected to X-ray crystallographic investigation. Complex 3 crystallized in the space group *Pcmm* (No. 62) with cell dimensions *a* = 11.803 (6) Å, *b* = 14.844 (8) Å, *c* = 18.752 (11) Å, *V* = 3285(3) Å<sup>3</sup>, *Z* = 8, and *R<sub>F</sub>* = 6.3%.

### Introduction

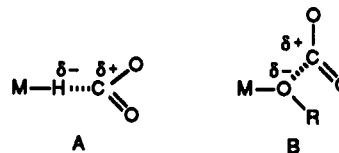
Catalytic reactions of carbon dioxide have recently attracted much attention. Reasons for this interest include the need for alternative hydrocarbon sources to petroleum, with CO<sub>2</sub> being the most abundant C<sub>1</sub> feedstock available, and the concern over increasing concentrations of CO<sub>2</sub> in the atmosphere, which prompts the possibility of recycling industrially produced CO<sub>2</sub>.<sup>1</sup> Relevant to these processes, a well-studied theme in our laboratories has been the mechanistic aspects of the insertion of carbon dioxide into metal–hydride and metal–carbon bonds, with special attention being paid to derivatives of chromium and tungsten.<sup>1a</sup> Reactions of these particular metal derivatives are thought to be prototypic of carboxylation reactions involving low-valent, saturated metal centers. In addition, there have been several studies reported related to the insertion of CO<sub>2</sub> into metal–oxygen bonds. Most of these have involved the reaction of CO<sub>2</sub> with a hydroxy ligand bound to a single, coordinatively saturated metal to form the corresponding bicarbonate or carbonate species,<sup>1c,d,2</sup> There are, as well, numerous studies of the reaction of complexes of the type M–OR (R = alkyl, aryl) with carbon dioxide to afford the alkyl or aryl carbonates.<sup>3</sup> Nevertheless, mechanistic information about

these insertion processes is lacking. This is particularly evident when the reaction pathway for the copolymerization of epoxides and CO<sub>2</sub> in the presence of metal alkoxides as catalysts<sup>4</sup> is considered.

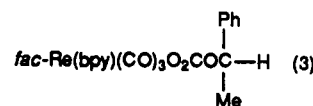
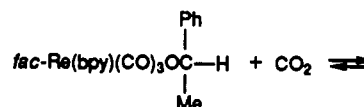
More recently, synthetic methods for providing pure samples of group 6 metal pentacarbonyl aryloxides have been developed that allow us to extend our investigation of CO<sub>2</sub> insertion processes to include various metal–aryloxy substrates.<sup>5</sup> As indicated in eq 1, the carbon dioxide insertion reaction is reversible.



This insertion process is akin to the more thoroughly investigated, both experimentally and theoretically, insertion reaction of CO<sub>2</sub> into metal hydrides to provide metal formates. In addition to this latter process also being reversible, both processes involve ligands (H<sup>-</sup> and OR<sup>-</sup>) that have occupied orbitals for interaction with the electrophilic site of carbon dioxide (species A and B).<sup>6</sup>



Mechanistic similarities have been noted for the two CO<sub>2</sub> insertion reactions involving Re(I) derivatives (eqs 2 and 3), where an



associative pathway is supported by the activation parameters determined for the processes.<sup>7</sup> That is,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were found

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to be 12.8 and 10.9 kcal/mol and –33.0 and –27.6 eu for reactions 2 and 3, respectively. In addition, a polar transition state was suggested by a significant rate increase upon changing the solvent from THF to CH<sub>3</sub>CN.

A rather detailed study of the mechanistic aspects of CO<sub>2</sub> insertion into metal–oxygen bonds in group 6 metal derivatives is currently underway, with emphasis being placed on steric influences on the insertion process. Herein, we report on the synthesis and characterization of the sterically crowded aryloxide derivatives [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1), and [Et<sub>4</sub>N][W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)OPh] (2), along with their reactivity toward CO<sub>2</sub> and COS. Furthermore, the solid-state structure of the product resulting from COS insertion into the W–O bond of 1, [Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3) has been determined.

### Experimental Section

**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 and hexane were purified by distillation from blue sodium benzophenone ketyl solutions under nitrogen. Acetonitrile was refluxed over and distilled twice from CaH<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. Solution spectra were taken in a 0.1-mm CaF<sub>2</sub> or NaCl cell on an IBM FT-IR Model 32 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL-200E spectrometer. High-pressure NMR experiments were conducted in a specially designed sapphire NMR tube.<sup>8</sup>

[Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1). W(CO)<sub>5</sub>THF was prepared by photolysis of W(CO)<sub>6</sub> (0.66 g, 1.9 mmol) in 50 mL of THF for 1.5 h (IR, ν(CO) in THF, 2076 (w), 1931 (s), and 1892 (m) cm<sup>-1</sup>). The W(CO)<sub>5</sub>THF solution was transferred via cannula to a flask containing [Et<sub>4</sub>N][O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (0.69 g, 1.84 mmol). After about 10 min of stirring at room temperature the reaction went to completion. The solution was cooled to –78 °C under an atmosphere of CO and then filtered through Celite. Crystals were obtained by slow layering of hexane over the THF solution, and the flask was kept at –11 °C. Anal. Calc for [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>]: C, 54.18; H, 4.56; N, 1.91; W, 25.15. Found: C, 55.56; H, 4.60; N, 2.15; W, 25.1. IR, ν(CO) in THF: 2054 (w), 1905 (s), and 1835 (m) cm<sup>-1</sup>. <sup>13</sup>C NMR (CD<sub>3</sub>CN), carbonyls (enriched in <sup>13</sup>CO by placing an atmosphere of <sup>13</sup>CO over a THF solution of 1): cis, δ 200.0 (4 CO, J<sub>W-C</sub> = 129.0 Hz); trans, δ 204.4 (1 CO).

[Et<sub>4</sub>N][cis-W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)OPh] (2). To a solution of W(CO)<sub>5</sub>OPh<sup>-</sup> prepared by the reaction of W(CO)<sub>5</sub>Me<sup>-</sup> with HOPh was added 3 equiv of PPh<sub>2</sub>Me via syringe. The reaction was monitored by infrared spectroscopy and found to convert completely to the cis-substituted product. The solid was precipitated by the addition of hexane and washed 3 times with 10 mL of hexane. Crystals were obtained by slow layering of hexane over a THF solution of the complex maintained at –11 °C. IR, ν(CO) in THF: 1993 (w), 1868 (s), 1847 (sh), 1808 (m) cm<sup>-1</sup>. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO), carbonyls: δ 206.3 (2 CO's cis to phosphine and OPh ligands, J<sub>C-P</sub> = 7.4 Hz, J<sub>W-C</sub> = 130.6 Hz), 211.5 (1 CO, cis to phosphine and trans to OPh ligands, J<sub>C-P</sub> = 3.2 Hz, J<sub>W-C</sub> = 145.9 Hz), 214.2 (1 CO, trans to phosphine and cis to OPh ligands, J<sub>C-P</sub> = 41.5 Hz, J<sub>W-C</sub> = 162.8 Hz).

