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Reductive Disproportionation of Carbon Dioxide by Dianionic Carbonylmetalates of the Transition Metals

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Abstract: Carbon dioxide reacts readily with $M_2[M'(CO)_5]$ (M = Li, Na, K, M' = W; M = K, M' = Cr, Mo, W) to give the corresponding group 6 hexacarbonyls $[M(CO)_6]$ and alkali metal carbonates. The reaction of $Li_2[W(CO)_5]$ with excess $^{13}CO_2$ at −78 °C gives $[W(CO)_5(^{13}CO)]$, confirming that the reaction involves reductive disproportionation of CO_2 to CO and CO_3^{2-}. The group 8 carbonylmetalates $Na_2[M(CO)_4]$ (M = Fe, Ru, Os) react with CO_2 to give $[M(CO)_5]$ and carbonate, and $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]$ reacts with CO_2 to give $[V(\eta\text{-}C_5H_5)(CO)_4]$ and carbonate, indicating that reductive disproportionation is a general reaction of dianionic carbonylmetalates with CO_2. Careful addition of 1 equiv of CO_2 to a solution of $Li_2[W(CO)_5]$ at −78 °C leads to an intermediate 1:1 adduct with an IR spectrum consistent with formulation as $Li_2[W(CO)_5(\eta^1\text{-}CO_2)]$. The principal ^{13}C absorption at 223.4 δ of a sample of $Li_2[W(CO)_5(\eta^1\text{-}^{13}CO_2)]$ prepared at −78 °C exhibits J_{W-C} = 92 Hz, consistent with the central C being directly bonded to W and sp^2 hybridized. Oxide scrambling from coordinated CO_2 to coordinated CO at higher temperatures results in complex signals between 205 and 201 δ assigned to the carbonyl ligands. Similar signals are observed in $Li_2[W(CO)_{5-n}(^{13}CO)_n(CO_2)]$ at −78 °C, and the CO_2 carbon of this complex becomes progressively enriched at higher temperatures. Carbon disulfide reacts with $Li_2[W(CO)_5]$ to give the η^1 adduct $Li_2[W(CO)_5(\eta^1\text{-}CS_2)]$, with ^{13}C NMR axial and equatorial carbonyl resonances at 204.8 and 199.7 δ. It is proposed that reductive disproportionation of CO_2 by a dianionic carbonylmetalate involves oxide transfer from an $\eta^1\text{-}CO_2$ adduct to a second molecule of CO_2 via an intermediate $C(O)OCO_2$ complex.

Recent interest in the reduction of carbon dioxide to carbon monoxide[1] has led to the recognition of a number of ways in which transition-metal complexes can promote or catalyze this reduction. The most important and extensively studied of these is the reverse of the water-gas-shift reaction (eq 1), a reaction catalyzed by a

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (1)$$

number of transition-metal systems, in which H_2 is the reductant and water is the oxygen sink. There are, however, several other transition-metal promoted reductions of CO_2 to CO, which may be conveniently classified in terms of the oxygen acceptor present in the system. Thus oxophilic early transition metals can react with CO_2 to give CO and metal oxides,[2] and complexes with easily oxidized ligands (such as phosphines and hydrides) can react with CO_2 to give CO and oxidized ligands.[3]

Reactions in which CO_2 acts as its own oxygen sink, to give CO and CO_3^{2-}, form a particularly important class of transition-metal-promoted reductions of CO_2, and the critical reaction in such systems (eq 2) is termed reductive disproportionation.

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \qquad (2)$$

The earliest reported example of the formation of both CO and CO_3^{2-} from the reaction of CO_2 with a transition-metal complex involved the reaction of $[Mo(PMe_2Ph)_4(N_2)_2]$ with CO_2 to give a dimer ($[\{Mo(PMe_2Ph)_3(CO)(CO_3)\}_2]$) in which both CO and CO_3^{2-} are coordinated to molybdenum.[4] Similar reactions involving $[Fe(PMe_3)_4]$ (to give $[Fe(PMe_3)_3(CO)(CO_3)]$[5]), $[Mo(PMe_3)_4(N_2)_2]$,[6] and $[Ni(triphos)(CS_2)]$[3c] have been observed, and Floriani has reported a detailed study of reductive disproportionation of CO_2 by $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$[2].

Transition-metal complexes which are powerful two-electron reductants should be particularly promising substrates for reductive disproportionation of CO_2, and we have indicated in preliminary communications[7] that CO_2 does indeed undergo facile reductive disproportionation with dianionic carbonylmetalates. We now wish to report details of those experiments, which indicate that reductive disproportionation is a general reaction of CO_2 with dianionic carbonylmetalates and that the reaction involves discrete CO_2 adducts containing η^1-C coordinated CO_2.

Experimental Section

General Methods. Reactions and manipulations were conducted under N_2 by means of standard Schlenk tube techniques or a Vacuum Atmospheres Dri-lab glovebox. Glassware was oven or flame dried before use. Infra-red spectra were recorded on a Perkin Elmer 457A or 683 spectrometer and calibrated relative to the 1601-cm^{-1} absorption of polystyrene. ^{13}C NMR spectra were recorded on a Bruker WM-300WB spectrometer and were referenced indirectly to tetramethylsilane by means of the carbonyl resonance at 206.0 δ of an external sample of acetone-d_6. Mass spectra were recorded on an AEI MS-9 instrument. Aliquots for solution IR spectra were placed in gas tight demountable cells with NaCl windows. Cells were purged with N_2 for 5–10 min and capped with 5-mm rubber septa before being filled, and solution spectra were recorded across the accessible carbonyl stretching region from the solvent cutoff at 1450 cm^{-1} to 2400 cm^{-1}.

Solvents and Reagents. Solvents were freshy distilled under N_2 from an appropriate desiccant (sodium/benzophenone ketyl for tetrahydrofuran (THF), $LiAlH_4$ for pentane, CaH_2 for toluene) and degassed before use. Matheson "bone dry" CO_2 was used as supplied without further purification: many of the anions studied are extremely proton sensitive, forming hydrides in the presence of traces of water, but we have not found water contamination to be a significant problem with this grade of CO_2. $Na_2[Fe(CO)_4]\cdot 1.5$dioxane was purchased from Ventron-Alfa and rinsed with THF before use to remove traces of $Na[FeH(CO)_4]$. Sodium reduction of the corresponding dodecacarbonyls (Strem) in liquid ammonia (dried by distillation from Na) was used to prepare $Na_2[Ru(CO)_4]$ and $Na_2[Os(CO)_4]$ as described in the literature.[8] Sodium

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amalgam reduction of [$V(\eta\text{-}C_5H_5)(CO)_4$] (Strem) was used to prepare $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]\cdot THF$,[9] and the solvate was used as prepared without further purification. Naphthalene free solutions of Li^+ and Na^+ salts of $[W(CO)_5]^{2-}$ in THF were prepared as described previously.[10] The K^+ salts of $[Cr(CO)_5]^{2-}$, $[Mo(CO)_5]^{2-}$, and $[W(CO)_5]^{2-}$ were prepared by a similar naphthalenide reduction of $[M(CO)_5(NMe_3)]$ substrates, taking advantage of the low solubility of the K^+ salts to obtain naphthalene free material by adding an equivalent volume of diethyl ether below 0 °C to precipitate $K_2[M(CO)_5]$ and then washing the precipitate with ether.

