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

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Carbon dioxide reduction; transition metal; carbonylmetalate.
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 $[M(CO)_5]$ and alkali metal carbonates. The reaction of $Li_2[W(CO)_5]$ with excess $^{13}CO_2$ at $-78^\circ C$ gives $[W(CO)_5(^{13}CO)]$, confirming that the reaction involves reductive disproportionation of $CO_2$ to CO and $CO_2$. 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 $Na_2[V(\eta^2-C_5H_5)(CO)_3]$ reacts with CO$_2$ to give $[V(\eta^2-C_5H_5)(CO)_4]$ and carbonate, indicating that reductive disproportionation is a general reaction of dianionic carbonylmetalate with CO$_2$. Careful addition of one equivalent of CO$_2$ to a solution of $Li_2[W(CO)_5]$ at $-78^\circ C$ leads to an intermediate 1:1 adduct with an IR spectrum consistent with formulation as $Li_2[W(CO)_5(\eta^1-CO_2)]$. The principal $^{13}C$ absorption at 223.4 $\delta$ of a sample of $Li_2[W(CO)_5(\eta^1-^{13}CO_2)]$ prepared at $-78^\circ C$ exhibits $J_{\text{w-c}} = 92$ 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 $\delta$ assigned to the carbonyl ligands. Similar signals are observed in $Li_2[W(CO)_4-n(^{13}CO_n)(CO_2)]$ at $-78^\circ C$, 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 $\eta^1$ adduct $Li_2[W(CO)_5(\eta^1-CS_2)]$, with $^{13}C$ NMR axial and equatorial carbonyl resonances at 204.8 and 199.7 $\delta$. It is proposed that reductive disproportionation of CO$_2$ by a dianionic carbonylmetalate involves oxide transfer from an $\eta^1$-CO$_2$ adduct to a second molecule of CO$_2$ via an intermediate $C_2O_4$ complex.
Introduction

Recent interest in the reduction of carbon dioxide to carbon monoxide 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 number of transition metal systems, in which H₂ is the reductant and water is the oxygen sink. There are, however, several other transition metal promoted reductions of CO₂ 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 CO₂ to give CO and metal oxides, and complexes with easily oxidized ligands (such as phosphines and hydrides) can react with CO₂ to give CO and oxidized ligands.

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (1)
\]

Reactions in which CO₂ acts as its own oxygen sink, to give CO and CO₃²⁻, form a particularly important class of transition metal promoted reductions of CO₂, and the critical reaction in such systems (eq. 2) is termed reductive disproportionation.

\[
2\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-} \quad (2)
\]

The earliest reported example of the formation of both CO and CO₃²⁻ from the reaction of CO₂ with a transition metal complex involved the reaction of [Mo(PMe₂Ph)₄(N₂)₂] with CO₂ to give a dimer ([{Mo(PMe₂Ph)₃(CO)(CO₃)}₂]) in which both CO and CO₃²⁻ are coordinated to molybdenum. Similar reactions involving [Fe(PMe₃)₄] (to give [Fe(PMe₃)₃(CO)(CO₃)]⁵), [Mo(PMe₂)₄(N₂)₂], and [Ni(triphos)(CS₂)] have been observed, and Floriani has reported a detailed study of reductive disproportionation of CO₂ by [Ti(η-C₅H₅)₂(CO)]²⁻.

Transition metal complexes which are powerful two electron reductants should be particularly promising substrates for reductive disproportionation of CO₂, and we have indicated in preliminary communications that CO₂ 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 CO₂ with dianionic carbonylmetalates and that the reaction involves...
discrete CO₂ adducts containing \( \eta^1-C \) coordinated CO₂.

**Experimental Section**

**General.** Reactions and manipulations were conducted under \( \text{N}_2 \) 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 \( \delta \) of an external sample of \( \delta^6 \)-acetone. Mass spectra were recorded on an ABI MS-9 instrument. Aliquots for solution spectra were placed in gas tight demountable cells with NaCl windows. Cells were purged with \( \text{N}_2 \) 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 freshly distilled under \( \text{N}_2 \) from an appropriate desiccant (sodium/benzophenone ketyl for tetrahydrofuran (THF), LiAlH₄ for pentane, CaH₂ for toluene) and degassed before use. Matheson "bone dry" CO₂ 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 CO₂. Na₂[Fe(CO)₄].1.5dioxane 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 Na₂[Ru(CO)₄] and Na₂[Os(CO)₄] as described in the literature. Sodium amalgam reduction of [V(\( \eta^7 \)-C₅H₅)(CO)₄] (Strem) was used to prepare Na₂[V(\( \eta^7 \)-C₅H₅)(CO)₃].THF, 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. 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(perm)] 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\(^\circ\)C to precipitate K\(_2\)M(CO)s\(s\) 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 using methyl orange indicator, and non-carbonate base was determined by titration of a second 1 mL aliquot with HCl using phenolphthalein indicator after precipitation of carbonate with Ba\(^{2+}\).

