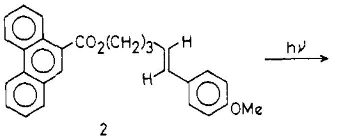

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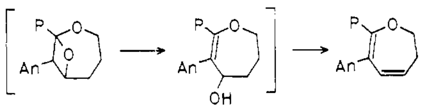

13 14 11

was no spot in the TLC of either reaction mixture that could be ascribed to a cyclobutane adduct. The only unidentified spots showed $R_f \sim 0$ and corresponded to small amounts of material. The products **10** and **11** can be rationalized by the initial formation of **12** and **13**, respectively, analogous to the **3** → **8** reaction, followed by obvious polar rearrangements and (for **11**) dehydration. That **10** and **11** are not primary photoproducts is shown by their absence in TLC of reaction mixtures.

Disappearance quantum yields and photophysical parameters for **1**–**4** are given in Table I.[9] The lower ϕ_f and shorter τ_f for **1**–**3** compared to **4** clearly demonstrate dominant intramolecular singlet interaction between the chromophores, and the high ϕ(disapp) values confirm its ultimate chemical nature. That exciplexes are indeed intermediates in at least the formation of the oxetanes from **1** and **2** is strongly suggested by a 10–20% greater quenching of product formation than of the phenanthroate fluorescence by molecular oxygen.[10]

Formation of cycloadducts is very efficient from the exciplexes. The lifetimes in the table and the reasonable assumption of a structure-independent fluorescence rate constant for the phenanthroate chromophore afford intramolecular quenching probabilities for **1**, **2**, and **3** of 0.74, 0.80, and 0.69. The corresponding exciplex → product probabilities are 0.49, 0.76, and 1.0, respectively.

That structures so different as cyclobutanes **6** and **7** and oxetanes **8** and **13** arise from exciplexes with identical fluorescence maxima suggests that the energies of these exciplexes are rather insensitive to their geometries. The intramolecular cycloadditions of McCullogh behave analogously.[3] Various photophysical measurements for intramolecular exciplexes[11] afford the same conclusion.

We believe that the strong preference for oxetane rather than cyclobutane formation from **1**–**3** arises from the conformational constraints of the aroyl ester group.[12-16] Esters in general strongly prefer a conformation for the C–O single bond in which the alkyl group and carbonyl oxygen are cis and the carbonyl and *O*-alkyl bonds are coplanar.[12-16] In all such conformations, the formation of cyclobutane is precluded as can readily be seen from Dreiding models. That **7** forms at all is evidence that this conformation is not absolutely enforced. It is also possible that restricted rotation around the phenanthrene–carbonyl bond[17] contributes to the disfavoring of cyclobutane formation, since models show that such rotation is probably necessary for close approach of the C═C double bonds. Finally, the models show that access of the carbonyl oxygen to the β position of the *p*-methoxystyryl moiety, which leads to all the oxetanes, can be accomplished in the favored conformation of the ester C–O single bond without serious difficulty.

Acknowledgment. We thank Dr. Takashi Tamaki, Research Institute for Polymers and Textiles, for valuable assistance with the fluorescence studies. R.A.C. acknowledges helpful conversations with Professor M. A. Winnik. Work at The University of Tsukuba was financially supported in part by a Grant-in-aid from the Ministry of Education, Science, and Culture of Japan. Work at the University of Texas at Dallas was partially supported by The Robert A. Welch Foundation (Grant AT-532).

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[9] Fluorescence lifetimes and quantum yields of esters A-1, A-4, B-1, B-3, and B-4 were also measured. Intramolecular fluorescence quenching was ineffective for all compounds except for B-3. Ester B-3 was similar to B-2 in photochemical and photophysical behavior according to preliminary results. Ester A-4 showed weak exciplex emission, but preparative irradiation[5] afforded almost quantitative recovery of starting material even on prolonged irradiation.

(10) Saltiel, J.; Townsend, D. *J. Am. Chem. Soc.* **1973**, *95*, 6140. Caldwell, R. A.; Smith, L. *Ibid.* **1974**, *96*, 2994.