[Et<sub>4</sub>N][W(CO)<sub>5</sub>O<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>]. [Et<sub>4</sub>N][W(CO)<sub>5</sub>OPh] was dissolved in 1 mL of (CD<sub>3</sub>)<sub>2</sub>CO, and the solution was injected into a NMR tube. An <sup>13</sup>C NMR spectrum was taken to characterize the alkoxide complex. The solution was cooled to –78 °C. The NMR tube was then evacuated and a small amount of <sup>13</sup>CO<sub>2</sub> bubbled into the solution. A <sup>13</sup>C NMR spectrum was then taken, and the appearance of resonances for the carbonate and for free CO<sub>2</sub> was observed. IR, ν(CO) in THF: 2063 (w), 1913 (s), 1854 (m) cm<sup>-1</sup>. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO): cation CH<sub>3</sub>, δ 7.55; cation CH<sub>2</sub>, δ 52.91; anion C<sub>6</sub>H<sub>5</sub>, δ 118.0, 116.6, 129.9, 169.3; O<sub>2</sub>COPh, δ 168.6 (identified by using <sup>13</sup>CO<sub>2</sub> in the synthesis).

[Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3). [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] was dissolved in THF. The atmosphere of N<sub>2</sub> was evacuated and replaced by an atmosphere of COS. An immediate darkening of the solution was observed, and the IR spectrum in the ν(CO) region shifted to higher energy. The solution was filtered through Celite, and crystals were isolated by the layering of hexane over the solution and storing the solution for 12 h at –11 °C. <sup>13</sup>C NMR (CD<sub>3</sub>CN), carbonyls (enriched

in <sup>13</sup>CO by placing an atmosphere of <sup>13</sup>CO over a THF solution of the complex): cis, δ 200.4 (4 CO, J<sub>W-C</sub> = 131.4 Hz); trans, δ 204.7 (1 CO); S<sup>\*</sup>C(O)OR, δ 179.6.

**X-ray Structure Determinations.** [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1). A bright yellow block was mounted on a glass fiber with vacuum grease, at room temperature, and cooled to 193 K in a N<sub>2</sub> cold stream. Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer. The scan range for the data collection was 1.20° plus Kα separation, with a variable scan rate of 1.50–15.00° min<sup>-1</sup>. 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 half of the total scan time. Lorentz and polarization corrections were applied to 11971 reflections. No absorption correction was applied. Reflection intensities were profiled by employing a learnt profile technique.<sup>9c</sup> The structure was solved by direct methods.<sup>9b</sup> Full-matrix least-squares isotropic refinement for O(400), C(400), C(401), C(402), and C(403) and anisotropic refinement for all remaining non-hydrogen atoms yielded R = 0.064, R<sub>w</sub> = 0.063, and S = 1.57 at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å<sup>2</sup>. Neutral-atom scattering factors were taken from ref 9a. Crystallographic data and experimental conditions are provided in Table I.

[Et<sub>4</sub>N][W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)OPh] (2). A yellow block was mounted on a glass fiber with vacuum grease, at room temperature, and cooled to 188 K in a N<sub>2</sub> cold stream. Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer. The scan range for the data collection was 1.20° plus Kα separation, with a variable scan rate of 2.00–15.00° min<sup>-1</sup>. 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 half of the total scan time. Lorentz and polarization corrections were applied to 6077 reflections. Reflection intensities were profiled by employing a learnt profile technique.<sup>9c</sup> The structure was solved by Patterson synthesis.<sup>9b</sup> Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R = 0.043, R<sub>w</sub> = 0.059, and S = 1.40 at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å<sup>2</sup>. Neutral-atom scattering factors were taken from ref 9a. Crystallographic data and experimental conditions are provided in Table I.

[Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3). A yellow plate was mounted on a glass fiber with epoxy cement, at room temperature, and cooled to 193 K in a N<sub>2</sub> cold stream. Preliminary examination and data collection was performed on a Nicolet R3m/V X-ray diffractometer. Scan range for data collection was 1.60° plus Kα separation, with a variable scan rate of 1.50–14.65° min<sup>-1</sup>. 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 half of the total scan time. Lorentz and polarization corrections were applied to 3686 reflections. The structure was solved by direct methods.<sup>9b</sup> Full-matrix least-squares isotropic refinement for all non-hydrogen atoms yielded R = 0.063, R<sub>w</sub> = 0.069, and S = 2.202 at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å<sup>2</sup>. Neutral-atom scattering factors were taken from ref 9a. Crystallographic data and experimental conditions are provided in Table I.

**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<sub>2</sub> purge. The tube was then charged with the desired pressure of <sup>13</sup>CO<sub>2</sub> up to 200 psi. If higher pressures were desired, the NMR tube was connected to a single-stage regulator and brought up to pressure with natural isotopic abundance 99.99% pure CO<sub>2</sub>. 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.

### Results

**Synthesis of [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1).** This complex was synthesized by the previously described procedure.<sup>5</sup> The route involves the preliminary photolytic generation of the W(CO)<sub>5</sub>THF adduct. This adduct, which possesses a very labile THF ligand,

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**Table I.** Crystallographic Data for [Et<sub>4</sub>N][W(CO)<sub>5</sub>(O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)] (1), [Et<sub>4</sub>N][W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)(OPh)] (2), and [Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3)

	1	2	3
(a) Crystal Data			
formula	C <sub>33</sub> H <sub>33</sub> NO <sub>6.5</sub> W	C <sub>31</sub> H <sub>38</sub> NO <sub>5</sub> PW	C <sub>32</sub> H <sub>33</sub> WSO <sub>7</sub> N
fw	731.5	719.4	759.6
cryst syst	monoclinic	monoclinic	orthorhombic
space grp	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n (No. 62)	Pcmm (No. 62)
a, Å	12.658 (3)	11.309 (7)	11.803 (6)
b, Å	15.136 (3)	16.939 (8)	14.844 (8)
c, Å	33.471 (6)	16.888 (13)	18.752 (11)
β, deg	95.388 (15)	102.39 (5)	
V, Å <sup>3</sup>	6385 (2)	3160 (3)	3285 (3)
Z	8	4	8
D(calc), g/mL	1.522	1.512	1.536
temp, K	193	188	193
cryst dimens, mm	0.12 × 0.20 × 0.22	0.2 × 0.3 × 0.4	0.15 × 0.25 × 0.30
μ(Mo Kα), mm <sup>-1</sup>	3.738	3.819	3.695
(b) Data Collection			
radiation	Mo Kα	Mo Kα	Mo Kα
wavelength, Å	0.710 73	0.710 73	0.710 73
scan limits, deg	4.0 < 2θ < 40.0	4.0 < 2θ < 40.0	4.0 < 2θ < 50.0
scan method	ω (Wyckoff)	θ-2θ	ω (Wyckoff)
no. of rflns colld	11 971	6077	3686
max h,k,l	15,0,39	13,8,0	14,17,22
min h,k,l	-15,-18,0	-13,-20,-20	0,0,-2
no. of indepdt obsd rflns	6981 [4.0σ(F <sub>o</sub> )]	3673 [4.0σ(F <sub>o</sub> )]	2475 [4.0σ(F <sub>o</sub> )]
(c) Refinement			
R <sup>a</sup>	0.064	0.043	0.063
R <sub>w</sub> <sup>a</sup>	0.063	0.059	0.069
N <sub>data</sub> /N <sub>params</sub>	12.9	10.4	10.4
S <sup>a</sup>	1.57	1.40	3.34
g <sup>a</sup>	0.0004	0.0010	0.0001