**Reaction of Li\(_2\)W(CO)s and Na\(_2\)W(CO)s with Excess CO\(_2\).** A naphthalene free solution of Li\(_2\)W(CO)s in THF (from 0.40 g (1.04 mmol) of [W(CO)s(NMe\(_3\))]\(s\)) was cooled to -78\(^\circ\)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 supernatent in the carbonyl region was the T\(_{1u}\) band of [W(CO)s\(s\)] at 1975 cm\(^{-1}\). The precipitate was collected by filtration and shown to be Li\(_2\)CO\(_3\) (0.056 g, 0.76 mmol \(\approx 73\%\)) by comparison (Nujol mull IR) with an authentic sample. The supernatent 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)s\(s\)] (0.30 g, 0.85 mmol \(\approx 82\%\)) were obtained by concentration of an ether extract. The reaction of Na\(_2\)W(CO)s with excess CO\(_2\) was carried out in a similar manner.

**Reaction of Li\(_2\)W(CO)s with Excess \(^{13}\)CO\(_2\) at Low Temperature.** A naphthalene free solution of Li\(_2\)W(CO)s in THF (30 mL) prepared from 0.10 g (0.26 mmol) of [W(CO)s(NMe\(_3\))]\(s\)) was cooled to -78\(^\circ\)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 supernatent 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 re-suspended 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 supernatent 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, then cooled to \(-78^\circ\)C for 1 hour. 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 (\(\equiv 68\%\)) 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)\(_4\)]\(\cdot\)1.5dioxane (0.202 g, 0.58 mmol) in THF (32 mL) was cooled to \(-78^\circ\)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 (\(c = 2910 \text{ M}^{-1} \text{ cm}^{-1}\)) indicated an effective [Fe(CO)\(_5\)] concentration of \(1.46 \times 10^{-2} \text{ M}\) (\(\equiv 82\%\) 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 (\(\equiv 93\%\)) carbonate.

Reaction of Na\(_2\)[Ru(CO)\(_4\)] with Excess CO\(_2\) and Conversion of the Product to
[Ru(CO)₄I₂]. Since [Ru(CO)₅] is light sensitive, this experiment was conducted in apparatus wrapped in Al foil. Excess CO₂ was bubbled for 15 min through a suspension of Na₂[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 A₂" and E' bands of [Ru(CO)₅].¹³ The solution was filtered on to 0.15 g (0.60 mmol) I₂ at 4°C, and the insoluble residue 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)₄I₂].¹³ The solvent was removed under reduced pressure to give a deep orange red solid from which excess I₂ 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)₄I₂] as a yellow powder.

Reaction of Na₂[Os(CO)₄] with Excess CO₂ and Conversion of the Product to [Os(CO)₄I₂]. Since [Os(CO)₅] is light sensitive, this reaction was carried out in apparatus covered in Al foil. The reaction was carried out in a similar manner to the reaction with Na₂[Ru(CO)₄], starting with a suspension of 0.21 g (0.60 mmol) of Na₂[Os(CO)₄] in THF. After addition of CO₂ 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 on to 0.15 g (0.60 mmol) I₂ at 4°C, and the insoluble residue 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)₄I₂].¹³ The solvent was removed from the mixture under reduced pressure and the excess I₂ 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 hours to give 0.20 g (0.37 mmol ± 61%) of [Os(CO)₄I₂] (IR) as an orange-yellow powder.

Preparation of Li₂[W(CO)₅(CO₂)]. A Schlenk vessel containing 19 mL of a 0.035 M solution of Li₂[W(CO)₅] (0.665 mmol) in THF at -78°C was evacuated to ca. 0.01 torr.
through a high vacuum manifold. Dry CO₂ (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 re-pressurization under N₂ indicated quantitative consumption of the initial dianion, with new ν₉ absorptions appearing at 2043 cm⁻¹ (w), 1900 cm⁻¹ (vs), and 1865 cm⁻¹ (s). 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 CO₂ in these solutions.

Preparation of an NMR Sample of Li₂[W(CO)₅(¹³CO₂)]. The vacuum line technique described above was used to add ¹³CO₂ (0.022 g, 0.49 mmol) to a Schlenk tube containing a rapidly stirred 0.042 M solution of Li₂[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 re-pressurization of the reaction vessel under N₂ revealed complete consumption of the initial Li₂[W(CO)₅] together with new ν₉ bands at 2042 cm⁻¹ (w), 1898 cm⁻¹ (vs), and 1865 cm⁻¹ (s). 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-d₆ in a sealed 5 mm tube (to provide a locking signal).