Determination of Carbonate.[11] Solid residues were analyzed for carbonate by a procedure in which the carbonate was first extracted into water (typically 10 mL on the scale of these experiments) and the CO_3^{2-} content of the filtered solution was then determined by double titration: total base was determined by titration of a 1-mL aliquot with 0.1 M HCl and methyl orange indicator, and non-carbonate base was determined by titration of a second 1-mL aliquot with HCl and phenolphthalein indicator after precipitation of carbonate with Ba^{2+}.

Reaction of $Li_2[W(CO)_5]$ and $Na_2[W(CO)_5]$ with Excess CO_2. A naphthalene free solution of $Li_2[W(CO)_5]$ in THF (from 0.40 g (1.04 mmol) of $[W(CO)_5(NMe_3)]$) was cooled to −78 °C, and dry CO_2 was bubbled into the solution through a stainless steel needle. The characteristic orange of the dianion faded rapidly to a light yellow and a white precipitate began to form. After the solution had warmed to room temperature and settled, the only significant IR absorption of the supernatant in the carbonyl region was the T_{1u} band of $[W(CO)_6]$ at 1975 cm^{-1}. The precipitate was collected by filtration and shown to be Li_2CO_3 (0.056 g, 0.76 mmol ≡ 73%) by comparison (Nujol mull IR) with an authentic sample. The supernatant was concentrated under reduced pressure (taking care that the volatile solid was under vacuum as little as possible) to give an off-white solid from which white crystals of $[W(CO)_6]$ (0.30 g, 0.85 mmol ≡ 82%) were obtained by concentration of an ether extract. The reaction of $Na_2[W(CO)_5]$ with excess CO_2 was carried out in a similar manner.

Reaction of $Li_2[W(CO)_5]$ with Excess $^{13}CO_2$ at Low Temperature. A naphthalene free solution of $Li_2[W(CO)_5]$ in THF (30 mL) prepared from 0.10 g (0.26 mmol) of $[W(CO)_5(NMe_3)]$ was cooled to −78 °C and attached to a vacuum line. The vessel was evacuated (10^{-4} torr), and 0.048 g (1.1 mmol) of $^{13}CO_2$ (93 atom% isotopic purity) was slowly added to the stirred solution. After the solution had been allowed to warm to room temperature, the supernatant was concentrated under reduced pressure to give an off white solid with a solution IR spectrum (2111 (vw), 1977 (vs), 1949 (s) cm^{-1}) similar to that reported for $[W(CO)_5(^{13}CO)]$.[12]

Reactions of $K_2[M(CO)_5]$ (M = Cr, Mo, W) with Excess CO_2. In a typical procedure, a freshly prepared sample of $K_2[Cr(CO)_5]$ prepared from 0.15 g (0.59 mmol) of $[Cr(CO)_5(NMe_3)]$ was resuspended in 10 mL of THF at ambient temperature, and CO_2 was bubbled through the stirred mixture at 200 mL/min for 2 min. After 5 min the fine yellow precipitate was allowed to settle, the supernatant was collected by filtration, and the insoluble residue was rinsed with 7 mL of THF. IR spectra of the solution showed $[Cr(CO)_6]$ (1980 cm^{-1}) as the only detectable metal carbonyl species. The solution was concentrated under reduced pressure to a volume of ca. 8 mL and then cooled to −78 °C for 1 h. The microcrystalline white $[Cr(CO)_6]$ precipitate was collected by filtration and dried by a series of rapid pump–purge cycles to give 0.06 g of neutral hexacarbonyl (0.27 mmol, 46.3%). The THF insoluble reaction product was determined titrimetrically to contain 0.40 mmol (≡ 68%) of carbonate. The reactions of $K_2[Mo(CO)_5]$ and $K_2[W(CO)_5]$ with CO_2 were carried out similarly to give the results tabulated in the Results and Discussion section.

Reaction of $Na_2[Fe(CO)_4]$ with Excess CO_2. A suspension of $Na_2[Fe(CO)_4]\cdot 1.4$dioxane (0.202 g, 0.58 mmol) in THF (32 mL) was cooled to −78 °C, and dry CO_2 was bubbled through the stirred solution for 5 min through a stainless steel needle. The tan suspension began to lighten in color during the addition, and the solution became a light yellow when the mixture was warmed to room temperature over 30 min. After the suspension had settled under N_2 for 2 h (this also allowed CO_2 to diffuse out of the solution), the IR spectrum of the solution contained two bands corresponding to the A_2'' and E' absorptions of $[Fe(CO)_5]$ at 2023 and 1993 cm^{-1}. The absorbance of the 2023-cm^{-1} band (ϵ = 2910 M^{-1} cm^{-1}) indicated an effective $[Fe(CO)_5]$ concentration of 1.46 × 10^{-2} M (≡ 82% yield). The solvent was removed from the reaction mixture under reduced pressure, and the pink powder obtained was determined titrimetrically to contain 0.54 mmol (≡ 93%) carbonate.

Reaction of $Na_2[Ru(CO)_4]$ with Excess CO_2 and Conversion of the Product to $[Ru(CO)_4I_2]$. Since $[Ru(CO)_5]$ is light sensitive, this experiment was conducted in an apparatus wrapped in Al foil. Excess CO_2 was bubbled for 15 min through a suspension of $Na_2[Ru(CO)_4]$ (0.15 g, 0.59 mmol) in THF (20 mL) which had been stirred for 20 min at 4 °C. IR spectra (recorded after the suspension had settled for 2 h) contained only two significant absorptions in the carbonyl stretching region at 2038 and 1995 cm^{-1}. These correspond to the A_2'' and E' bands of $[Ru(CO)_5]$.[13] The solution was filtered onto 0.15 g (0.60 mmol) of I_2 at 4 °C, and the insoluble residue was shown to contain 0.36 mmol (≡ 61%) of carbonate. After 30 min the solution was warmed to room temperature to give a clear, orange-red solution with IR absorptions at 2165 (m), 2115 (vs), and 2078 (ms) cm^{-1} corresponding to those of *cis*-$[Ru(CO)_4I_2]$.[13] The solvent was removed under reduced pressure to give a deep orange-red solid from which excess I_2 was removed by sublimation at 0.05 torr for 3 h. Extraction with THF (10 mL) yielded 0.20 g (0.43 mmol ≡ 73%) of $[Ru(CO)_4I_2]$ as a yellow powder.

Reaction of $Na_2[Os(CO)_4]$ with Excess CO_2 and Conversion of the Product to $[Os(CO)_4I_2]$. Since $[Os(CO)_5]$ is light sensitive, this reaction was carried out in an apparatus covered in Al foil. The reaction was carried out in a similar manner to the reaction with $Na_2[Ru(CO)_4]$, starting with a suspension of 0.21 g (0.60 mmol) of $Na_2[Os(CO)_4]$ in THF. After addition of CO_2 the only carbonyl absorptions in the IR spectrum of the solution were those of $[Os(CO)_5]$ at 2043 (vs) and 1987 (vs) cm^{-1}. The solution was filtered onto 0.15 g (0.60 mmol) of I_2 at 4 °C, and the insoluble residue was shown to contain 0.56 mmol (≡ 91%) carbonate as described above. After 30 min at 4 °C and 30 min at room temperature the IR spectrum of the iodination reaction contained absorptions at 2171 (m), 2097 (vs), 2088 (sh), and 1987 (vs) cm^{-1} assigned to $[Os(CO)_4I_2]$.[13] The solvent was removed from the mixture under reduced pressure, and the excess I_2 was sublimed off at 60 °C and 0.05 torr over 30 min. The product was extracted into toluene and precipitated by concentration under vacuum over 2 h to give 0.20 g (0.37 mmol ≡ 61%) of $[Os(CO)_4I_2]$ (IR) as an orange-yellow powder.