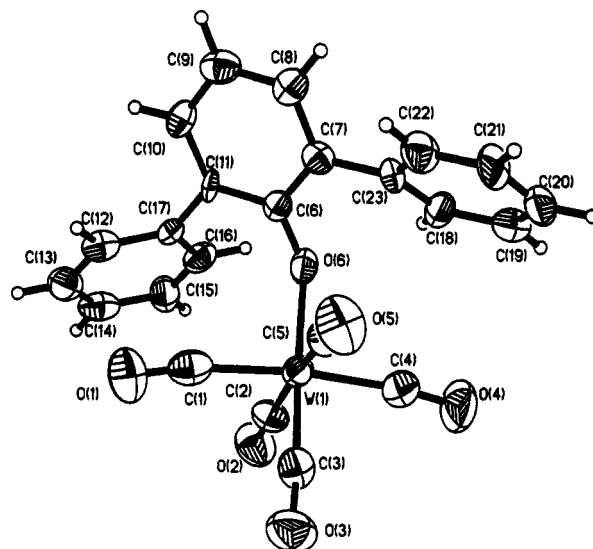
$$^a R = (\sum |F_o - F_c| / \sum F_o), R_w = (\sum w(F_o - F_c)^2 / \sum w(F_o)^2)^{1/2}, w^{-1} = \sigma^2 F + gF^2, S = (\sum w(F_o - F_c)^2 / N_{data} - N_{params})^{1/2}.$$

rapidly reacts with [Et<sub>4</sub>N][O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] to quantitatively afford the desired [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] complex. Complex 1 undergoes decomposition by clusterfication following carbonyl loss to give complexes of varying nuclearity.<sup>5,10</sup> This instability problem was alleviated by performing the isolation of the complex, as well as its reactivity studies, at low temperature and under an atmosphere of carbon monoxide. Infrared (ν(CO)) and <sup>13</sup>C NMR spectra typical of complexes containing the [W(CO)<sub>5</sub>] fragment were noted for 1 and are reported in the Experimental Section.

**Structure of [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1).** The structure of 1 has been determined by X-ray crystallography. The complex crystallized in the space group P2<sub>1</sub>/c with two independent anions and cations and a THF solvent molecule of crystallization per asymmetric unit. One of the two independent anions is illustrated in Figure 1 with its atomic labeling scheme. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Pertinent bond distances and bond angles are listed in Tables III and IV, respectively.

The two anions possess the same gross structural features with only slight differences in bond distances and angles being noted. In both, the geometry about the tungsten atom is a slightly distorted octahedron due mainly to the steric demands of the bulky 2,6-diphenylphenoxide ligand. This is observable in the OC<sub>6</sub>H<sub>3</sub>-W-O bond angles, which span a range from 88.7 (5) to 96.3 (5)°, where the largest deviations from 90° involve the carbonyls on the same side as the bulky 2,6-diphenylphenyl group.

The tungsten-oxygen bond distances in the two anions are 2.174 (9) and 2.168 (9) Å, averaging 2.171 (9) Å. These distances are



**Figure 1.** ORTEP diagram of the anion of [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (1), showing 50% probability thermal motion ellipsoids with atomic labeling scheme.

similar to the W-O bond distance in the W(CO)<sub>5</sub>OPh<sup>-</sup> anion of 2.192 (20) Å. The W-O-C bond angles are 123.7 (8) and 128.4 (7)°. These angles are significantly smaller than the analogous bond angle in W(CO)<sub>5</sub>OPh<sup>-</sup> of 132.5°.

**Reactions with CO<sub>2</sub> and COS.** Complex 1 was found to be unreactive toward CO<sub>2</sub>. This lack of reactivity was determined by exposure of a solution of the aryloxy to carbon dioxide, both at atmospheric pressure and at high pressure (900 psi). No detectable shift in the ν(CO) region in the infrared was observed nor was there the appearance of a resonance in the <sup>13</sup>C NMR spectrum corresponding to a carbonate. On the other hand, in the cases where the M-O bond is reactive toward CO<sub>2</sub>, the alkyl or aryl carbonate is formed readily under mild conditions, room

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Table II. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for Complex 1