Preparation of Li₂[W(CO)₅(CS₂)]. A colorless solution of CS₂ (38.0 μL, 0.63 mmol) in 3.0 mL of THF was added in three equal portions over 5 min through a cannula to a rapidly stirred 0.043 M solution of Li₂[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 ν₉ absorptions at 2054 cm⁻¹ (w), 1912 cm⁻¹ (vs), and 1859 cm⁻¹ (ms).

Preparation of Li₂[W(CO)₅₋ₙ(¹³CO)ₙ] and Na₂[W(CO)₅₋ₙ(¹³CO)ₙ]. A sample of partially ¹³C-labelled [W(CO)₅] was prepared from the reaction of Na₂[W(CO)₅] with 2.1 equiv ¹³CO₂ and converted into [W(CO)₅₋ₙ(¹³CO)ₙ(NMe₃)], and hence into Li₂[W(CO)₅₋ₙ(¹³CO)ₙ] and Na₂[W(CO)₅₋ₙ(¹³CO)ₙ], as previously described.¹⁰ Mass spectra established that the [W(CO)₅₋ₙ(¹³CO)ₙ(NMe₃)], and presumably the dianions
prepared from it, was labelled as follows: unlabelled, 41%; 1 X $^{13}$C, 42%; 2 X $^{13}$C, 14%; 3 X $^{13}$C, 2%; 4 X $^{13}$C, 1%.

Preparation of an NMR sample of Na$_2$[W(CO)$_{5-n}$(1$^{13}$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 mono-labelled Na$_2$[W(CO)$_{5-n}$(1$^{13}$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 cm$^{-1}$ (w), 2044 cm$^{-1}$ (w), 1961 cm$^{-1}$ (m), 1912 cm$^{-1}$ (vs), and 1859 cm$^{-1}$ (s). 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, 240K) δ 204.8 ($^{1}J_{W-C}$ = 154 Hz), 199.7 ($^{1}J_{W-C}$ = 128 Hz), with 1:4.5 integrated relative intensities.

Preparation of Li$_2$[W(CO)$_{5-n}$(1$^{13}$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)$_{5-n}$(1$^{13}$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 cm$^{-1}$ (vw), 1900 cm$^{-1}$ (vs), and 1866 cm$^{-1}$ (s). 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($\eta$-C$_5$H$_5$)(CO)$_3$] with Excess CO$_2$. A yellow suspension of Na$_2$[V($\eta$-C$_5$H$_5$)(CO)$_3$].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 for 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 to those of an authentic sample of [V($\eta$-C$_5$H$_5$)(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 \([\mathrm{V(\eta-C_5H_5)(CO)_4}]\) (IR and \(^1\)H NMR; 0.12 g, 0.51 mmol \(\equiv 67\%\)) were obtained from this material by concentration of a pentane (3 \(\times\) 20 mL) extract under reduced pressure. The pentane-insoluble residue was analyzed for carbonate as described above (0.43 mmol \(\equiv 57\%\)). The suspension obtained from a separate experiment in which some of the same batch of \(\mathrm{Na_2[V(\eta-C_5H_5)(CO)_3]THF}\) (0.136 g) was treated with excess \(\mathrm{CO}_2\) 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 \([\mathrm{V(\eta-C_5H_5)(CO)_4}]\) 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 \(\mathrm{Li_2[W(CO)_5]}\) in THF a rapid reaction occurs, as evidenced by bleaching of the characteristic orange of \([\mathrm{W(CO)_5}]^{2-}\) and precipitation of a white solid. The only observable carbonyl containing product was \([\mathrm{W(CO)_6]}\) (IR), which could be isolated in 82\% yield. The ether insoluble material was shown to be \(\mathrm{Li_2CO_3}\) (74\%) by comparison of its IR spectrum with that of an authentic sample, suggesting that the reaction involved reductive disproportionation of \(\mathrm{CO}_2\) (eq. 2) to give one equivalent of carbonate and one equivalent of CO coordinated to tungsten (Eq. 3).

\[
\mathrm{Li_2[W(CO)_5]} + 2\mathrm{CO}_2 \rightarrow [\mathrm{W(CO)_6}] + \mathrm{Li_2CO_3}
\]  

(3)