Preparation of $Li_2[W(CO)_5(CO_2)]$. A Schlenk vessel containing 19 mL of a 0.035 M solution of $Li_2[W(CO)_5]$ (0.665 mmol) in THF at −78 °C was evacuated to ca 0.01 torr through a high vacuum manifold. Dry CO_2 (0.025 g, 0.57 mmol) was slowly condensed into the vigorously stirred solution over 20 min by repeated filling of the butyl rubber tubing connecting the vessel to a fixed volume reservoir. Solution IR spectra obtained after repressurization under N_2 indicated quantitative consumption of the initial dianion, with new ν_{CO} absorptions appearing at 2043 (w), 1900 (vs), and 1865 (s) cm^{-1}. The formation of small quantities of $[W(CO)_6]$ was indicated by a moderately weak absorption at 1975 cm^{-1}. IR spectra did not indicate the presence of any free CO_2 in these solutions.

Preparation of an NMR Sample of $Li_2[W(CO)_5(^{13}CO_2)]$. The vacuum line technique described above was used to add $^{13}CO_2$ (0.022 g, 0.49 mmol) to a Schlenk tube containing a rapidly stirred 0.042 M solution of $Li_2[W(CO)_5]$ in THF (13.2 mL, 0.55 mmol) at −78 °C over 30 min. During the addition the mixture lightened to a clear, golden yellow. Solution IR spectra recorded after repressurization of the reaction vessel under N_2 revealed complete consumption of the initial $Li_2[W(CO)_5]$ together with new ν_{CO} bands at 2042 (w), 1898 (vs), and 1865 (s) cm^{-1}. A small quantity of $[W(CO)_6]$ was evident (1974 cm^{-1}). An NMR sample was prepared by transferring ca. 4 mL of this solution into a serum capped 10-mm NMR tube maintained at −78 °C containing acetone-d_6 in a sealed 5-mm tube (to provide a locking signal).

Preparation of $Li_2[W(CO)_5(CS_2)]$. A colorless solution of CS_2 (38.0 μL, 0.63 mmol) in 3.0 mL of THF was added in 3 equal portions over 5 min through a cannula to a rapidly stirred 0.043 M solution of $Li_2[W(CO)_5]$ in THF (15.4 mL, 0.66 mmol) at −78 °C. The solution immediately turned an intense deep red-purple color, and IR spectra recorded at room temperature exhibited ν_{CO} absorptions at 2054 (w), 1912 (vs), and 1859 (ms) cm^{-1}.

Preparation of $Li_2[W(CO)_{5-n}(^{13}CO)_n]$ and $Na_2[W(CO)_{5-n}(^{13}CO)_n]$. A sample of partially ^{13}C-labeled $[W(CO)_6]$ was prepared from the reaction of $Na_2[W(CO)_5]$ with 2.1 equiv of $^{13}CO_2$ and converted into $[W(CO)_{5-n}(^{13}CO)_n(NMe_3)]$ and hence into $Li_2[W(CO)_{5-n}(^{13}CO)_n]$ and $Na_2[W(CO)_{5-n}(^{13}CO)_n]$, as previously described.[10] Mass spectra established that the $[W(CO)_{5-n}(^{13}CO)_n(NMe_3)]$, and presumably the dianions prepared from it, was labeled as follows: unlabeled, 41%, 1 × ^{13}C; 42%, 2 × ^{13}C; 14%, 3 × ^{13}C; 2%, 4 × ^{13}C, 1%.

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Table I. Yields for the Reductive Disproportionation of CO_2 by Dianionic Carbonylmetalates

$M'_2[ML_n]$	initial prod (IR)	isolated prod	isoltd yield (%)	yield M'_2CO_3 (%)
$Li_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$	82	74[a]
$Na_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$	83	*b*
$K_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$	48	78[c]
$K_2[Cr(CO)_5]$	$[Cr(CO)_6]$	$[Cr(CO)_6]$	46	68[c]
$K_2[Mo(CO)_5]$	$[Mo(CO)_6]$	$[Mo(CO)_6]$	42	73[c]
$Na_2[Fe(CO)_4]$	$[Fe(CO)_5]$	not isoltd	82 ± 10[d]	94[c]
$Na_2[Ru(CO)_4]$	$[Ru(CO)_5]$	*cis*-$[Ru(CO)_4I_2]$	73	61[c]
$Na_2[Os(CO)_4]$	$[Os(CO)_5]$	*cis*-$[Os(CO)_4I_2]$	61	92[c]
$Na_2[V(\eta\text{-}C_5H_5)(CO)_3]$	$[V(\eta\text{-}C_5H_5)(CO)_4]$	$[V(\eta\text{-}C_5H_5)(CO)_4]$	67 (96)[e]	57 (84)[c,e]

[a] Isolated yield. [b] Not determined. [c] Titrimetric yield. [d] Infrared yield. [e] After correction for Hg contamination of the starting dianion.

Preparation of an NMR sample of $Na_2[W(CO)_{5-n}(^{13}CO)_n(CS_2)]$. Neat CS_2 (32.0 μL, 0.040 g, 0.53 mmol) was injected into a vigorously stirred 0.045 M solution of largely monolabeled $Na_2[W(CO)_{5-n}(^{13}CO)_n]$ in THF (11.0 mL, 0.50 mmol, see above) at −78 °C. The mixture immediately darkened to a translucent deep red-purple, and solution IR spectra recorded after 15 min at −78 °C revealed >90% consumption of initial pentacarbonyltungstate together with the appearance of ν_{CO} bands at 2051 (w), 2044 (w), 1961 (m), 1912 (vs), and 1859 (s) cm^{-1}. An NMR sample was prepared by transferring ca. 4 mL of this solution into a serum capped 10-mm NMR tube maintained at −78 °C containing acetone-d_6 in a sealed 5-mm tube (to provide a locking signal). ^{13}C NMR (75.47 MHz, 240 K) δ 204.8 ($^1J_{W-C}$ = 154 Hz), 199.7 ($^1J_{W-C}$ = 128 Hz), with 1:4.5 integrated relative intensities.

Preparation of $Li_2[W(CO)_{5-n}(^{13}CO)_n(CO_2)]$. Dry $^{12}CO_2$ (10.5 mL, 0.43 mmol) was slowly injected into a Schlenk vessel containing a vigorously stirred 0.034 M solution of $Li_2[W(CO)_{5-n}(^{13}CO)_n]$ in THF (14.1 mL, 0.48 mmol) at −78 °C by means of a mechanically driven polypropylene syringe. IR spectra of the homogeneous solution revealed essentially quantitative consumption of $Li_2[W(CO)_5]$ and contained new ν_{CO} absorptions at 2037 (vw), 1900 (vs), and 1866 (s) cm^{-1}. The presence of a small quantity of $[W(CO)_6]$ was also indicated by a band at 1974 cm^{-1}. An NMR sample was prepared by transferring ca. 4 mL of this solution into a serum capped 10-mm NMR tube maintained at −78 °C containing acetone-d_6 in a sealed 5-mm tube (to provide a locking signal).