(11) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press; London, 1979; Vol. 2, pp 1–78, and references therein. See especially pp 37 ff.

(12) Lowe, J. P. *Prog. Phys. Org. Chem.* **1968**, *6*, 1.

(13) Lister, D. G.; McDonald, J. N.; Owen, N. L. "Internal Rotation and Inversion"; Academic Press: London, 1978.

(14) Riveros, J. M.; Wilson, E. B., Jr. *J. Chem. Phys.* **1967**, *46*, 4605.

(15) Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529.

(16) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.

(17) Although apparently undocumented for esters, the analogous restriction for benzaldehydes and acetophenones is well-known,[13,14] as is its relevance to aryl ketone photochemistry.[18]

(18) Wagner, P. J.; Chen, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 239. Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1977**, *99*, 7713.

Evidence for Oxide Transfer from Coordinated CO_2 to Coordinated CO in an Anionic CO_2 Complex

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We recently reported that CO_2 could be reduced to coordinated CO by reaction with transition-metal carbonylate dianions and suggested that the reactions might involve formation of intermediate carbon dioxide complexes such as $[W(CO)_5CO_2]^{2-}$ ($\mathbf{1}^{2-}$, eq 1).[1] We now report experiments that support the intermediacy

$$\underset{\mathbf{2}^{2-}}{[W(CO)_5]^{2-}} \xrightarrow{CO_2} \underset{\mathbf{1}^{2-}}{[W(CO)_5CO_2]^{2-}} \xrightarrow{CO_2} \underset{\mathbf{3}}{[W(CO)_6]} + CO_3^{2-} \quad (1)$$

of a species with a composition corresponding to that of $\mathbf{1}^{2-}$ in the reaction of $Li_2[W(CO)_5]$ ($Li_2\mathbf{2}$) with CO_2, spectral studies consistent with its formulation as an η^1-CO_2 complex, and labeling studies that suggest that transfer of oxide from coordinated CO_2 to coordinated CO is facile in this anionic complex.

The infrared spectrum shown in Figure 1 is obtained when 1 equiv of CO_2 is added slowly (30 min) to a 0.05 M solution of $Li_2[W(CO)_5$1[2] in tetrahydrofuran (THF) at −78 °C and the mixture allowed to warm to room temperature. The spectra of such solutions have been observed to remain unchanged after storage for 40 h at 0 °C, and since the characteristic absorptions of $Li_2\mathbf{2}$ are not observed[4] and only small quantities of $[W(CO)_6]$ have been formed, this suggests the formation of a relatively thermally stable complex whose composition is that of the simple CO_2 adduct $Li_2[W(CO)_5CO_2]$ ($Li_2\mathbf{1}$).

The spectrum in Figure 1 is consistent with formulation of $\mathbf{1}^{2-}$ as a species with C_{4v} symmetry.[5,6] The absorptions at 1899 (vs) cm^{-1} and 1865 (s) cm^{-1} can be assigned to the IR-active E symmetry stretch of the equatorial carbonyls and the A_1 symmetry stretch of the axial carbonyl, respectively, in agreement with the relative intensities of the bands, while the weak band at 2043 cm^{-1} can be assigned to the A_1 stretching mode of the equatorial

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† Fellow of the Alfred P. Sloan Foundation, 1982–1984.

(1) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604.

(2) Typically prepared on a 1-mmol scale by lithium napthalide reduction of $[W(CO)_5NMe_3]$.[3]

(3) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215.

(4) $Li_2[W(CO)_5]$:[3] 1820 (vs), 1775 (s, sh), 1690 (s), 1608 (s).

(5) Orgel, L. E. *Inorg. Chem.* **1962**, *1*, 25.

(6) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975; Chapter 7 and references therein.