The stoichiometry of the reaction indicates that one of the carbonyls of the product \([\mathrm{W(CO)_6]}\) must be derived from the added \(\mathrm{CO}_2\), and this has been confirmed by carrying out the reaction at \(-78^\circ\mathrm{C}\) with 93\% labelled \(^{13}\mathrm{CO}_2\). The hexacarbonyl obtained was 90\% \([\mathrm{W(CO)_5}(^{13}\mathrm{CO})]\) and 10\% unlabelled \([\mathrm{W(CO)_6}]\) with only traces of \([\mathrm{W(CO)_4}(^{13}\mathrm{CO})_2]\), 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 \(\mathrm{CO}_2\) by carbonylmetalates
was established by examining the reaction of \( \text{CO}_2 \) with a number of other dianionic carbonylmetalates, including the \( \text{Na}^+ \) and \( \text{K}^+ \) salts of \([\text{W(CO)}_5]^{2-}\), the \( \text{K}^+ \) salts of the pentacarbonyl dianions of the other group 6 metals, and the \( \text{Na}^+ \) 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 \( \text{Na}_2[\text{Fe(CO)}_4] \), \( \text{Na}_2[\text{Ru(CO)}_4] \), and \( \text{Na}_2[\text{Os(CO)}_4] \) 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 thirty minutes 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 \( \text{CO}_2 \) was bubbled through a suspension of \( \text{Na}_2[\text{Fe(CO)}_4] \) in THF at \(-78^\circ \text{C}\), for example, there was a distinct lightening of the color of the solution during the addition.

IR spectra suggested that the reaction of \( \text{CO}_2 \) with the group 8 carbonylmetalates is very clean, but quantification of pentacarbonyl formation was hampered by handling problems for all the metals: \([\text{Fe(CO)}_5]\) is a volatile liquid, while \([\text{Ru(CO)}_5]\) and \([\text{Os(CO)}_5]\) are not only volatile but also both thermally and photochemically unstable with respect to the corresponding dodecacarbonyls. The yield of \([\text{Fe(CO)}_5]\) was determined by absorption mode IR spectroscopy based on an experimentally determined extinction coefficient for the \( A_{2}^{\text{a}} \) absorption in THF. This procedure was complicated by the presence of \( \text{CO}_2 \) dissolved in the THF, but outgassing of the solution for two h under \( \text{N}_2 \) allowed determination of the yield as \( 82 \pm 10\% \).

Minimum yields of the unstable pentacarbonyls of Ru and Os were determined by chemical derivitization. Calderazzo and L'Eplattenier have reported that reaction of \([\text{Ru(CO)}_5]\) with \( \text{I}_2 \) results in high yield conversion to the relatively involatile and stable di-iodide \([\text{Ru(CO)}_4\text{I}_2]\).\(^{13}\) Treatment with \( \text{I}_2 \) of the filtered solution obtained
from the reaction of CO\(_2\) with Na\(_2[\text{Ru(CO)}_4]\) led to isolation of a 73% yield of this di-iodide, establishing a minimum yield of 73% for the reductive disproportionation reaction. It has been indicated\(^1\)\(^3\) 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\(_2[\text{Os(CO)}_4]\) 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%.

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\(_2\)CO\(_3\), 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\(^1\)\(^1\)). This involved initial determination of the total base followed by redetermination of the base content after precipitation of the carbonate with Ba\(^{2+}\).\(^1\)\(^5\)

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\(_2[V(\pi-C_5H_5)(CO)_3].THF^9\) (Table I). Although the solvate is insoluble in THF, a suspension reacted readily with added CO\(_2\) to give a solution in which [V(\pi-C_5H_5)(CO)_4] was the only significant carbonyl containing product observable by IR. The [V(\pi-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(\pi-C_5H_5)(CO)_4] corresponded to a minimum yield of 67%, but correction for the mercury contamination (see Experimental) 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\(_2[\text{W(CO)}_5]\) with One Equivalent 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 
CO₂. Determining the mechanism of the reaction is essential to understanding this 
activation, and we accordingly investigated possible intermediates in the reaction 
in some detail using Li₂[W(CO)₆] as a model substrate.

The gradual addition of one equivalent₁⁶ of CO₂ to a stirred solution of 
Li₂[W(CO)₆] in THF at -78°C led to slight lightening of the orange-brown color without 
the formation of any of the Li₂CO₃ precipitate characteristic of the reductive 
disproportionation reaction. Infrared spectra of the solution indicated that the 
Li₂[W(CO)₆] had been completely consumed and that a new species had been formed with a 
characteristic spectrum (Figure 1 (a)) 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, CO₂ 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 CO₂. Rapid transfer of an equivalent of CO₂ into THF 
solutions of Li₂[W(CO)₆] led to the production of substantial [W(CO)₆] production and 
incomplete consumption of the monomeric dianion, presumably because the intermediate 
reacts almost as rapidly with CO₂ as does Li₂[W(CO)₆].₁⁷

The stoichiometry of the reaction with one equivalent of CO₂ indicates that the new 
species may be formulated as a simple 1:1 CO₂ adduct (eq. 4).₁⁸ The CO₂ 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.

