# Transfer of an Oxide Ion from an Anionic Carbon Dioxide Complex to a Cationic Carbonyl Complex

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*Summary:* Reaction of Li$_2$[W(CO)$_5$(CO$_2$)] with [Fp(CO)]BF$_4$ leads principally to [W(CO)$_6$] and [Fp$_2$]. It is proposed that Li[Fp(CO)$_2$] is the initial product, but that this reacts readily with [Fp(CO)]BF$_4$ to give [Fp$_2$], CO, and CO$_2$. Initial oxide transfer to [Fp(CO)]BF$_4$ is supported by labeling studies using $^{13}$CO$_2$ and C$^{18}$O$_2$ which show that oxygen, but not carbon, is incorporated into the product [Fp$_2$] from the CO$_2$ of Li$_2$[W(CO)$_5$(CO$_2$)].

Oxide ion transfer reactions appear to be characteristic of the nucleophilic oxygen atoms in anionic transition-metal CO$_2$ complexes. Thus the dianionic complex [W(CO)$_5$(CO$_2$)]$^{2-}$ reacts with CO$_2$ to give CO and CO$_3^{2-}$,[1] and isotopic scrambling experiments suggest that this complex also transfers oxide between CO$_2$ and CO ligands.[2] The unprecedented nature of oxide transfer to CO, together with its potential as a route to novel CO$_2$ complexes, has led us to explore the scope of the reaction: we now wish to report evidence, including $^{13}$C and $^{18}$O labeling studies, for the first intermolecular oxide transfer from a coordinated CO$_2$ to a coordinated CO, together with the unusual decomposition reaction of the transient CO$_2$ complex formed.

Oxide transfer from CO$_2$ to CO should be facilitated by the use of an anionic CO$_2$ complex and a cationic CO complex, and we therefore chose Li$_2$[W(CO)$_5$(CO$_2$)], prepared in tetrahydrofuran (THF) as described previously,[2] as the oxide source, and [Fe($\eta$-C$_5$H$_5$)(CO)$_3$]$^+$ [3-6] as the carbonyl substrate. Formation of [Fp(CO$_2$)]$^-$ [4,7] was anticipated (eq 1), but [Fp$_2$][3] was the principal iron-containing product observed when an 80 mM solution of [Fp(CO)]BF$_4$ in CH$_3$CN (0.6 molar equiv) was added to a 40 mM solution of Li$_2$[W(CO)$_5$(CO$_2$)] at −78 °C. The mixture darkened within 5 min from yellow to the characteristic purple of [Fp$_2$], and after 30 min IR spectra indicated that the principal species in solution were [W(CO)$_6$] and [Fp$_2$] together with excess Li$_2$[W(CO)$_5$(CO$_2$)] and some Li$_2$[W$_2$(CO)$_{10}$]. Absorption mode IR[8] established that the quantities of [W(CO)$_6$] and [Fp$_2$] present corresponded to yields of 58% (based on CO$_2$) and 68% (based on [Fp(CO)]BF$_4$), respectively, but separation problems precluded mass balance determination.

$$\mathrm{Li_2[W(CO)_5(CO_2)] + [Fp(CO)]BF_4 \rightarrow [W(CO)_6] + Li[Fp(CO_2)] + LiBF_4} \quad (1)$$

Determining whether Li[Fp(CO$_2$)] was a minor product of the reaction was complicated by the strong carbonyl absorption of [W(CO)$_6$], which would have masked the relatively weak carbonyl absorptions of a small quantity of Li[Fp(CO$_2$)] at 2015 and 1950 cm$^{-1}$. The mixture was therefore treated with 3 equiv of HBF$_4$ in ether; this should convert Li[Fp(CO$_2$)] into [Fp(CO)]BF$_4$,[4] and a 15% yield of [Fp(CO)]BF$_4$ was indeed obtained after extraction of the resulting precipitate with CH$_3$NO$_2$ and addition of diethyl ether, indicating the presence of a comparable amount of Li[Fp(CO$_2$)] in solution before protonation.[9]