	x	y	z	U(eq) <sup>a</sup>		x	y	z	U(eq) <sup>a</sup>
O(400)	9080 (19)	4521 (17)	1105 (5)	292 (12)	C(104)	1501 (10)	2484 (11)	1877 (5)	52 (6)
C(400)	9771 (14)	4083 (13)	1402 (7)	179 (7)	O(104)	971 (9)	2231 (7)	1595 (3)	66 (5)
C(401)	9799 (19)	4684 (17)	1753 (5)	199 (11)	C(105)	3742 (10)	2509 (10)	2115 (4)	43 (5)
C(402)	8725 (23)	5087 (19)	1719 (7)	231 (14)	O(105)	4515 (8)	2336 (8)	1982 (3)	72 (5)
C(403)	8392 (17)	5128 (17)	1289 (8)	199 (12)	C(106)	2992 (10)	1399 (10)	2886 (4)	43 (5)
W(1)	2100 (1)	6435 (1)	5023 (1)	35 (1)	O(106)	2199 (6)	1906 (6)	2723 (3)	39 (3)
C(1)	3176 (12)	6958 (11)	5444 (5)	52 (6)	C(107)	3409 (11)	683 (9)	2679 (5)	44 (5)
O(1)	3762 (9)	7163 (8)	5715 (4)	80 (5)	C(108)	4268 (11)	206 (10)	2868 (5)	54 (6)
C(2)	992 (11)	6878 (10)	5359 (4)	46 (5)	C(109)	4664 (11)	399 (10)	2357 (5)	53 (6)
O(2)	345 (8)	7086 (8)	5570 (3)	70 (5)	C(110)	4253 (11)	1066 (10)	3467 (5)	55 (6)
C(3)	2165 (11)	5412 (10)	5348 (5)	47 (5)	C(111)	3413 (10)	1598 (9)	3294 (4)	38 (5)
O(3)	2270 (10)	4777 (8)	5564 (4)	81 (5)	C(112)	3721 (14)	2849 (10)	3781 (5)	58 (6)
C(4)	1004 (12)	5790 (11)	4662 (5)	55 (6)	C(113)	3344 (15)	3535 (12)	4008 (5)	68 (7)
O(4)	371 (9)	5350 (9)	4482 (4)	89 (6)	C(114)	2271 (15)	3734 (11)	3988 (5)	65 (7)
C(5)	3281 (11)	5821 (9)	4742 (4)	43 (5)	C(115)	1598 (14)	3213 (11)	3736 (5)	67 (7)
O(5)	3931 (8)	5420 (8)	4627 (3)	73 (5)	C(116)	1940 (12)	2537 (10)	3506 (5)	53 (6)
C(6)	2758 (9)	8056 (9)	4511 (4)	31 (4)	C(117)	3012 (11)	2363 (9)	3534 (4)	41 (5)
O(6)	1990 (6)	7576 (6)	4631 (3)	39 (3)	C(118)	1878 (12)	360 (10)	2188 (5)	51 (6)
O(7)	3222 (10)	7826 (9)	4160 (4)	35 (5)	C(119)	1447 (14)	76 (10)	1823 (5)	65 (7)
C(8)	4020 (10)	8363 (8)	4020 (4)	41 (5)	C(120)	2110 (16)	-116 (11)	1522 (6)	73 (8)
C(9)	4404 (10)	9109 (10)	4242 (4)	47 (5)	C(121)	3187 (16)	-45 (10)	1599 (5)	69 (7)
C(10)	3961 (9)	9317 (9)	4602 (5)	40 (5)	C(122)	3600 (13)	240 (9)	1972 (5)	58 (6)
C(11)	3145 (9)	8795 (7)	4731 (3)	25 (4)	C(123)	2954 (11)	451 (9)	2273 (5)	46 (5)
C(12)	3293 (12)	9271 (9)	5450 (5)	45 (6)	N(1)	2608 (7)	2687 (7)	280 (3)	36 (4)
C(13)	2846 (12)	9579 (9)	5791 (5)	49 (6)	C(200)	3095 (10)	2855 (9)	710 (4)	45 (5)
C(14)	1769 (12)	9661 (9)	5777 (5)	51 (6)	C(201)	3172 (12)	2044 (9)	982 (4)	59 (6)
C(15)	1121 (12)	9456 (10)	5436 (4)	50 (6)	C(202)	3246 (9)	1979 (10)	81 (4)	49 (5)
C(16)	1573 (11)	9165 (9)	5100 (5)	45 (5)	C(203)	4386 (9)	2220 (10)	30 (5)	69 (6)
C(17)	2667 (10)	9064 (9)	5099 (4)	35 (5)	C(204)	1488 (9)	2312 (9)	274 (4)	46 (5)
C(18)	1821 (10)	6827 (9)	3839 (4)	43 (5)	C(205)	733 (10)	2907 (10)	480 (5)	61 (6)
C(19)	1499 (13)	6102 (11)	3598 (5)	61 (6)	C(206)	2632 (10)	3552 (9)	63 (4)	49 (5)
C(20)	2284 (14)	5580 (11)	3433 (5)	60 (6)	C(207)	2222 (12)	3546 (10)	-373 (4)	66 (6)
C(21)	3354 (14)	5826 (9)	3504 (4)	53 (6)	N(2)	2217 (8)	7273 (7)	2226 (3)	45 (4)
C(22)	3650 (13)	6530 (10)	3738 (4)	51 (6)	C(301)	1572 (13)	7540 (11)	1833 (5)	75 (7)
C(23)	2874 (11)	7058 (10)	3918 (4)	42 (5)	C(302)	1476 (17)	6846 (12)	1513 (5)	113 (10)
W(2)	2430 (1)	3029 (1)	2335 (1)	35 (1)	C(303)	3331 (10)	6958 (10)	2151 (5)	72 (7)
C(101)	3419 (11)	3711 (11)	2743 (5)	49 (6)	C(304)	3989 (13)	7635 (12)	1956 (6)	109 (9)
O(101)	3997 (9)	4123 (9)	2948 (4)	75 (5)	C(305)	1688 (10)	6495 (9)	2410 (5)	58 (6)
C(102)	1173 (10)	3641 (10)	2564 (4)	43 (5)	C(306)	589 (10)	6645 (11)	2530 (5)	75 (7)
O(102)	506 (8)	4025 (8)	2678 (3)	70 (5)	C(307)	2268 (12)	8083 (9)	2482 (5)	56 (6)
C(103)	2542 (11)	4020 (11)	1988 (5)	55 (6)	C(308)	2822 (13)	7948 (11)	2899 (5)	78 (7)
O(103)	2623 (9)	4662 (8)	1776 (4)	73 (5)					

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table III. Bond Lengths from One of the Independent Anions of Complex 1 ( $\text{\AA}$ )

W(1)–C(2)	1.993 (15)	W(1)–C(1)	2.024 (15)
W(1)–C(4)	2.007 (16)	W(1)–C(3)	1.887 (15)
W(1)–O(6)	2.168 (9)	W(1)–C(5)	2.061 (14)
C(2)–O(2)	1.173 (19)	C(1)–O(1)	1.160 (19)
C(4)–O(4)	1.165 (20)	C(3)–O(3)	1.205 (19)
C(6)–O(6)	1.306 (19)	C(5)–O(5)	1.120 (18)

Table IV. Bond Angles from One of the Independent Anions of Complex 1 (deg)

C(1)–W(1)–C(3)	86.1 (6)	C(1)–W(1)–C(2)	86.1 (6)
C(1)–W(1)–C(4)	172.3 (7)	C(2)–W(1)–C(3)	87.0 (6)
C(3)–W(1)–C(4)	86.5 (6)	C(2)–W(1)–C(4)	91.1 (6)
C(2)–W(1)–C(5)	171.1 (6)	C(1)–W(1)–C(5)	91.4 (6)
C(4)–W(1)–C(5)	89.7 (6)	C(3)–W(1)–C(5)	84.2 (6)
C(2)–W(1)–O(3)	93.7 (5)	C(1)–W(1)–O(6)	96.3 (5)
C(4)–W(1)–O(6)	91.1 (5)	C(3)–W(1)–O(6)	177.5 (5)
W(1)–C(1)–O(1)	171.0 (14)	C(5)–W(1)–O(6)	95.2 (5)
W(1)–C(3)–O(3)	175.7 (13)	W(1)–C(2)–O(2)	175.5 (13)
W(1)–C(5)–O(5)	171.7 (12)	W(1)–C(4)–O(4)	173.0 (14)
W(1)–O(6)–C(6)	128.4 (7)		

temperature and 1 atm of CO<sub>2</sub>. For example, the reaction of CO<sub>2</sub> with W(CO)<sub>5</sub>OPh<sup>−</sup> is complete within 30 min.<sup>5,7</sup>

By comparison, the reaction of COS with the W(CO)<sub>5</sub>OR<sup>−</sup> (R = Ph and 2,6-Ph<sub>2</sub>Ph) derivatives occurs rapidly under conditions identical with those for CO<sub>2</sub> to form the alkyl or aryl monothiocarbonate product. The insertion reaction with the M–O bond is rapid and is complete in 2 min upon exposure of the solution to an atmosphere of COS. Though, unlike the CO<sub>2</sub> insertion

reaction, the COS reaction is irreversible.