\[
\begin{align*}
\text{CO}_2 \ (1 \text{ equiv}) & \\
\text{Li}_2[\text{W(CO)}_6] & \rightarrow \text{Li}_2[\text{W(CO)}_6(\text{CO}_2)] \\
\text{THF, -78°C} & \quad (4)
\end{align*}
\]

Spectroscopic Evidence for Formulation of Li₂[W(CO)₆(ÇO₂)] as an η¹-C Complex of 
CO₂. The limited number of known discrete, well characterized complexes of CO₂ with

11
transition metals\textsuperscript{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 \([\text{Ph}_3\text{PNPPPh}_3]^+ ([\text{PPN}]^+ \text{ introduced as } [\text{PPN}]\text{Cl})\) were all unsuccessful, and \([\text{W(CO)}_6]\) was the only identifiable organometallic product formed. Addition of the cryptand Kryptofix 2.2.1 (4,7,13,16,21-pentaaza-1,10-diazabicyclo[8.8.5]tricosane) to a solution of the adduct at \(-78^\circ\text{C}\) resulted in formation of an orange precipitate, but this decomposed rapidly to \([\text{W(CO)}_6]\) at higher temperatures.

The failure to isolate the \text{CO}_2 adduct focussed attention on solution IR and \textsuperscript{13}\text{C} NMR studies of samples prepared in situ. Solution infrared spectra (Figure 1 (a)) support formulation as a \([\text{W(CO)}_5\text{L}]\) complex with effective \text{C}_4\text{v} symmetry, suggesting that the adduct is the \(\eta^1-\text{C}\) complex \(\text{Li}_2[\text{W(CO)}_5(\eta^1-\text{CO}_2)]\): \([\text{W(CO)}_5\text{L}]\) complexes typically exhibit three bands, corresponding to the \(\text{A}_1\) stretching mode of the equatorial carboxylics (weakly active, generally above 2000 \text{ cm}^{-1}\), the \(\text{E}\) stretch of the equatorial carboxylics, (usually very strong) and the \(\text{A}_1\) stretch of the axial carboxyl (usually strong, and lower in energy than the equatorial \(\text{E}\) band). Such an assignment excellently describes the spectrum of \(\text{Li}_2[\text{W(CO)}_5(\text{CO}_2)]\),\textsuperscript{19} which is strikingly similar, for example, to that of \([\text{K.crypt2:2:2}][\text{W(CO)}_5\text{C(O)OCH}_3]\),\textsuperscript{22} which should have a similar degree of back donation to the carboxylic ligands.

Formation of a complex in which the \text{CO}_2 acts as an \(\eta^1\) Lewis acid ligand to the 18-electron \([\text{W(CO)}_5]^{2-}\) dianion is consistent with the tendency of low valent carboxylic complexes of tungsten to obey the 18-electron rule, and with the \(\eta^1-\text{C}\) coordination found by Floriani in \([\text{Co(n-Pr-salen)K(CO}_2\text{THF}]\), the only structurally characterized complex of \text{CO}_2 with an anionic transition metal complex.\textsuperscript{20}

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

$$[(\eta^2-\text{C}_5\text{H}_4\text{CH}_3)_2\text{Nb(\text{CH}_2\text{SiMe}_3)(CO}_2)] (220.5 \delta^{25})$$

and $[\text{Mo(CO)}_2(\text{PMe}_3)_2]$ (206.1 $\delta^6$).

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$_2[\text{W(CO)}_5(\text{CO}_2)]$ 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$_2[\text{W(CO)}_5(\text{CO}_2)]$ was complicated by solution ion pairing, and by the dramatic activation (established by previous mass spectral studies$^7$) of the CO$_2$ ligand in Li$_2[\text{W(CO)}_5(\text{CO}_2)]$ with respect to oxide transfer from coordinated CO$_2$ to coordinated CO. When an NMR sample of Li$_2[\text{W(CO)}_5(^{13}\text{CO}_2)]$ was warmed to 240 K a complicated series of peaks in the 205-201 $\delta$ 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$_2[\text{W(CO)}_5(\text{CO}_2)]$ which are being progressively labelled by oxide transfer reactions of the type shown in eq 5. Consistent with this interpretation, the changes in the spectrum of labelled Li$_2[\text{W(CO)}_5(\text{CO}_2)]$ 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 unlabelled Li$_2[\text{W(CO)}_5(\text{CO}_2)]$. The correlation reported by Buchner and Schenk between Cotton-Kraihanzel CO force constants and carbonyl $^{13}$C chemical shifts for a series of octahedral $[\text{W(CO)}_5L]$ complexes$^{28}$ was used to predict a chemical shift of 203 $\delta$ for the equatorial carbonyls of Li$_2[\text{W(CO)}_5(\text{CO}_2)]$ from the
solution IR data, in good agreement with observation.