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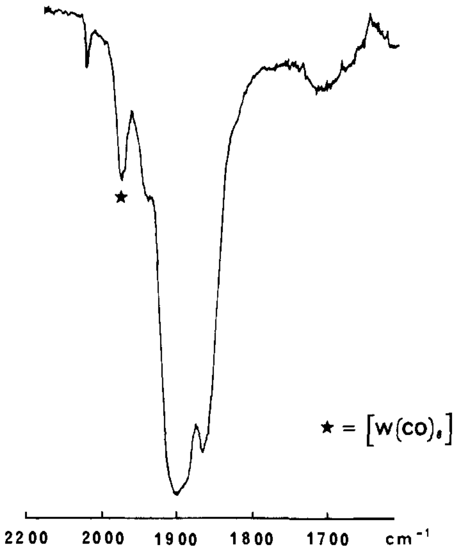


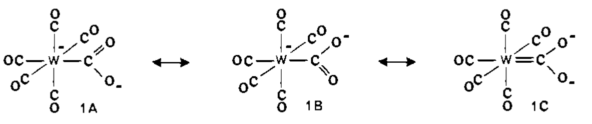
Figure 1. IR spectrum resulting from reaction of $Li_2[W(CO)_5]$ in THF with 1 equiv of CO_2 at −78 °C.

Table I. Chemical Shifts and W–C Coupling Constants for Carbon Ligands Bonded Directly to the Pentacarbonyl Tungsten Moiety

	δ C	J_{W-C}, Hz	T, K	ref
$Li_2[W(CO)_5CO_2]$	223.4	93	200	this work[a]
$[W(CO)_5C(OMe)Ph]$[13a]	321.7	111	298	this work[a]
$[W(CO)_5C(OEt)C{\equiv}CPh]$	286.1	102.5		12
$[W(CO)_5CPh_2]$[13b]	356.5	96	240	this work[a]
$[W(CO)_5COCH_3]NEt_4$[13a,7]	275.9	76	298	this work[a]
$[W(CO)_5CH_3]NEt_4$[13c]	−34.6	44	298	this work[a]

[a] Recorded in THF at 75.47 MHz, calibrated by using the carbonyl resonance of $(CD_3)_2CO$ at 206 ppm as an external standard.

carbonyls. The spectrum is remarkably similar to that of the acyl anion $[W(CO)_5COCH_3]^-$, with reported absorptions[7] at 2045 (w), 1969 (w sh), 1889 (vs), and 1866 (vs) cm^{-1}, while the major absorptions occur at lower frequencies than those of neutral carbene complexes with two heteroatomic substituents.[8] These data suggest that **1**$^{2-}$ is an η^1-CO_2 complex (eq 2) analogous to



(2)

the monoanionic Co complex, reported by Floriani,[9] which is the only example of a structurally characterized η^1-CO_2 complex. As in the case of the Co complex, interaction with the cation probably plays a crucial role in the bonding within the complex: the difference between cation interactions with monoanionic and with dianionic substrates may be responsible for the failure to observe (within the window above 1400 cm^{-1} allowed by the solvent) an IR absorption assignable to the CO_2 ligand corresponding to that reported for the Co complex at 1650 cm^{-1}.[9]

The formation of a single major species in the reaction with CO_2, and its formulation as an η^1-CO_2 complex, is supported by ^{13}C NMR spectra. When Li_2**1** is prepared from $^{13}CO_2$ (93%) the NMR spectrum (Figure 2) contains only one major ^{13}C resonance, which must arise from a C bonded directly to W since it has ^{183}W satellites with a large W–C coupling constant of 93 Hz. Comparison of this value with those reported in Table I for other complexes of $[W(CO)_5]$ containing single and double metal–carbon bonds suggests that there is a significant π component to the bond (canonical 1C).[10] This is consistent with the low-field position of the resonance: although it occurs at higher field than the resonances of the sp^2 carbons in the acyl complex and the carbene complexes, the CO_2 carbon is strongly deshielded relative to the sp^3 carbon of the methyl tungstate (Table I). The CO_2 carbon resonates at a somewhat lower field in $[PtCl(CO_2H)(PEt_3)_2]$,[14] which should have a similar metal–carbon bonding interaction.