Reaction of $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]$ with Excess CO_2. A yellow suspension of $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]\cdot THF$ (0.245 g, 0.77 mmol) in THF (15 mL) turned olive green and then deep red-brown when gaseous CO_2 was bubbled through the suspension of 5 min at room temperature. The IR spectrum of the cloudy solution obtained after brief removal of excess CO_2 under vacuum contained two major absorptions at 2034 (s) and 1921 (vs) cm^{-1} identical with those of an authentic sample of $[V(\eta\text{-}C_5H_5)(CO)_4]$ in THF, together with unassigned very weak absorptions at 1854 and 1820 cm^{-1}. The mixture was gradually concentrated under reduced pressure at room temperature until a free flowing amorphous solid formed. Orange-yellow crystals of $[V(\eta\text{-}C_5H_5)(CO)_4]$ (IR and ^1H NMR; 0.12 g, 0.51 mmol ≡ 67%) were obtained from this material by concentration of a pentane (3 × 20 mL) extract under reduced pressure. The pentane-insoluble residue was analyzed for carbonate as described above (0.43 mmol ≡ 57%). The suspension obtained from a separate experiment in which some of the same batch of $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]\cdot THF$ (0.136 g) was treated with excess CO_2 in THF was allowed to sit for 2 weeks. The drop of mercury formed was mechanically separated and weighed (0.044 g), and this weight was used to calculate that the yield of $[V(\eta\text{-}C_5H_5)(CO)_4]$ and carbonate in the original experiment corresponded to yields of 96% and 84%, respectively.

Results and Discussion

Reactions of Carbonylmetalates with Excess Carbon Dioxide. When carbon dioxide is bubbled through solutions of $Li_2[W(CO)_5]$ in THF, a rapid reaction occurs, as evidenced by bleaching of the characteristic orange of $[W(CO)_5]^{2-}$ and precipitation of a white solid. The only observable carbonyl containing product was $[W(CO)_6]$ (IR), which could be isolated in 82% yield. The ether insoluble material was shown to be Li_2CO_3 (74%) by comparison of its IR spectrum with that of an authentic sample, suggesting that the reaction involved reductive disproportionation of CO_2 (eq 2) to give 1 equiv of carbonate and 1 equiv of CO coordinated to tungsten (eq 3).

$$Li_2[W(CO)_5] + 2CO_2 \rightarrow [W(CO)_6] + Li_2CO_3 \qquad (3)$$

The stoichiometry of the reaction indicates that one of the carbonyls of the product $[W(CO)_6]$ must be derived from the added CO_2, and this has been confirmed by carrying out the reaction at −78 °C with 93% labeled $^{13}CO_2$. The hexacarbonyl obtained was 90% $[W(CO)_5(^{13}CO)]$ and 10% unlabeled $[W(CO)_6]$ with only traces of $[W(CO)_4(^{13}CO)_2]$,[14] as established by analysis of the envelope of the parent ion peak in the mass spectrum of the material using the iterative method outlined previously.[7b]

The generality of the reductive disproportionation of CO_2 by carbonylmetalates was established by examining the reaction of CO_2 with a number of other dianionic carbonylmetalates, including the Na^+ and K^+ salts of $[W(CO)_5]^{2-}$, the K^+ salts of the pentacarbonyl dianions of the other group 6 metals, and the Na^+ salts of the tetracarbonyl dianions of the group 8 metals. The results of these reactions are summarized in Table I.

Visual evidence for the progress of reductive disproportionation is less obvious in the case of the group 8 carbonylmetalates than in the case of the group 6 carbonylmetalates since $Na_2[Fe(CO)_4]$, $Na_2[Ru(CO)_4]$, and $Na_2[Os(CO)_4]$ have only limited solubility in THF, and the sodium carbonate formed is also insoluble in THF. The reactions were, however, readily monitored by IR, which indicated, in the case of all three metals, that the carbonylmetalates had been converted into the corresponding pentacarbonyls within 30 min at room temperature after treatment of suspensions of the salts in THF with carbon dioxide. It is, however, probable that the reactions proceed at significant rates even at low temperatures: when CO_2 was bubbled through a suspension of $Na_2[Fe(CO)_4]$ in THF at −78 °C, for example, there was a distinct lightening of the color of the solution during the addition.

IR spectra suggested that the reaction of CO_2 with the group 8 carbonylmetalates is very clean, but quantification of pentacarbonyl formation was hampered by handling problems for all the metals: $[Fe(CO)_5]$ is a volatile liquid, while $[Ru(CO)_5]$ and $[Os(CO)_5]$ are not only volatile but also both thermally and photochemically unstable with respect to the corresponding dodecacarbonyls. The yield of $[Fe(CO)_5]$ was determined by absorption mode IR spectroscopy based on an experimentally determined extinction coeffient for the A_2'' absorption in THF. This procedure was complicated by the presence of CO_2 dissolved in the THF, but outgassing of the solution for 2 h under N_2 allowed determination of the yield as 82 ± 10%.

Minimum yields of the unstable pentacarbonyls of Ru and Os were determined by chemical derivatization. Calderazzo and L'Eplattenier have reported that reaction of $[Ru(CO)_5]$ with I_2 results in high yield conversion to the relatively involatile and stable diiodide $[Ru(CO)_4I_2]$.[13] Treatment with I_2 of the filtered solution obtained from the reaction of CO_2 with $Na_2[Ru(CO)_4]$ led to isolation of a 73% yield of this diiodide, establishing a minimum yield of 73% for the reductive disproportionation reaction. It has been indicated[13] that the analogous reaction of $[Os(CO)_5]$ with I_2 does not proceed as cleanly as the Ru reaction, and we did indeed observe a lower (61%) yield of $[Os(CO)_4I_2]$ when the $[Os(CO)_5]$ solution formed by reaction of CO_2 with $Na_2[Os(CO)_4]$ was treated with I_2. This establishes a minimum yield of 61% for the reductive disproportionation reaction in the Os system, but it seems probable that the true yield is higher, particularly since the carbonate yield was 92%.

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[14] As previously reported[7b] the isotopic labeling of the hexacarbonyl is much more complex if the reaction is carried out under conditions under which the intermediate CO_2 complex is allowed to warm significantly above −78 °C. This promotes extensive scrambling of oxide between the coordinated CO_2 and coordinated CO.

Mull IR spectra of the THF insoluble materials from the reactions between CO_2 and the carbonylmetalates of the group 6 and group 8 metals indicated that they were primarily Na_2CO_3, and this was confirmed and the yields quantified (Table I) by application of a titrimetric procedure (recommended by Vögel for the determination of carbonate in the presence of hydroxide or bicarbonate[11]). This involved initial determination of the total base followed by redetermination of the base content after precipitation of the carbonate with Ba^{2+}.[15]

There is no reason why reductive disproportionation of CO_2 should be limited to simple carbonylmetalates, and we have indeed observed a similar reaction with the dianionic complex $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]\cdot THF$[9] (Table I). Although the solvate is insoluble in THF, a suspension reacted readily with added CO_2 to give a solution in which $[V(\eta\text{-}C_5H_5)(CO)_4]$ was the only significant carbonyl containing product observable by IR. The $[V(\eta\text{-}C_5H_5)(CO)_4]$ could be isolated following extraction with pentane, but quantification was complicated by mercury contamination of the starting dianion. The isolated $[V(\eta\text{-}C_5H_5)(CO)_4]$ corresponded to a minimum yield of 67%, but correction for the mercury contamination (see Experimental Section) indicated that the true yield was ca. 96%. Minimum and corrected yields of carbonate as determined titrimetrically were 57% and 84%, respectively.