Both insertion products have been spectroscopically characterized. In either case upon reaction with CO<sub>2</sub> or COS the infrared band pattern of the carbonyl region for monomeric complex shifts to higher energy. This is expected on the basis of the lesser donating ability of the formed insertion products relative to the aryloxide. For example, the complex W(CO)<sub>5</sub>OPh<sup>−</sup> displays an infrared spectrum in the  $\nu(\text{CO})$  region containing three bands characteristic of the  $C_{4v}$  symmetry of the pentacarbonyl moiety. The bands for W(CO)<sub>5</sub>OPh<sup>−</sup> are at 2057 (w), 1904 (s), and 1852 (m) cm<sup>−1</sup>, which upon reaction with CO<sub>2</sub> and COS shift to 2063 (w), 1913 (s), 1854 (m), and 2059 (w), 1916 (s), 1859 (m) cm<sup>−1</sup>, respectively.

More conclusive in the characterization has been the appearance of a very diagnostic resonance in the <sup>13</sup>C NMR spectrum of the formed carbonate or thiocarbonate. This resonance is a good indication for the insertion reaction because the resonance falls within a characteristic range for carbonates, of 155–170 ppm, as compared to that for free CO<sub>2</sub> of 124 ppm. This resonance has been found to be relatively uninfluenced by varying substituents on either the metal or the alkyl and aryl groups.<sup>11</sup>

**Structure of [Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (3).** The complex [Et<sub>4</sub>N][W(CO)<sub>5</sub>SC(O)O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] crystallized in

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**Table V.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for Complex 3

	x	y	z	$U(\text{eq})^a$
W	5451 (1)	7500	5255 (1)	35 (1)
S	4461 (3)	7500	6483 (2)	40 (1)
C(1)	6110 (15)	7500	4297 (10)	51 (6)
O(1)	6470 (15)	7500	3716 (8)	90 (6)
C(2)	6583 (9)	6518 (8)	5547 (6)	47 (4)
O(2)	7235 (7)	5984 (6)	5673 (6)	78 (4)
C(3)	4365 (10)	6492 (9)	4927 (7)	53 (4)
O(3)	3823 (8)	5918 (7)	4730 (6)	89 (4)
C(4)	3030 (11)	7500	6286 (8)	29 (4)
O(4)	2586 (7)	7500	5710 (5)	35 (3)
O(5)	2395 (7)	7500	6912 (5)	35 (3)
C(6)	1186 (11)	7500	6800 (8)	37 (5)
C(7)	639 (8)	6678 (7)	6780 (6)	36 (3)
C(8)	-559 (8)	6696 (8)	6717 (6)	44 (4)
C(9)	-1104 (12)	7500	6686 (9)	47 (6)
C(10)	2061 (9)	5489 (8)	6433 (7)	50 (4)
C(11)	2555 (10)	4646 (8)	6538 (8)	57 (5)
C(12)	2197 (13)	4125 (10)	7076 (9)	78 (6)
C(13)	1352 (17)	4391 (10)	7526 (10)	95 (7)
C(14)	881 (12)	5234 (9)	7418 (8)	73 (5)
C(15)	1188 (9)	5773 (8)	6872 (6)	47 (4)
N	693 (14)	7056 (11)	4069 (9)	38 (6)
C(16)	1662 (18)	7500	4002 (14)	107 (12)
C(17)	1483 (27)	8452 (19)	3477 (15)	59 (11)
C(18)	713 (21)	6547 (19)	3389 (14)	50 (9)
C(19)	1870 (22)	6019 (21)	3302 (18)	79 (13)
C(20)	874 (20)	6474 (16)	4687 (13)	51 (8)
C(21)	55 (22)	5648 (17)	4768 (14)	62 (9)
C(22)	-509 (13)	7500	4064 (10)	50 (6)
C(23)	-719 (22)	8074 (21)	4701 (16)	85 (12)

<sup>a</sup>Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table VI.** Bond Lengths from the Anion of Complex 3 ( $\text{\AA}$ )

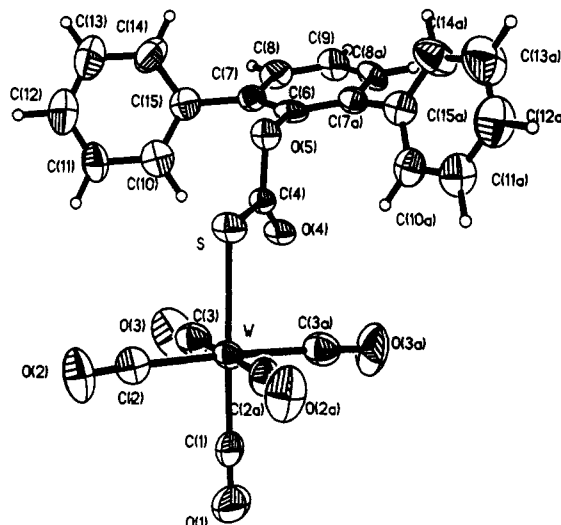
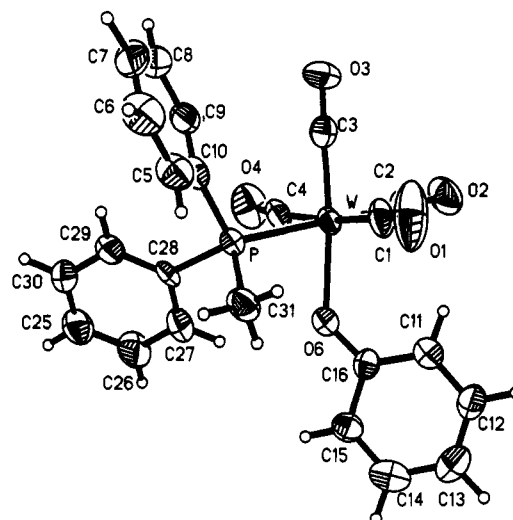
W-S	2.582 (4)	W-C(1)	1.957 (19)
W-C(2)	2.052 (11)	W-C(3)	2.064 (13)
W-C(2A)	2.052 (11)	W-C(3A)	2.064 (13)
S-C(4)	1.729 (13)	C(1)-O(1)	1.169 (25)
C(2)-O(2)	1.130 (14)	C(3)-O(3)	1.128 (16)
C(4)-O(4)	1.200 (17)	C(4)-O(5)	1.393 (17)
O(5)-C(6)	1.442 (16)		

**Table VII.** Bond Angles from the Anion of Complex 3 (deg)

S-W-C(1)	176.5 (5)	S-W-C(2)	93.3 (3)
C(1)-W-C(2)	89.2 (5)	S-W-C(3)	89.1 (3)
C(1)-W-C(3)	88.5 (5)	C(2)-W-C(3)	88.2 (5)
S-W-C(2A)	93.3 (3)	C(1)-W-C(2A)	89.2 (5)
C(2)-W-C(2A)	90.5 (6)	C(3)-W-C(2A)	177.4 (5)
S-W-C(3A)	89.1 (3)	C(1)-W-C(3A)	88.5 (5)
C(2)-W-C(3A)	177.4 (5)	C(3)-W-C(3A)	92.9 (7)
C(2A)-W-C(3A)	88.2 (5)	W-S-C(4)	104.6 (5)
W-C(1)-O(1)	177.9 (17)	W-C(2)-O(2)	176.3 (11)
W-C(3)-O(3)	176.0 (10)	S-C(4)-O(4)	128.2 (11)
S-C(4)-O(5)	110.2 (10)	O(4)-C(4)-O(5)	121.6 (11)
C(4)-O(5)-C(6)	114.2 (10)		

the orthorhombic space group  $Pcmm$  (No. 62). The anion is illustrated in Figure 2 with its atomic labeling scheme. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table V, whereas bond distances and bond angles are provided in Tables VI and VII.