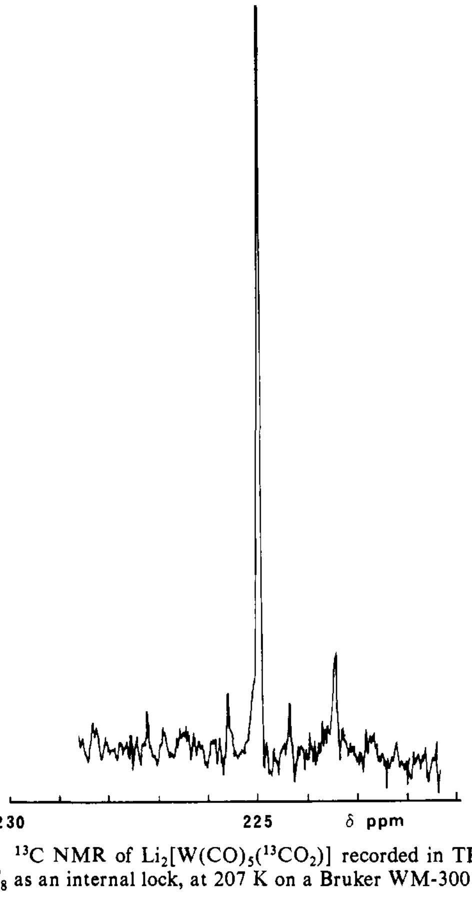


Figure 2. ^{13}C NMR of $Li_2[W(CO)_5(^{13}CO_2)]$ recorded in THF, with toluene-d_8 as an internal lock, at 207 K on a Bruker WM-300 at 75.47 Hz.

IR spectra very similar to those of Li_2**1** are otbained when Li_2**2** is treated with 1 equiv of CS_2 in THF at −78 °C (no tractable products are obtained with excess CS_2). This suggests that CS_2 forms a **2**$^{2-}$ adduct with a structure that is closely related to that of the CO_2 adduct, and the positions and intensities of the IR bands are again consistent with formulation as a C_{4v} complex containing an η^1–heteroallene ligand (1859 (s) cm^{-1}, axial A_1; 1912 (vs) cm^{-1}, equatorial E; 2054 (w) cm^{-1}, equatorial A_1). Further support for a C_{4v} structure for $[W(CO)_5CS_2]^{2-}$ was obtained from an experiment in which $Li_2[W(CO)_5]$ was prepared from $Li_2[W(CO)_5]$ that had been enriched in ^{13}C.[15] ^{13}C NMR spectra of the enriched adduct showed that the carbonyl ligands gave rise to absorptions at 204.8 and 199.7 ppm (THF, 200 K), both of which exhibited

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(7) Fischer, E. O.; Weiss, K. *Chem. Ber.* **1976**, *109*, 1128.

(8) (a) Fischer, E. O.; Kollmeier, H. J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 309. (b) Fischer, E. O.; Winkler, E.; Kreiter, C. G.; Huttner, G.; Kreig, B. *Ibid.* **1971**, *10*, 922.

(9) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405.

(10) The values obtained by Schrock and co-workers for J_{W-C} in tungsten alkyl, alkylidene, and alkylidyne complexes support the assumption that *J* correlates with bond order,[11] although the values that they observe for single and double bonds in high-valent complexes are consistently larger than those that we observe in low-valent carbonyl complexes.

(11) (a) Schrock, R. R., personal communication. (b) Wengrovious, J. H.; Schrock, R. R. *Organometallics*, **1982**, *1*, 148. (c) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(12) Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *85*, C19.

(13) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (c) Casey, C. P.; Polichnowski, S. W. *Ibid.* **1978**, *100*, 7565.