Formation of a CO_2 Adduct from the Reaction of $Li_2[W(CO)_5]$ with 1 equiv of CO_2. While it is not thermodynamically unreasonable that strongly reducing dianionic carbonylmetalates should promote reductive disproportionation of CO_2, the facility of the reaction under mild conditions represents a dramatic kinetic activation of CO_2. Determining the mechanism of the reaction is essential to understanding this activation, and we accordingly investigated possible intermediates in the reaction in some detail by using $Li_2[W(CO)_5]$ as a model substrate.

The gradual addition of 1 equiv[16] of CO_2 to a stirred solution of $Li_2[W(CO)_5]$ in THF at −78 °C led to slight lightening of the orange-brown color without the formation of any of the Li_2CO_3 precipitate characteristic of the reductive disproportionation reaction. Infrared spectra of the solution indicated that the $Li_2[W(CO)_5]$ had been completely consumed and that a new species had been formed with a characteristic spectrum (Figure 1a) consisting of three bands at 2043 (w), 1900 (vs), and 1865 (s) cm^{-1}. A small quantity of $[W(CO)_6]$ was also produced in the course of the reaction, but this could be minimized by adding the gas in small aliquots from a fixed volume reservoir on a high vacuum line over a period of 45 min. Alternatively, CO_2 could be delivered by means of a mechanically driven polypropylene syringe, with the rate of addition gradually reduced over time. In each case, best results were obtained when the THF solution was vigorously shaken or stirred to minimize local excesses of CO_2. Rapid transfer of an equivalent of CO_2 into THF solutions of $Li_2[W(CO)_5]$ led to substantial $[W(CO)_6]$ production and incomplete consumption of the monomeric dianion, presumably because the intermediate reacts almost as rapidly with CO_2 as does $Li_2[W(CO)_5]$.[17]

The stoichiometry of the reaction with 1 equiv of CO_2 indicates that the new species may be formulated as a simple 1:1 CO_2 adduct (eq 4).[18] The CO_2 adduct is relatively stable once it has been formed, and IR spectra of a solution maintained at 0 °C for 40 h gave no indication of decomposition.

$$Li_2[W(CO)_5] \xrightarrow[\text{THF, -78 °C}]{CO_2\text{ (1 equiv)}} Li_2[W(CO)_5(CO_2)] \qquad (4)$$

Spectroscopic Evidence for Formulation of $Li_2[W(CO)_5(CO_2)]$ as an η^1-C Complex of CO_2. The limited number of known discrete, well-characterized complexes of CO_2 with transition metals[1] led to extensive attempts to isolate the adduct. Isolation by concentration of THF solutions at low temperatures, by precipitation from concentrated solutions by addition of pentane or diethyl ether, and by counterion exchange with $[Ph_3PNPPh_3)]^+$

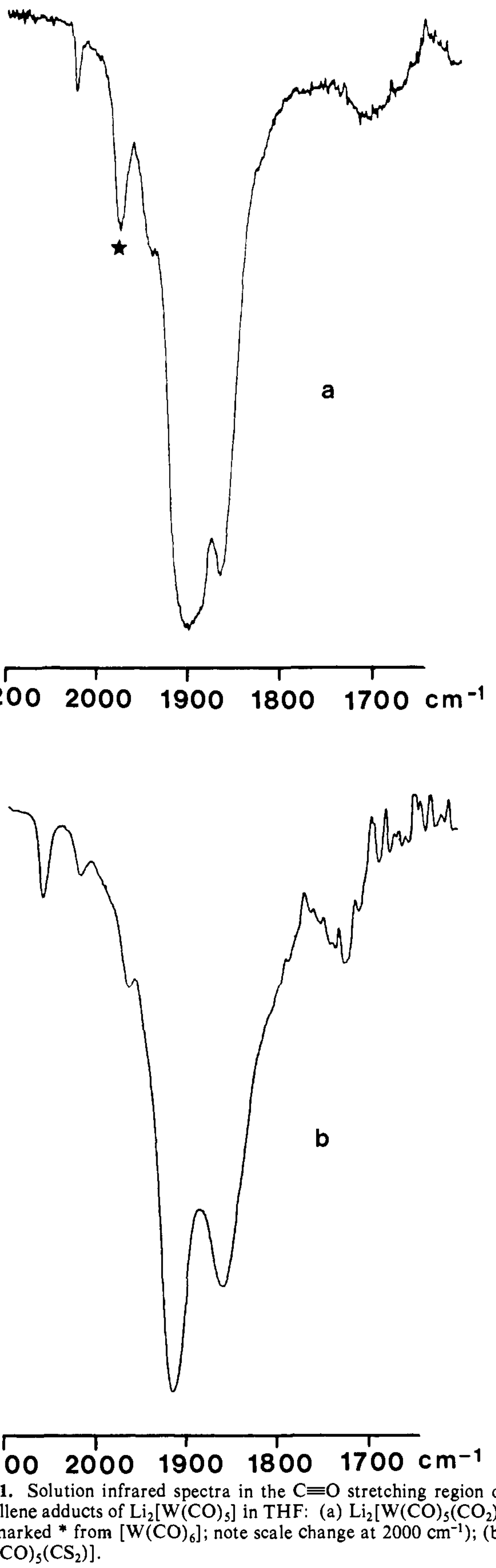

Figure 1. Solution infrared spectra in the C≡O stretching region of heteroallene adducts of $Li_2[W(CO)_5]$ in THF: (a) $Li_2[W(CO)_5(CO_2)]$ (peak marked * from $[W(CO)_6]$; note scale change at 2000 cm^{-1}); (b) $Li_2[W(CO)_5(CS_2)]$.

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(15) This procedure also eliminates the possibility that oxalates formed a significant portion of the precipitated solids.

(16) On the basis of the quantity of $[M(CO)_5(NMe_3)]$ from which the $Li_2[W(CO)_5]$ was prepared by naphthalenide reduction[10] on the assumption of an 85% yield in the reduction.

(17) Similar results were obtained when CO_2 was sublimed onto the frozen surface of the $Li_2[W(CO)_5]$ solution at −196 °C, and the resulting mixture was permitted to thaw at −78 °C.

(18) There was also no IR evidence for the presence of unreacted CO_2 under these conditions.

Table II. ^{13}C NMR Data for Carbon Ligands Directly Bound to Tungsten in $[W(CO)_5L]$ Complexes[a]

complex	δ CO_{eq}	δ CO_{ax}	δ C_L	T (K)
$[W(CO)_5C(OMe)Ph]$	197.2	203.4	321.7	298
	(128)	(116)	(111)	
$[W(CO)_5C(Ph)_2]$	196.8	213.7	356.5	240
	(129)	(105)	(96)	
$[W(CO)_5C(p\text{-}C_6H_4OMe)Ph]$	197.2	211.7	346.3	240
	(129)	(107)	(89)	
$NEt_4[W(CO)_5C(O)Me]$	204.1	208.1	275.9	298
	(128)	(137)	(76)	
$NEt_4[W(CO)_5CH_3]$	207.0	208.2	−34.6	298
	(126)	(149)	(44)	

[a] $^1J_{W-C}$ values in Hz in parentheses.