The geometry around the tungsten atom is again that of a distorted octahedron. In this structure there is no apparent steric influence from the phenyl rings with the equatorial carbonyls in that they have returned to an almost idealized plane. The W-S bond distance in the anion is 2.582 (2)  $\text{\AA}$ , which is anticipated for an anionic W-S bond. For example, the W-S bond length in  $W(\text{CO})_5\text{SH}^-$  has been found to be 2.567 (5)  $\text{\AA}$ .<sup>12</sup> A distance of 3.487  $\text{\AA}$  found for the W and O(4) separation supports a

**Figure 2.** ORTEP diagram of the anion of  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{SC}(\text{O})\text{O}-2,6\text{-Ph}_2\text{-C}_6\text{H}_3]$  (3), showing 50% probability thermal motion ellipsoids with atomic labeling scheme.**Figure 3.** ORTEP diagram of the anion of  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_4(\text{PPh}_2\text{Me})(\text{OPh})]$  (2), showing 50% probability thermal motion ellipsoids with atomic labeling scheme.

nonbonding  $W\cdots\text{O}$  interaction. The C-O(4) bond was found to be 1.20 (2)  $\text{\AA}$ , typical of carboxylic esters. This distance is also similar to the C-O distance found for the complexes  $\text{Cr}(\text{CO})_4\text{SC}(\text{O})\text{H}^-$ <sup>13</sup> and  $\text{trans-}[\text{PtH}(\text{OC}(\text{O})\text{OCH}_3)(\text{PCy}_3)_2]$ <sup>14</sup> of 1.21 and 1.206 (6)  $\text{\AA}$ , respectively. Also, the C-S bonds of  $\text{Cr}(\text{CO})_5\text{SC}(\text{O})\text{H}^-$  and  $W(\text{CO})_5\text{SC}(\text{O})\text{O}-2,6\text{-Ph}_2\text{-C}_6\text{H}_3^-$  are comparable at 1.725 (5) and 1.729 (13)  $\text{\AA}$ , respectively. A W-S-C angle of 104.6 (6) $^\circ$  was found for complex 3, which is significantly different from the corresponding Pt-O-C angle of 122.2 (7) $^\circ$  found in the methyl carbonate. This difference in angles is as expected on the basis of an increase in p character for the hybridization around the sulfur atom.<sup>15</sup>

**Synthesis of  $[\text{Et}_4\text{N}][\text{cis-}W(\text{CO})_4(\text{PPh}_2\text{Me})(\text{OPh})]$  (2).** The phosphine anion,  $\text{cis-}W(\text{CO})_4(\text{PPh}_2\text{Me})(\text{OPh})^-$ , was synthesized by the addition of 3 equiv of the phosphine to a solution of  $W(\text{CO})_5\text{OPh}^-$ . The facility of CO displacement from the cis position provided for exclusive production of the cis product. Upon removal of excess phosphine by washing with hexane there was the appearance in the infrared spectrum of a small concentration of the monosubstituted  $W(\text{CO})_5\text{OPh}^-$  species. This is presumed

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**Table VIII.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for Complex 2

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
W	1931 (1)	2480 (1)	4342 (1)	34 (1)
C(1)	653 (8)	1677 (6)	4451 (7)	51 (4)
O(1)	-45 (7)	1203 (5)	4502 (7)	113 (5)
C(2)	685 (9)	3309 (6)	4260 (7)	55 (4)
O(2)	-71 (7)	3788 (4)	4169 (5)	72 (3)
C(3)	1399 (9)	2354 (5)	3188 (7)	46 (4)
O(3)	1028 (7)	2286 (5)	2468 (5)	70 (3)
C(4)	3196 (8)	3235 (6)	4111 (6)	45 (3)
O(4)	3914 (7)	3642 (5)	3909 (6)	81 (4)
P	3464 (2)	1370 (1)	4490 (2)	33 (1)
C(5)	3384 (9)	-90 (5)	3639 (7)	54 (4)
C(6)	3384 (10)	-533 (6)	2954 (8)	66 (5)
C(7)	3431 (9)	-165 (7)	2232 (7)	65 (5)
C(8)	3435 (9)	649 (6)	2177 (7)	60 (4)
C(9)	3433 (8)	1085 (5)	2874 (6)	46 (3)
C(10)	3411 (8)	728 (5)	3608 (6)	40 (3)
O(6)	2711 (6)	2534 (3)	5645 (3)	45 (2)
C(11)	970 (8)	2608 (5)	6230 (6)	48 (3)
C(12)	479 (9)	2598 (6)	6917 (6)	60 (4)
C(13)	1192 (11)	2463 (6)	7672 (7)	62 (4)
C(14)	2424 (11)	2349 (5)	7731 (7)	57 (4)
C(15)	2923 (9)	2362 (5)	7044 (6)	43 (3)
C(16)	2182 (8)	2491 (5)	6266 (5)	36 (3)
N	3521 (7)	4857 (4)	6805 (5)	49 (3)
C(17)	2879 (10)	5330 (7)	6059 (7)	70 (5)
C(18)	2028 (13)	4863 (9)	5429 (10)	137 (8)
C(19)	4327 (10)	5427 (6)	7304 (7)	65 (4)
C(20)	5061 (13)	5092 (10)	8107 (9)	134 (9)
C(21)	4241 (10)	4175 (6)	6570 (9)	88 (6)
C(22)	5183 (10)	4397 (7)	6069 (8)	85 (6)
C(23)	2612 (11)	4507 (7)	7233 (9)	89 (6)
C(24)	1809 (2)	5079 (2)	7539 (8)	92 (6)
C(25)	7506 (10)	2048 (7)	5267 (7)	65 (5)
C(26)	6661 (10)	2320 (6)	5686 (8)	66 (5)
C(27)	5432 (9)	2124 (7)	5439 (7)	56 (4)
C(28)	5074 (7)	1636 (5)	4766 (5)	38 (3)
C(29)	5908 (8)	1367 (6)	4355 (6)	47 (3)
C(30)	7141 (9)	1576 (6)	4602 (6)	55 (4)
C(31)	3342 (8)	705 (5)	5305 (6)	50 (4)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U<sub>ij</sub>* tensor.