\[ \text{O} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{W} \Rightarrow \text{C} \end{array} \begin{array}{c} \text{O} \end{array} \rightarrow \text{O} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{W} \Rightarrow \text{C} \end{array} \begin{array}{c} \text{O} \end{array} \rightarrow \text{O} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{W} \Rightarrow \text{C} \end{array} \begin{array}{c} \text{O} \end{array} \]

The surprising complexity of the 205-201 \( \delta \) signals probably indicates that \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \) 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 \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \) would be consistent with the non-Lorenztian line shape of the IR absorption assigned to the equatorial carbonyls, which is probably a composite band. The weak resonance at 221.8 \( \delta \) in freshly prepared \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \) is probably also a consequence of ion pairing and can be assigned to the \( \text{CO}_2 \) resonance of a minor ion pair.

The assignment of the 205-201 \( \delta \) signals to the carbonyl ligands (despite their surprising complexity) was supported by the spectrum of a sample prepared from partially \(^{13}\text{C}\) labelled \( \text{Li}_2[\text{W(CO)}_5-n(\text{CO}_2)_n] \) and unlabelled \( \text{CO}_2 \). As expected, freshly prepared solutions of this material maintained at \(-78^\circ\text{C}\) did not exhibit any \(^{13}\text{C}\) signals attributable to the \( \text{CO}_2 \), but did exhibit a complicated series of peaks in the 205-201 \( \delta \) region. These closely resembled the signals in this region in a sample of \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \) 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 \( \text{CO}_2 \) complex.

Facile oxide transfer from coordinated \( \text{CO}_2 \) to coordinated \( \text{CO} \) in solutions of \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \) was confirmed by the change in the \(^{13}\text{C}\) spectrum when the sample of \( \text{Li}_2[\text{W(CO)}_5-n(\text{CO}_2)_n(\text{CO}_2)] \) was warmed to 270 K: resonances appeared corresponding to the 223.4 and 221.8 \( \delta \) absorptions of freshly prepared \( \text{Li}_2[\text{W(CO)}_5(\text{CO}_2)] \), indicating gradual enrichment of the carbon of the coordinated \( \text{CO}_2 \).

Formation and Spectral Characteristics of the Model \( \eta^1 \)-Heteroallene Complex \( \text{Li}_2[\text{W(CO)}_5(\text{CS}_2)] \). 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 one equivalent 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 1 (b)), and indicate the formation of the 1:1 adduct Li$_2$[W(CO)$_5$(CS$_2$)],$^{30}$ with C$_4$ 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[($\mu^2$-C$_5$H$_5$)Fe(CO)$_2$] with CS$_2$, but this species could not be isolated from THF solution,$^{31}$ and no $\pi^1$-CS$_2$ complexes with alkali metal counterions have been structurally characterized to date. The closest model for this coordination mode is probably [Cl(Ph$_3$P)$_2$Pt($\mu$-CS$_2$)Pt(PPh$_3$)$_2$][BF$_4$]·0.2CH$_2$Cl$_2$, in which the CS$_2$ ligand is $\pi^1$-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 to that of the Li$^+$ salt) is the essentially Lorentzian lineshape 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 labelled Na$_2$[W(CO)$_5$-$n$(1$^{3}$CO)$_n$(CS$_2$)] gave the simple $^{13}$C spectrum expected for a [W(CO)$_5$L] complex (see Table II for comparative data), with two distinct carbonyl resonances with appropriate intensities at 204.8 and 199.7 $\delta$ which can be assigned to the axial and equatorial carbonyls of Na$_2$[W(CO)$_5$-$n$(1$^{3}$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 $^{12}$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.

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$_2$O$_4$ 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$_2$O$_4$ ligand does make this an attractive hypothesis. He reported that the neutral iridium (I) complex [IrCl(C$_8$H$_{14}$)(PMe$_3$)$_3$] reacts with CO$_2$ to give an iridium (III) species [IrCl(PMe$_3$)$_3$(C$_2$O$_4$)] containing a C$_2$O$_4$ 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 cyclo-octene ligand in the iridium system opens a coordination site through which the C$_2$O$_4$ unit can act as bis-chelate ligand; (b) carbonate loss from the neutral iridium complex would involve marked charge separation.

The applicability of the mechanism in 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 $-78^\circ$C to give a mixture of Na$_2$[W(CO)$_5$], [W(CO)$_5$] and a new species with a principal C=O stretching absorption at 1890 cm$^{-1}$. This is probably
Na₂[W(CO)₅(CO₂)], but the complex could not be obtained as cleanly as Li₂[W(CO)₅(CO₂)]. No intermediate species could be detected in the reductive disproportionation of CO₂ by K₂[W(CO)₅], and the stability of intermediate Na₂[W(CO)₅(CO₂)] 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 CO₂ 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 Na₂[V(η-C₅H₅)(CO)₃] were limited by the heterogeneous nature of these reactions.