($[PPN]^+$: introduced as [PPN]Cl) were all unsuccessful, and $[W(CO)_6]$ was the only identifiable organometallic product formed. Addition of the cryptand Kryptofix 2.2.1 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) to a solution of the adduct at −78 °C resulted in formation of an orange precipitate, but this decomposed rapidly to $[W(CO)_6]$ at higher temperatures.

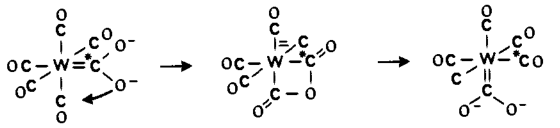
The failure to isolate the CO_2 adduct focussed attention on solution IR and ^{13}C NMR studies of samples prepared in situ. Solution infrared spectra (Figure 1a) support formulation as a $[W(CO)_5L]$ complex with effective C_{4v} symmetry, suggesting that the adduct is the η^1-C complex $Li_2[W(CO)_5(\eta^1\text{-}CO_2)]$: $[W(CO)_5L]$ complexes typically exhibit three bands, corresponding to the A_1 stretching mode of the equatorial carbonyls (weakly active, generally above 2000 cm^{-1}), the E stretch of the equatorial carbonyls (usually very strong), and the A_1 stretch of the axial carbonyl (usually strong and lower in energy than the equatorial E band). Such an assignment excellently describes the spectrum of $Li_2[W(CO)_5(CO_2)]$,[19] which is strikingly similar, for example, to that of $[K\cdot crypt2{:}2{:}2][W(CO)_5C(O)OCH_3]$,[22] which should have a similar degree of back donation to the carbonyl ligands.

Formation of a complex in which the CO_2 acts as an η^1 Lewis acid ligand to the 18-electron $[W(CO)_5]^{2-}$ dianion is consistent with the tendency of low-valent carbonyl complexes of tungsten to obey the 18-electron rule and with the η^1-C coordination found by Floriani in $[Co(n\text{-}Pr\text{-}salen)K(CO_2)THF]$, the only structurally characterized complex of CO_2 with an anionic transition-metal complex.[20]

Although ^{13}C NMR studies of $Li_2[W(CO)_5(CO_2)]$ are more difficult to interpret, they are consistent with formulation as an η^1-C complex of CO_2. Low-temperature spectra of a sample freshly prepared from $^{13}CO_2$ contained a major resonance at 223.4 δ with ^{183}W satellites corresponding to a W–C coupling constant of 92 Hz, together with a minor peak at 221.8 δ (J_{W-C} = 90 Hz). The chemical shift of the major resonance is well downfield from that of free CO_2 (132.2 δ[23]) and is similar to that of the carbenoid carbon in, for example, $[Cr(CO)_5C(OEt)_2]$ (206.6 δ[24]), as anticipated for an η^1-C coordinated CO_2. The chemical shift could also, however, arise from an η^2-C,O bound CO_2 given the shifts observed for established η^2-C,O complexes of CO_2 such as $[(\eta^5\text{-}C_5H_4CH_3)_2Nb(CH_2SiMe_3)(CO_2)]$ (220.5 δ[25]) and $[Mo(CO_2)_2(PMe_3)_4]$ (206.1 δ[6]).

The 92-Hz coupling constant is more informative than the chemical shift of the major resonance and strongly suggests an sp^2 hybridized carbon bonded to tungsten. Tungsten-carbon coupling constants tend to increase with the order of the W–C bond,[26] probably because of the increasing s-character of the bond as the hybridization at carbon changes. Comparison with Schrock's data for high valent tungsten complexes[26] suggests that the coupling constant for $Li_2[W(CO)_5(CO_2)]$ is on the borderline between that of an sp^2 C and an sp^3 C, but comparison with the more closely related data base reported in Table II places the value in exactly the range expected for an sp^2 C in a low-valent carbonyl complex.

Interpretation of ^{13}C NMR studies of $Li_2[W(CO)_5(CO_2)]$ was complicated by solution ion pairing and by the dramatic activation (established by previous mass spectral studies[7b]) of the CO_2 ligand in $Li_2[W(CO)_5(CO_2)]$ with respect to oxide transfer from coordinated CO_2 to coordinated CO. When an NMR sample of $Li_2[W(CO)_5(^{13}CO_2)]$ was warmed to 240 K a complicated series of peaks in the 205–201 δ region, present as weak peaks in the fresh sample, grew rapidly in intensity.[27] These peaks most probably arise from the cis and trans carbonyls of $Li_2[W(CO)_5(CO_2)]$ which are being progressively labeled by oxide-transfer reactions of the type shown in eq 5. Consistent with this interpretation, the changes in the spectrum of labeled $Li_2[W(CO)_5(CO_2)]$ were not reversed by cooling the sample back to 200 K, and IR spectra of the solution recorded before and after the scrambling reaction were identical and virtually the same as those of unlabeled $Li_2[W(CO)_5(CO_2)]$. The correlation reported by Buchner and Schenk between Cotton-Kraihanzel CO force constants and carbonyl ^{13}C chemical shifts for a series of octahedral $[W(CO)_5L]$ complexes[28] was used to predict a chemical shift of 203 δ for the equatorial carbonyls of $Li_2[W(CO_5)(CO_2)]$ from the solution IR data, in good agreement with observation.


(5)

The surprising complexity of the 205–201 δ signals probably indicates that $Li_2[W(CO)_5(CO_2)]$ exists in solution as a mixture of ion pairs which equilibrate slowly on the NMR time scale. In medium polarity solvents carbonylmetalates with alkali metal counterions characteristically ion pair,[29] and the existence of several types of ion pairs in THF solutions of $Li_2[W(CO)_5(CO_2)]$ would be consistent with the non-Lorentzian line shape of the IR absorption assigned to the equatorial carbonyls, which is probably a composite band. The weak resonance at 221.8 δ in freshly prepared $Li_2[W(CO)_5(^{13}CO_2)]$ is probably also a consequence of ion pairing and can be assigned to the CO_2 resonance of a minor ion pair.

The assignment of the 205–201 δ signals to the carbonyl ligands (despite their surprising complexity) was supported by the spec-

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(19) The failure to see an absorption above the solvent cutoff at 1450 cm^{-1} which can be assigned to the assymetric mode of the coordinated CO_2 does not invalidate these assignments. The frequency of this absorption in monoanionic η^1-CO_2 complexes of cobalt depends markedly on the counterion and the alkyl substitution on the salen ligand, ranging from 1680 to below 1600 cm^{-1},[20] and the additional back-donation expected in a dianionic complex could easily shift the absorption below 1450 cm^{-1}. We have even observed examples of monoanionic η^1-CO_2 complexes in which this absorption is below 1450 cm^{-1}.[21]

(20) (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(21) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794.

(22) IR (THF, ν_{CO} only) 2050 (w), 1905 (s), and 1865 (m) cm^{-1}: Darensbourg, D. J.; Gray, R. L,; Ovalles, C.; Pala, M. *J. Mol. Catal.* **1985**, *29*, 285.

(23) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience: New York, 1972; p 133.

(24) Fischer, E. O.; Scherzer, K.; Kreissl, F. R. *J. Organomet. Chem.* **1976**, *118*, C33.