(14) Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

(15) Prepared[3] from labeled $[W(CO)_6]$ obtained by reaction of $Na_2[W(CO)_5]$ with $^{13}CO_2$.[1]

Table II

section[a]		none	1 × ^{13}C	1 × ^{18}O and/or 2 × ^{13}C	1 × ^{13}C + 1 × ^{18}O	2 × ^{18}O and/or 2 × ^{13}C + 1 × ^{18}O	1 × ^{13}C + 2 × ^{18}O	3 × ^{18}O and/or 2 × ^{13}C + 2 × ^{18}O	3 × ^{18}O + ^{13}C
a	time, h								
	0	11	37	42	10				
	5	14	31	30	9	14	1		
	28	27	15	26	13	11	4	4	1
b	random distribution of labels	25	13	27	12	12	5	3	1
c	distribution expected if there is no ^{13}C exchange	22	18	22	18	9	7	2	2

[a] Key: (a) isotopic composition of the [W(CO)$_6$] formed by quenching a 1:1 mixture of Li$_2$[W(CO)$_5$(C^{18}O$_2$)] (99% labeled) and Li$_2$[W(CO)$_5$(^{13}CO$_2$)] (93% labeled) after varying periods at 0 °C. The data presented are the percentages of the [W(CO)$_6$] containing the specified number of ^{13}C and ^{18}O labels per molecule. Some label combinations cannot be distinguished—in those cases the combinations given in the column heading are in order of descending importance (as indicated by the statistical distributions below); (b and c) calculated label distributions (see text for assumptions).

^{183}W–C coupling. These can be assigned to the trans and cis carbonyls of a [W(CO)$_5$L] complex, respectively, on the basis of their chemical shifts (cf. 208.1 and 204.1 ppm for NEt$_4$[W(CO)$_5$COCH$_3$]) and, most importantly, the ≈1:4 ratio of their integrated intensities. In light of the similarities between the IR spectra of the CS$_2$ and CO$_2$ adducts, these data also provide an indirect argument in favor of a C_{4v} structure for **1**$^{2-}$ and against alternative formulations consistent with the stoichiometric data, such as formulation as the metalloanhydride {W(CO)$_4$[(CO)$_2$O]}$^{2-}$.

While exploring the chemistry of **1**$^{2-}$ we have observed that it undergoes several facile exchange reactions, as illustrated by the data in Table II. In the experiment reported in section a, a solution of Li$_2$**1** (solution IR), prepared by reaction of Li$_2$**2** with a 1:1 mixture of C^{18}O$_2$ (99%) and ^{13}CO$_2$ (93%), was allowed to stand at 0 °C. Subsequent exchange was monitored by quenching aliquots of the solution with excess CO$_2$ at −78 °C. The solutions of [W(CO)$_6$] (**3**) formed were treated with aqueous NEt$_4$Br to convert any unreacted (and volatile) [W(CO)$_5$(NMe$_3$)] to [W(CO)$_5$Br]$^-$, and the **3** was extracted into Et$_2$O together with the napthalene remaining from the formation of **2**$^{2-}$.[3] The isotopic compositions of the samples of **3** were then determined by recording the mass spectra of the mixtures and analyzing the parent ion envelopes on the assumption that each was the sum of the tungsten isotope envelopes of the variously labeled molecules present. The lowest mass peak in an envelope, for example, would be assumed to correspond to the ^{182}W peak of **3** containing only ^{12}C and ^{16}O, and the height of this would be used to calculate the contribution of this species to higher mass peaks. Subtraction then generated a new isotope envelope, and the process was repeated until a negligible fraction (<1% in most cases) of the total intensity of the peak remained unaccounted for.[16]

The data suggest that **1**$^{2-}$ probably undergoes at least three exchange reactions, the least surprising of which occurs during the reaction of an aliquot of freshly prepared **1**$^{2-}$ with excess CO$_2$. This results in the formation of a significant quantity of unlabeled **3**, suggesting that exchange of added CO$_2$ for coordinated CO$_2$ (eq 3) can compete effectively with [W(CO)$_6$] formation. This

$$[\mathrm{W(CO)_5(^{13}CO_2)}]^{2-} + \mathrm{CO_2} \rightarrow [\mathrm{W(CO)_5(CO_2)}]^{2-} + \mathrm{^{13}CO_2} \qquad (3)$$

has been confirmed by an experiment in which **1**$^{2-}$, freshly prepared from ^{13}CO$_2$ (93%), was reacted with CO$_2$ at room temperature. The bulk of the resulting **3** (49%) was unlabeled while 38% contained a single ^{13}C atom, indicating, as anticipated, a much greater degree of exchange at higher temperatures. The **3** formed also contained small quantities (10% and 3%) of doubly and triply labeled molecules.