Reactions of Li₂[W(CO)₅(CO₂)] with Electrophiles. The reactivity of the oxygen atoms in Li₂[W(CO)₅(CO₂)] towards the mild CO₂ electrophile suggested that characterization of Li₂[W(CO)₅(CO₂)] could be completed, and conversion of the CO₂ ligand into an organic derivative initiated, by electrophilic derivatization of the anion. This strategy has been successfully used to convert [[Fe(η-C₅H₅)(CO)₂(CO₂)]₂Mg] into a metalloester, but we have not discovered conditions under which it can be applied to Li₂[W(CO)₅(CO₂)]. [W(CO)₅] was the principal product of the reaction of Li₂[W(CO)₅(CO₂)] with a variety of electrophiles, including CF₃CO₂H, MesSiOSO₂CF₃, [Ti(η-C₅H₅)₂Cl₂] and {CH₂OSO₂C₆H₄CH₃}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 bistriflate ethylene (eq. 6).°

\[
\begin{array}{c}
\text{OC}^-\text{W}=\text{CO}^- \\
\text{OC}^-\text{W}=\text{CO}^- \\
\end{array}
\rightarrow
\begin{array}{c}
\text{OC}^-\text{W}=\text{CO}^- \\
\text{OC}^-\text{W}=\text{CO}^- \\
\end{array}
\rightarrow
\begin{array}{c}
\text{OC}^-\text{W}=\text{CO}^- \\
\text{OC}^-\text{W}=\text{CO}^- \\
\end{array}
\]

(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
metals, and Na$_2$[V(η-C$_5$H$_5$)(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 to 290°C.$^{13,19}$ Reaction of CO$_2$ with Na$_2$[Ru(CO)$_5$] or Na$_2$[Os(CO)$_5$] 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 labelled 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)$_5$(η$^1$-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 on to 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$_2$. 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 \(M'[(R\text{-salen})Co(CO_2)]^{2+}\), and is consistent with tighter binding of the more polarizing cations to the basic oxygens of the bound \(CO_2\).

Acknowledgement. This work was supported in part by the Office of Naval Research.


(14) As previously reported\textsuperscript{7b} the isotopic labelling of the hexacarbonyl is much more complex if the reaction is carried out under conditions under which the intermediate CO\textsubscript{2} complex is allowed to warm significantly above \(-78^\circ\text{C}\). This promotes extensive scrambling of oxide between the coordinated CO\textsubscript{2} and coordinated CO.

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

(16) Based on the quantity of [M(CO)\textsubscript{5}(NMe\textsubscript{3})] from which the Li\textsubscript{2}[W(CO)\textsubscript{5}] was prepared by naphthalenide reduction\textsuperscript{10} on the assumption of an 85 \% yield in the reduction.

(17) Similar results were obtained when CO\textsubscript{2} was sublimed onto the frozen surface of the Li\textsubscript{2}[W(CO)\textsubscript{5}] solution at \(-196^\circ\text{C}\) and the resulting mixture permitted to thaw at \(-78^\circ\text{C}\).

(18) There was also no IR evidence for the presence of unreacted CO\textsubscript{2} under these conditions.

(19) The failure to see an absorption above the solvent cut-off at 1450 cm\textsuperscript{-1} which can be assigned to the the assymmetric mode of the coordinated CO\textsubscript{2} does not invalidate these assignments. The frequency of this absorption in monoanionic \(\eta^1\)-CO\textsubscript{2} complexes of cobalt depends markedly on the counterion and the alkyl substitution on the salen ligand, ranging from 1680 to below 1600 cm\textsuperscript{-1},\textsuperscript{20} and the additional back-donation expected in a dianionic complex could easily shift the absorption below 1450 cm\textsuperscript{-1}. We have even observed examples of monoanionic \(\eta^1\)-CO\textsubscript{2} complexes in which this absorption is below 1450 cm\textsuperscript{-1}.\textsuperscript{21}


(22) IR (THF, νco only) 2050 (w), 1905 (s), and 1865 (m) cm⁻¹: Darensbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. J. Mol. Cat. 1985, 29, 285.


(27) The ¹³CO₂ resonance and the 201 to 205 δ resonances also shifted downfield by 0.2 to 1.7 δ when the sample was warmed to 240 K, but these changes were fully reversible on cooling the sample.


This adduct is indefinitely stable at -78°C, and stable for hours at room temperature. It does slowly decompose in the presence of excess CS₂, but the reaction gives intractable purple solids rather than the [W(CO)₅(CS)] anticipated if CS₂ underwent a reductive disproportionation reaction with dianionic carbonylmetalates analogous to that observed with CO₂.