(25) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

(26) Schrock, R. R., personal communication. The data in the following references indicate ranges of 60–120 Hz for single bonds, 120–190 Hz for double bonds, and above 190 Hz for triple bonds. (a) Clark, D. N.; Shrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. (b) Pedersen, S. F.; Shrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483. (c) Fernstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Shrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305. (d) Wengrovius, J. H.; Shrock, R. R. *Organometallics* **1982**, *1*, 148. (e) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Shrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (f) Sharp, P. R.; Holmes, S. J.; Shrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.

(27) The $^{13}CO_2$ resonance and the 201–205 δ resonances also shifted downfield by 0.2–1.7 δ when the sample was warmed to 240 K, but these changes were fully reversible on cooling the sample.

(28) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132.

(29) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

trum of a sample prepared from partially ^{13}C labeled $Li_2[W(CO)_{5-n}(^{13}CO)_n]$ and unlabeled CO_2. As expected, freshly prepared solutions of this material maintained at -78 °C did not exhibit any ^{13}C signals attributable to the CO_2 but did exhibit a complicated series of peaks in the 205–201 δ region. These closely resembled the signals in this region in a sample of $Li_2[W(CO)_5(^{13}CO_2)]$ which had been allowed to warm to 240 K, consistent with assignment of the signals in both samples to carbonyl ligands in different ion pairs of the CO_2 complex.

Facile oxide transfer from coordinated CO_2 to coordinated CO in solutions of $Li_2[W(CO)_5(CO_2)]$ was confirmed by the change in the ^{13}C spectrum when the sample of $Li_2[W(CO)_{5-n}(^{13}CO)_n(CO_2)]$ was warmed to 270 K: resonances appeared corresponding to the 223.4 and 221.8 δ absorptions of freshly prepared $Li_2[W(CO)_5(^{13}CO_2)]$, indicating gradual enrichment of the carbon of the coordinated CO_2.

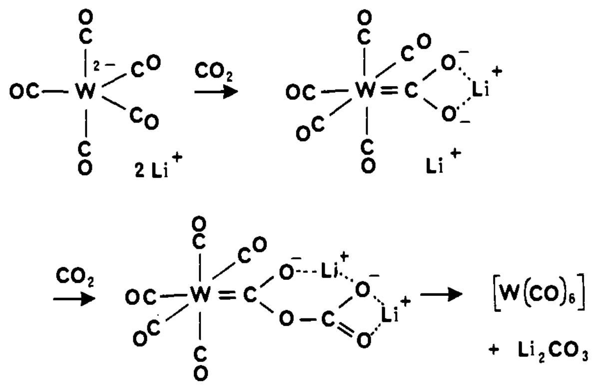
Formation and Spectral Characteristics of the Model η^1-Heteroallene Complex $Li_2[W(CO)_5(CS_2)]$. The problems which the facile oxide scrambling characteristic of $Li_2[W(CO)_5(CO_2)]$ added to spectral characterization led us to investigate the reaction of CS_2 with $Li_2[W(CO)_5]$, in search of a model heteroallene adduct which would not be subject to such complications. The addition of 1 equiv of CS_2 to a THF solution of $Li_2[W(CO)_5]$ at -78 °C produced an intensely deep red-purple solution, and IR spectra showed that the CS_2 and the pentacarbonyl dianion had both been consumed. The ν_{CO} absorptions of the product are similar to those of $Li_2[W(CO)_5(CO_2)]$ (Figure 1b) and indicate the formation of the 1:1 adduct $Li_2[W(CO)_5(CS_2)]$,[30] with C_{4v} symmetry and absorptions at 2054 (w, equatorial A_1), 1912 (vs, equatorial E), and 1859 (ms, axial A_1) cm^{-1}. Solvent absorptions precluded the observation of the asymmetric ν_{CSS} stretching mode absorption.

An anionic CS_2 complex has been previously reported by Ellis from the reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with CS_2, but this species could not be isolated from THF solution,[31] and no η^1-CS_2 complexes with alkali metal counterions have been structurally characterized to date. The closest model for this coordination mode is probably $[Cl(Ph_3P)_2Pt(\mu\text{-}CS_2)Pt(PPh_3)_2][BF_4]\cdot 0.2CH_2Cl_2$, in which the CS_2 ligand is η^1-C coordinated to one Pt center.[32]

The most encouraging feature of the IR spectra of $Li_2[W(CO)_5(CS_2)]$ and $Na_2[W(CO)_5(CS_2)]$ (which can be prepared similarly and has a spectrum identical with that of the Li^+ salt) is the essentially Lorentzian line shape of the carbonyl absorptions. This suggests that, although the complexes are almost certainly ion paired in THF, ion pairing probably involves interaction with sulfur rather than with carbonyl sites as in $Li_2[W(CO)_5(CO_2)]$. Consistent with this, the species formed by reaction of CS_2 with partially labeled $Na_2[W(CO)_{5-n}(^{13}CO)_n(CS_2)]$ gave the simple ^{13}C spectrum expected for a $[W(CO)_5L]$ complex (see Table II for comparative data), with two distinct carbonyl resonances with appropriate intensities at 204.8 and 199.7 δ which can be assigned to the axial and equatorial carbonyls of $Na_2[W(CO)_{5-n}(^{13}CO)_n(CS_2)]$. Since the IR spectra of $Li_2[W(CO)_5(CO_2)]$ and $Li_2[W(CO)_5(CS_2)]$ are very similar except for the evidence for ion pairing with the equatorial carbonyls of the former, the straightforward ^{13}C spectrum of $[W(CO)_5(CS_2)]^{2-}$ strongly supports the interpretation advanced above of the ^{13}C spectra of the CO_2 complex.

The Mechanism of the Reductive Disproportionation Reaction. The intermediacy of $Li_2[W(CO)_5(CO_2)]$ in the reductive disproportionation of CO_2 by $Li_2[W(CO)_5]$ was confirmed by the addition of further CO_2 to a sample of the CO_2 adduct to give $[W(CO)_6]$ and CO_3^{2-}, but the details of this reaction are unclear.

Scheme I. Mechanism Proposed for the Reductive Disproportionation of CO_2 by $Li_2[W(CO)_5]$



The CO_2 adduct could give $[W(CO)_6]$ by direct expulsion of an oxide ion, scavenged by excess CO_2 to give carbonate. Oxide is, however, an exceedingly poor leaving group, and it would be difficult within this mechanism to account for the marked decrease in the stability of $Li_2[W(CO)_5(CO_2)]$ in the presence of excess CO_2. It seems more probable that excess CO_2 plays an active role in the reductive disproportionation by coordinating to the nucleophilic oxygen atoms of the CO_2 in $Li_2[W(CO)_5(CO_2)]$ to give a $C(O)OCO_2$ complex (Scheme I) which could eliminate carbonate directly.

Although no experimental evidence has been obtained for a second intermediate in the reductive disproportionation reaction, the precedent from the work of Herskovitz for the formation of a 2:1 CO_2 adduct containing a $C(O)OCO_2$ ligand does make this an attractive hypothesis. He reported[33] that the neutral iridium(I) complex $[IrCl(C_8H_{14})(PMe_3)_3]$ reacts with CO_2 to give an iridium(III) species $[IrCl(PMe_3)_3(C(O)OCO_2)]$ containing a $C(O)OCO_2$ ligand derived from CO_2. The relative stability of this complex, which contrasts markedly with the reactivity of the proposed 2:1 adduct in the tungsten system, probably arises from two factors: (a) the lability of the cyclooctene ligand in the iridium system opens a coordination site through which the $C(O)OCO_2$ unit can act as bischelate ligand, and (b) carbonate loss from the neutral iridium complex would involve marked charge separation.