**Table IX.** Bond Lengths from the Anion of Complex 2 (Å)

W–C(1)	2.021 (10)	W–C(2)	1.974 (10)
W–C(3)	1.924 (11)	W–C(4)	2.018 (10)
W–P	2.532 (3)	W–O(6)	2.191 (6)
C(1)–C(1)	1.142 (13)	C(2)–O(2)	1.165 (13)
C(3)–O(3)	1.204 (13)	C(4)–O(4)	1.171 (13)
P–C(10)	1.835 (10)	P–C(28)	1.836 (8)
P–C(31)	1.806 (10)		

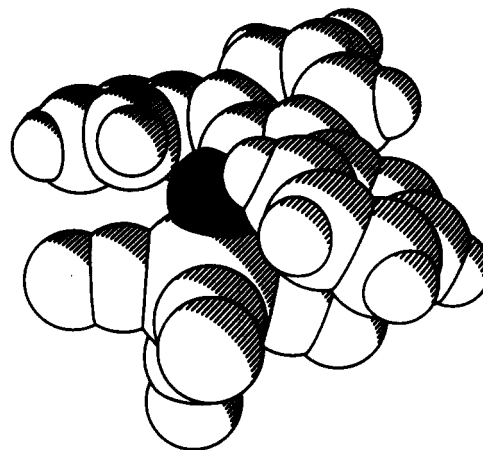
to be due to phosphine dissociation from the complex in solution followed by reaction with CO present in solution to re-form the monomer. Indeed exposure of *cis*-W(CO)<sub>4</sub>(PR<sub>3</sub>)OPh<sup>-</sup> to CO results in re-formation of the W(CO)<sub>5</sub>OPh<sup>-</sup> anion.

**Structure of [Et<sub>4</sub>N][*cis*-W(CO)<sub>4</sub>(PPh<sub>2</sub>Me)(OPh)] (2).** The complex was structurally characterized in order to further study the steric interactions of the phosphine substituent relative to the reactive lone pairs on the ligated oxygen atom. This complex crystallized in the space group *P2<sub>1</sub>/n*. The anion with atomic labeling scheme is illustrated in Figure 3. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table VIII, whereas bond distances and bond angles are provided in Tables IX and X.

Steric interaction is obvious in the crystal structure in that the lone pairs on the oxygen point toward the phosphine due to the steric requirements of the aryl group of the ligated aryloxy and the bulky phosphine. Furthermore, the phosphine ligand is oriented with the less bulky methyl substituent pointing toward the lone pairs to minimize steric interference. The tungsten–oxygen bond distance in this anion is 2.191 (6) Å. This distance is identical with the W–O bond distance in the W(CO)<sub>5</sub>OPh<sup>-</sup> anion

**Table X.** Bond Angles from the Anion of Complex 2 (deg)

C(1)–W–C(2)	88.3 (4)	C(1)–W–C(3)	86.8 (4)
C(2)–W–C(3)	86.8 (4)	C(1)–W–C(4)	173.8 (4)
C(2)–W–C(4)	93.5 (4)	C(3)–W–C(4)	87.4 (4)
C(1)–W–P	88.8 (3)	C(2)–W–P	176.8 (3)
C(3)–W–P	94.4 (3)	C(4)–W–P	89.5 (3)
C(1)–W–O(6)	94.5 (4)	C(2)–W–O(6)	99.7 (4)
C(3)–W–O(6)	173.4 (3)	C(4)–W–O(6)	91.0 (3)
P–W–O(6)	79.2 (2)	W–C(1)–O(1)	177.5 (9)
W–C(2)–O(2)	176.4 (9)	W–C(3)–O(3)	177.8 (9)
W–C(4)–O(4)	173.9 (9)	W–P–C(10)	117.2 (3)
W–P–C(28)	117.6 (3)	W–P–C(31)	112.1 (3)



**Figure 4.** Space-filling model of the anion of 1 utilizing van der Waals radii, demonstrating the crowded environment around the metal–oxygen center.

of 2.192 (20) Å. The W–O–C bond angle is 130.1 (5)°, which is quite similar to the corresponding angle in W(CO)<sub>5</sub>OPh<sup>-</sup> of 132.5°. This implies that even though the phosphine ligand is a better electron donor as compared to CO, any increased electron density on the tungsten center has negligible influence on the ligation of the aryloxy moiety, both with respect to bond length and bond angle.

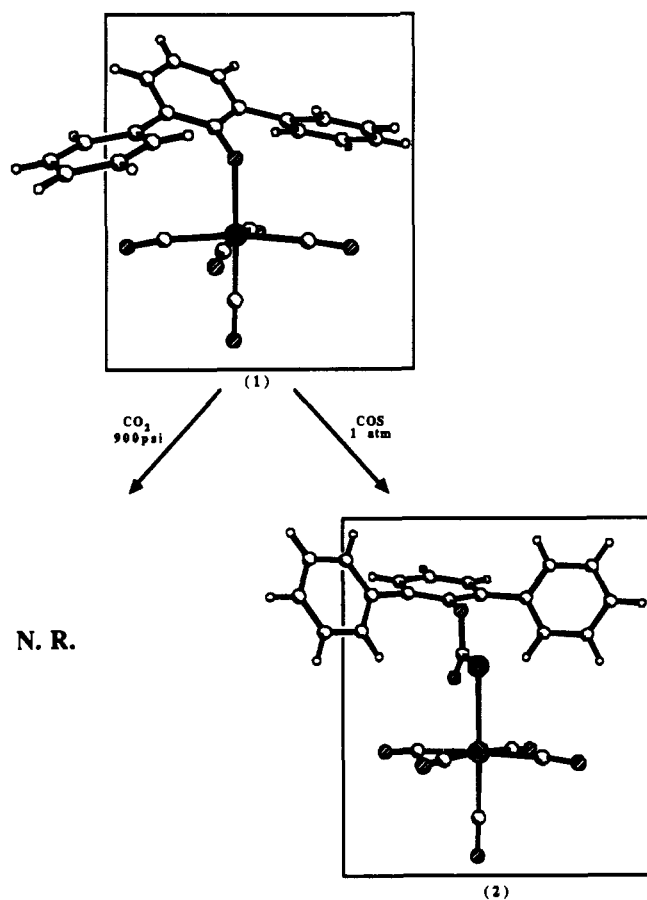
### Discussion

The sterically crowded aryloxy complex [Et<sub>4</sub>N][W(CO)<sub>5</sub>O-2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>] (see Figure 4 for the space-filling model of 1) has been shown by IR and <sup>13</sup>C NMR spectroscopies to be unreactive toward CO<sub>2</sub> even at pressures of carbon dioxide sufficient to induce its condensation at room temperature. By way of contrast the sterically unhindered but electronically quite similar complex<sup>16</sup> [Et<sub>4</sub>N][W(CO)<sub>5</sub>OPh] undergoes a facile, reversible insertion reaction with CO<sub>2</sub> at ambient temperature and atmospheric pressure to afford the corresponding phenyl carbonate complex.<sup>5</sup> This lack of CO<sub>2</sub> reactivity in the diphenyl derivative is presumed to be due to the steric interference of the phenyl rings around the metal–oxygen bond. The complex 1, however, reacts rapidly with 1 atm of COS to yield the tungsten–aryl thiocarbonate insertion product (Scheme 1). Upon comparison of structure 1 and the structure of the insertion product, 3, there is an obvious release of the steric interaction. In 1 the phenyl rings are forced parallel to the equatorial plane of the “W(CO)<sub>5</sub>” fragment. After insertion the entire aryl group in 3 is moved away from the W(CO)<sub>5</sub> fragment and the steric interaction is relieved, which allows the phenyl rings to orient directly toward the equatorial carbonyls.