Significant quantities of [W(CO)₅H]⁻ were also produced in this reaction (¹³C NMR of the product obtained by reaction of CF₃CO₂H with a ¹³C enriched sample of Li₂[W(CO)₅(CO₂)]), as would be anticipated from the established conversion of [W(CO)₆] to [W(CO)₅H]⁻ by treatment with OH⁻.

(a) Darensbourg, D. J.; Rokicki, A. Organometallics 1982, 1, 1685.

The formation of an unstable anionic metalloester from the reaction of an alkoxide with [W(CO)₆] has been reported, and alkoxide loss is analogous to reversible OH⁻ loss from the corresponding metallocarboxylic acid.

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$_2$)].

Scheme I. Mechanism proposed for the reductive disproportionation of CO$_2$ by Li$_2$[W(CO)$_5$].
Table I. Yields for the Reductive Disproportionation of CO₂ by Dianionic Carbonylmetallates

<table>
<thead>
<tr>
<th>M'₂[MLₙ] Initial Product (IR)</th>
<th>Isolated Product</th>
<th>Isolated Yield (%)</th>
<th>Yield M'₂CO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂[W(CO)₅] [W(CO)₆]</td>
<td>[W(CO)₆]</td>
<td>82</td>
<td>74a</td>
</tr>
<tr>
<td>Na₂[W(CO)₅] [W(CO)₆]</td>
<td>[W(CO)₆]</td>
<td>83</td>
<td>-b</td>
</tr>
<tr>
<td>K₂[W(CO)₅] [W(CO)₆]</td>
<td>[W(CO)₆]</td>
<td>48</td>
<td>78c</td>
</tr>
<tr>
<td>K₂[Cr(CO)₅] [Cr(CO)₆]</td>
<td>[Cr(CO)₆]</td>
<td>46</td>
<td>68c</td>
</tr>
<tr>
<td>K₂[Mo(CO)₅] [Mo(CO)₆]</td>
<td>[Mo(CO)₆]</td>
<td>42</td>
<td>73c</td>
</tr>
<tr>
<td>Na₂[Fe(CO)₄] [Fe(CO)₅]</td>
<td>Not isolated</td>
<td>82 ± 10d</td>
<td>94c</td>
</tr>
<tr>
<td>Na₂[Ru(CO)₄] [Ru(CO)₅]</td>
<td>cis-[Ru(CO)₄]I₂</td>
<td>73</td>
<td>61c</td>
</tr>
<tr>
<td>Na₂[Os(CO)₄] [Os(CO)₅]</td>
<td>cis-[Os(CO)₄]I₂</td>
<td>61</td>
<td>92c</td>
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<tr>
<td>Na₂[V(η-C₅H₅)-] V(η-C₅H₅)-</td>
<td>[V(η-C₅H₅)(CO)₄]</td>
<td>67 (96)c</td>
<td>57(84)c, e</td>
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<tr>
<td>(CO)₃]  *(CO)₄]</td>
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a Isolated yield.

b Not determined.

c Titrimetric yield.

d Infrared yield.

e After correction for Hg contamination of the starting dianion.
Table II. $^{13}$C NMR Data for Carbon Ligands Directly Bound to Tungsten in \([W(CO)_5L]\) Complexes ($^1J_{W-C}$ Values in Hz in Parentheses)

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<tr>
<th>Complex</th>
<th>$\delta$ CO$_{eq}$</th>
<th>$\delta$ CO$_{ax}$</th>
<th>$\delta$ Cl</th>
<th>T (K)</th>
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<tr>
<td>([W(CO)]_5C(O)Ph)</td>
<td>197.2 (128)</td>
<td>203.4 (116)</td>
<td>321.7 (111)</td>
<td>298</td>
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<tr>
<td>([W(CO)]_5C(Ph)$_2$]</td>
<td>196.8 (129)</td>
<td>213.7 (105)</td>
<td>356.5 (96)</td>
<td>240</td>
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<tr>
<td>([W(CO)]_5C(p-C_6H_4OMe)Ph]</td>
<td>197.2 (129)</td>
<td>211.7 (107)</td>
<td>346.3 (89)</td>
<td>240</td>
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<tr>
<td>NEt$_4[W(CO)_5C(O)Me]$</td>
<td>204.1 (128)</td>
<td>208.1 (137)</td>
<td>275.9 (76)</td>
<td>298</td>
</tr>
<tr>
<td>NEt$_4[W(CO)_5CH$_3$]</td>
<td>207.0 (126)</td>
<td>208.2 (149)</td>
<td>-34.6 (44)</td>
<td>298</td>
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