The second and most remarkable exchange process can be interpreted in terms of the transfer of nucleophilic O^{2-} ions from coordinated CO$_2$ to coordinated CO (eq 4), in a reaction remi-

$$\mathrm{MCO_2}^{2-} + \mathrm{M'CO} \rightarrow \mathrm{MCO} + \mathrm{M'CO_2}^{2-} \qquad (4)$$

niscent of the O-transfer reaction which is believed to be the key step (eq 5; L$_2$ = (PEt$_3$)$_2$ or Ph$_2$PCH$_2$CH$_2$PPh$_2$) in the oxidation

$$\mathrm{L_2Ni(NO_2)_2(CO)} \rightarrow \mathrm{L_2Ni(NO_2)(NO)(CO_2)} \rightarrow \mathrm{L_2Ni(NO_2)(NO)} + \mathrm{CO_2} \qquad (5)$$

of CO by NO$_2$ (isoelectronic with CO$_2^-$) complexes of Ni[17] and related catalytic reactions.[18] An intermolecular analogue of this reaction, probably involving simultaneous O^{2-} transfer from the CO$_2$ ligands of two reacting molecules of **1**$^{2-}$, would account for the significant quantity of **3** containing both ^{13}C and ^{18}O formed in all the experiments. A similar intramolecular reaction, although it is not ruled out by the present experiments, could not by itself account for the incorporation of both ^{13}C and ^{18}O in the same molecule. Previous reports of oxygen exchange between H$_2$^{18}O and [W(CO)$_6$] under basic phase-transfer conditions provide supporting evidence for the ability of coordinated carbonyls to undergo reversible reactions with oxygen nucleophiles.[19]

The label distribution within **1**$^{2-}$ is close to being random after the solution has been kept for 28 h at 0 °C, as can be seen by comparing the experimental data with the random distribution in Table IIb calculated on the assumption that 0.99/7 of the oxygen atoms in **1**$^{2-}$ are ^{18}O and 0.93/6 of the carbon atoms are ^{13}C. At the level of precision of the present experiment, the data do not clearly distinguish between this completely random distribution, which would require the existence of another exchange reaction to allow for C exchange as well as O exchange, and one in which there has been no ^{13}C exchange (Table IIc). Attempts to isolate Li$_2$**1** have so far been unsuccessful, but further experiments are in progress. We are also exploring the scope and mechanism of the O^{2-}-transfer reaction.

Acknowledgment. We thank the National Science Foundation (Grant CHE80-16162) and the Exxon Educational Foundation for their support of this research. We thank Professor R. R. Schrock for helpful discussions of his unpublished data on W–C coupling constants.

Registry No. Li$_2$·**1**, 83416-48-2; Li$_2$·**2**, 75706-82-0; **3**, 14040-11-0; CO$_2$, 124-38-9; W(CO)$_5$C(OMe)Ph, 37823-96-4; W(CO)$_5$CPh$_2$, 50276-12-5; [W(CO)$_5$COCH$_3$]NEt$_4$, 59610-08-1; [W(CO)$_5$CH$_3$]NEt$_4$, 57574-51-3; CS$_2$, 75-15-0; C^{18}O$_2$, 18983-82-9; Li$_2$[W(CO)$_5$CS$_2$], 83416-49-3; ^{13}CO$_2$, 1111-72-4.

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(16) An iterative calculation of this type is very sensitive to adventitious variations in peak heights, and the spectrum of a sample often had to be recorded several times before one was obtained that could be analyzed by using this approach.

(17) (a) Doughty, D. T.; Gordon, G.; Stewart, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 2645. (b) Feltham, R. D.; Kriege, J. C. *Ibid.* **1979**, *101*, 5064.

(18) See, for example: (a) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3325. (b) Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3278 and references therein.

(19) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4688.