These results are consistent with evidence from other experiments where bulky phosphine-substituted derivatives *cis*-M-(CO)<sub>4</sub>(PR<sub>3</sub>)(OPh)<sup>-</sup> reacted more slowly with CO<sub>2</sub> than their unsubstituted analogues. This retardation in rate is due to the fact that the metal–oxygen reaction center is made sterically less

(16) The electronic similarity in these two phenoxide derivatives is manifested in their  $\nu(\text{CO})$  spectra (2057, 1904, 1852 and 2054, 1905, 1835  $\text{cm}^{-1}$ ), <sup>13</sup>C NMR spectra (200.0, 203.6 and 200.0, 204.4 ppm), and W–O bond distances (2.192 (20) and 2.171 (9) Å) for the phenoxide and 2,6-diphenylphenoxide derivative, respectively.

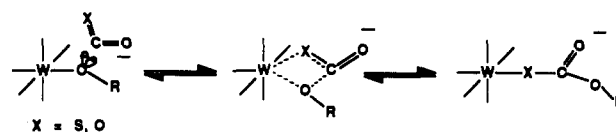
Scheme I



accessible through *cis* substitution. Although carbon dioxide insertion into the  $(\text{CO})_5\text{CrOPh}^-$  complex is faster than for the tungsten analogue, a reversal in the order of the rates of reactivity is observed upon *cis* phosphine substitution (i.e.,  $\text{W} > \text{Cr}$ ). It was also found that for the *cis*- $(\text{CO})_4\text{W}(\text{L})\text{OPh}^-$  complexes the relative rate of reaction with  $\text{CO}_2$  follows  $\text{L} = \text{CO} \gg \text{P}(\text{OMe})_3 > \text{PMe}_3 > \text{PPH}_3$ , which parallels an increase in the L's cone angle.<sup>5</sup> The solid-state structure of one of these *cis*-phosphine-substituted derivatives, *cis*- $\text{W}(\text{CO})_4(\text{PPH}_2\text{Me})(\text{OPh})^-$ , was performed. The structure reveals obvious steric interaction in that the phenoxide adopts a conformation that places its lone pairs in the direction of the phosphine ligand (Figure 3). In other words, the incoming  $\text{CO}_2$  molecule encounters steric interference upon approach to the metal-oxygen center from the phosphine on the substituted species that it does not experience in the pentacarbonyl derivative. This reduced reactivity toward  $\text{CO}_2$  is counter to what would be expected on the basis of the increased electron donation from phosphines vs carbonyls. The more donating phosphines should increase the electron density on the tungsten center thus making the phenoxide ligand more basic and more prone to reaction with  $\text{CO}_2$ . This is indeed the case for the analogous  $\text{CO}_2$  insertion reactions involving tungsten-alkyl derivatives, where substitution of phosphines for CO significantly accelerate the rate of  $\text{CO}_2$  insertion into the W-R bond.<sup>17</sup> Thus, in the case of metal aryloxides where there is directed reactivity of the  $\text{CO}_2$  toward

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Scheme II



the lone pairs on the oxygen, steric influences are important but in the instance where there is no directionality to the  $\text{CO}_2$  approach for insertion, as in metal alkyls, steric hindrance is less important and electronic effects determine the energetics of the process.

As mentioned, in an alternative approach to studying carbon dioxide activation these aryloxide complexes have been reacted with COS and  $\text{CS}_2$  as models for  $\text{CO}_2$ .<sup>5,18</sup> The proposed mechanism for insertion involves the prior interaction of the Lewis acid site carbon of  $\text{CO}_2$  with the lone pairs on the alkoxide oxygen followed by a concerted transformation to a four-centered transition state (Scheme II). This four-centered transition state appears not to require an open coordination site. Evidence for this arises from the independence of the rate of insertion on added CO.<sup>5</sup> Furthermore, when the carboxylation reaction is carried out in a large excess of carbon monoxide, no  $\text{W}(\text{CO})_6$  is formed during the reaction, strongly supportive of a process involving insertion of  $\text{CO}_2$  at the metal-oxygen center.<sup>5</sup>

An aspect of the mechanism that changes significantly in switching from  $\text{CO}_2$  to COS is the M-O interaction vs the corresponding M-S interaction (M-X interaction, Scheme II). The metal-sulfur interaction in the transition state is expected to be stronger than the corresponding metal-oxygen interaction. Additionally, the carbon-sulfur double bond in COS, which is weakened in the transition state, is inherently weaker than the carbon-oxygen double bond in  $\text{CO}_2$  ( $\Delta\text{CO}$  in  $\text{CO}_2$  is 126 kcal/mol vs  $\Delta\text{CS}$  in COS, which is 72 kcal/mol).<sup>18c,19</sup> Hence, all of these factors lead to a destabilization of the transition state in those instances where there is a weak aryloxide-carbon dioxide interaction without a concomitant strong M-X interaction. This is indeed the case for  $\text{CO}_2$  insertion into a M-OR bond when the R substituent is sterically encumbering. The M-S involvement in the COS's reactivity vs  $\text{CO}_2$ 's is supported by the fact that its insertion into complexes  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OR}]$  is irreversible while the analogous carbonates formed in these cases readily decarboxylate to re-form the alkoxide or aryloxide metal complexes.<sup>5</sup> Thus it should be concluded that  $\text{CO}_2$  does not react with compound 1 due to steric reasons and that the difference between 1's reactivity with  $\text{CO}_2$  vs COS is not steric but due to inherent differences in the sulfur atom vs oxygen atom's bonding nature. Further, it can be concluded that carbonyl sulfide and carbon disulfide are not especially good models for  $\text{CO}_2$ .

**Acknowledgment.** The financial support of this research by the National Science Foundation (Grant 88-17873) is greatly appreciated.

**Supplementary Material Available:** Tables of bond distances and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{O}-2,6\text{-Ph}_2\text{-C}_6\text{H}_3]$ ,  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{SC}(\text{O})\text{O}-2,6\text{-Ph}_2\text{-C}_6\text{H}_3]$ , and  $[\text{Et}_4\text{N}][\text{W}(\text{CO})_4(\text{PPH}_2\text{Me})(\text{OPh})]$  (14 pages); listings of calculated and observed structure factors (72 pages). Ordering information is given on any current masthead page.

- (18) (a) Lee, G. R.; Cooper, N. J. *Organometallics* **1989**, *8*, 1538. (b) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956. (c) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57.
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