The applicability of the mechanism of Scheme I to the reaction of CO_2 with other pentacarbonyl dianions of the group 6 metals is supported by the observation of an intermediate 1:1 adduct in the reaction of CO_2 with $Li_2[Cr(CO)_5]$, with very similar IR characteristics to those of $Li_2[W(CO)_5(CO_2)]$. $Na_2[W(CO)_5]$ reacts with CO_2 in THF at -78 °C to give a mixture of $Na_2[W(CO)_5]$, $[W(CO)_6]$, and a new species with a principal C≡O stretching absorption at 1890 cm^{-1}. This is probably $Na_2[W(CO)_5(CO_2)]$, but the complex could not be obtained as cleanly as $Li_2[W(CO)_5(CO_2)]$. No intermediate species could be detected in the reductive disproportionation of CO_2 by $K_2[W(CO)_5]$, and the stability of intermediate $M_2[W(CO)_5(CO_2)]$ salts would appear to increase in the sequence $K^+ < Na^+ < Li^+$.

A mechanism similar to that in Scheme I probably applies to reductive disproportionation of CO_2 by all the dianionic carbonylmetalates which we have studied, but mechanistic investigations of the reactions with the tetracarbonyl dianions of the group 8 metals and with $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]$ were limited by the heterogeneous nature of these reactions.

Reactions of $Li_2[W(CO)_5(CO_2)]$ with Electrophiles. The reactivity of the oxygen atoms in $Li_2[W(CO)_5(CO_2)]$ toward the mild CO_2 electrophile suggested that characterization of $Li_2[W(CO)_5(CO_2)]$ could be completed, and conversion of the CO_2 ligand into an organic derivative initiated, by electrophilic derivatization of the anion. This strategy has been successfully used to convert $[\{Fe(\eta\text{-}C_5H_5)(CO)_2(CO_2)\}_2Mg]$ into a metalloester,[34]

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[30] This adduct is indefinitely stable at -78 °C and stable for hours at room temperature. It does slowly decompose in the presence of excess CS_2, but the reaction gives intractable purple solids rather than the $[W(CO)_5(CS)]$ anticipated if CS_2 underwent a reductive disproportionation reaction with dianionic carbonylmetalates analogous to that observed with CO_2.

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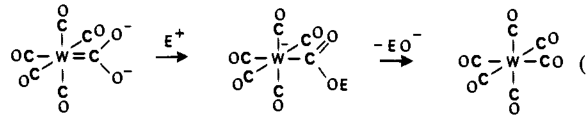
[32] Lisy, J. M.; Dobryzinski, E. D.; Angelici, R. J.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 656.

[33] Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

[34] Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121.

but we have not discovered conditions under which it can be applied to $Li_2[W(CO)_5(CO_2)]$. $[W(CO)_6]$ was the principal product of the reaction of $Li_2[W(CO)_5(CO_2)]$ with a variety of electrophiles, including CF_3CO_2H,[35] $Me_3SiOSO_2CF_3$ $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$, and $\{CH_2OSO_2C_6H_4CH_3\}_2$. The mechanism of the titanocene dichloride reaction is unclear, but the others presumably involve formation of intermediate anionic metalloesters which lose alkoxide ions faster than they react with further electrophile, even in the intramolecular case of bistosylate ethylene (eq 6).[37]



(6)

Conclusions

Reductive disproportionation of carbon dioxide to carbonate and coordinated carbon monoxide is a general reaction of dianionic carbonylmetalates, including the pentacarbonyl dianions of the group 6 metals, the tetracarbonyl dianions of the group 8 metals, and $Na_2[V(\eta\text{-}C_5H_5)(CO)_3]$.

The reaction can provide synthetically valuable routes to the corresponding neutral carbonyls. This is particularly true for $[Ru(CO)_5]$ and $[Os(CO)_5]$, which are unstable with respect to the corresponding dodecacarbonyls and which are currently prepared by high-pressure carbonylations of Ru or Os precursors at 160–290 °C.[13,39] Reaction of CO_2 with $Na_2[Ru(CO)_4]$ or $Na_2[Os(CO)_4]$ provides a low-pressure alternative which has marked advantages for small scale or exploratory work. Reductive disproportionation is also convenient for the preparation of samples of either group 8 pentacarbonyls or group 6 hexacarbonyls partially labeled with ^{13}C or ^{18}O.

In the case of $Li_2[W(CO)_5]$ it has been established that reductive disproportionation proceeds through a 1:1 adduct, and solution IR and ^{13}C NMR spectra suggest formulation of the adduct as $Li_2[W(CO)_5(\eta^1\text{-}CO_2)]$ and also suggest that this exists in solution as a mixture of ion pairs. The complex contains an η^1-C coordinated CO_2, and the increase in nucleophilicity resulting from the associated transfer of negative charge onto the oxygen atoms is probably responsible for the kinetic facility of subsequent reaction with a second molecule of CO_2, for the facile transfer of oxide from coordinated CO_2 to coordinated CO, and for the ready loss of oxide in reactions with other electrophiles. There is spectroscopic evidence for similar η^1-C adducts between CO_2 and $Li_2[Cr(CO)_5]$ and $Na_2[W(CO)_5]$, and CS_2 forms a relatively stable η^1-C adduct with $Li_2[W(CO)_5]$.

The failure to obtain clean CO_2 adducts except with Li^+ salts of the pentacarbonyl dianions of the group 6 metals probably reflects the importance of the "supported" coordination mode in these systems. Floriani has previously reported that coordination of CO_2 to an anionic transition metal can be counterion sensitive and has established in the case of K^+ salt of a Co complex that complexation involves binding of the alkali metal counterion to the basic oxygens of the CO_2.[20] Similar supporting interactions are probably at least as important for the dianionic complexes $[M(CO)_5(CO_2)]^{2-}$, and although we do not have direct evidence, the existence of a supported coordination mode is indicated by the counterion dependence of the stability of $[W(CO)_5(CO_2)]^{2-}$. This parallels the counterion stability reported by Floriani for $M'[(R\text{-salen})Co(CO_2)]$[20] and is consistent with tighter binding of the more polarizing cations to the basic oxygens of the bound CO_2.

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[35] Significant quantities of $[W(CO)_5H]^-$ were also produced in this reaction (^{13}C NMR of the product obtained by reaction of CF_3CO_2H with a ^{13}C enriched sample of $Li_2[W(CO)_5(CO_2)]$), as would be anticipated from the established conversion of $[W(CO)_6]$ to $[W(CO)_5H]^-$ by treatment with OH^-.[36]

[36] (a) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (b) Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.* **1981**, *152*, 107. (c) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4688.

[37] The formation of an unstable anionic metalloester from the reaction of an alkoxide with $[W(CO)_6]$ has been reported,[33] and alkoxide loss is analogous to reversible OH^- loss from the corresponding metallocarboxylic acid.[36]

[38] Darensbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. *J. Mol. Catal.* **1985**, *29*, 285.

[39] Rushman, P.; van Buuren, G. N.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.