The sequence by which [Fp$_2$] was formed was at first unclear, particularly since Li[Fp(CO$_2$)] is indefinitely stable in THF at −78 °C,[11] but is seemed probable that the initial product was Li[Fp(CO$_2$)] and that this reacted with the dissolving [Fp(CO)]BF$_4$ more rapidly than did Li$_2$[W(CO)$_5$(CO$_2$)]. This possibility led us to investigate the reaction between Li[Fp(CO$_2$)] and [Fp(CO)]BF$_4$, and we have determined that these complexes react readily to give [Fp$_2$] as shown in eq 2. The purple of [Fp$_2$] appeared within 5 min of addition of a slurry of [Fp(CO)]BF$_4$ (1 equiv) in THF to a 40 mM solution of Li[Fp(CO$_2$)][11] at −78 °C, and the reaction was complete in less than 30 min as judged by dissolution of the [Fp(CO)]BF$_4$. The mixture was warmed to room temperature, and it was shown (GC) that 1.01 equiv of CO and 1.05 equiv of CO$_2$ had been evolved. The organometallic product was confirmed by IR and $^1$H NMR to be [Fp$_2$], isolated in 85% yield after recrystallization from pentane.

$$\mathrm{Li[Fp(CO_2)] + [Fp(CO)]BF_4 \rightarrow [Fp_2] + CO + CO_2 + LiBF_4} \quad (2)$$

A reasonable mechanism for the oxidative decomposition involves initial electron transfer from [Fp(CO$_2$)]$^-$ to [Fp(CO)]$^+$ to generate paramagnetic intermediates which could form [Fp]·, and hence [Fp$_2$], by loss of CO$_2$ and CO (eq 3); this reaction may provide another example of the importance of Fe(I) species in the organometallic chemistry of iron.[12-15] Alternatively, the observed products may be formed via a transient metalla-anhydride [Fp(CO)O(CO)Fp].

$$\mathrm{[Fp(CO_2)]^- + [Fp(CO)]^+ \rightarrow [Fp(CO)_2]\cdot + [Fp(CO)]\cdot \rightarrow [Fp_2] + CO + CO_2} \quad (3)$$

Evidence supporting initial oxide transfer in the reaction of Li$_2$[W(CO)$_5$(CO$_2$)] with [Fp(CO)]BF$_4$ was obtained from $^{18}$O and $^{13}$C labeling studies in which 99% labeled Li$_2$[W(CO)$_5$(C$^{18}$O$_2$)] and 93% labeled Li$_2$[W(CO)$_5$($^{13}$CO$_2$)] were reacted with [Fp(CO)]BF$_4$ as described above. The [W(CO)$_6$] and [Fp$_2$] formed in each reaction were separated (in low yield) by selective adsorption of the [Fp$_2$] on to silica gel and were analyzed by mass spectrometry. The [Fp$_2$] from the $^{18}$O experiment contained significant quantities of $^{18}$O: 16% was monolabeled and 1% contained two $^{18}$O, and since we have recently shown that there is

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[9] Although other [Fp(L)]$^+$ salts (L = a donor ligand) can be formed by treatment of [Fp$_2$] with HBF$_4$ in CH$_3$CN or CH$_3$NO$_2$,[10] we have confirmed that [Fp(CO)]$^+$ is not formed from [Fp$_2$] under our conditions, even in the presence of [W(CO)$_6$], and it is reasonable to infer that there is a 15% yield of Li[Fp(CO$_2$)] in the solution before protonation.

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facile scrambling of the $CO_2$ and CO oxygen atoms in $Li[Fp(CO_2)]$,[11] the appearance of $C^{18}O$ in $[Fp_2]$ supports the intermediacy of $Li[Fp(CO^{18}O)]$. This is most reasonably formed by oxide transfer from $Li_2[W(CO)_5(C^{18}O_2)]$, and alternative interpretations involving $CO_2$ transfer were ruled out by the results of the $^{13}C$ experiment, which gave $[Fp_2]$ which was 99% unlabeled.

The $[W(CO_6]$ samples formed in the $^{18}O$ and $^{13}C$ labeling experiments were determined to be 61% and 68% monolabeled, respectively, while a further 3% of the material from each experiment contained two labels,[16] suggesting that ca. 30% of the observed $[W(CO)_6]$ had not been formed from $Li_2[W(CO)_5(CO_2)]$, but was a byproduct of the sequence used to prepare $Li_2[W(CO)_5(CO_2)]$. This further implies that the yield of $[W(CO)_6]$ from the reaction with $[Fp(CO)]BF_4$ was ca. 30% less than the spectroscopic yield, bringing the yield into reasonable agreement with the stoichiometry predicted for the formation of $[Fp_2]$ according to eq 1 and 2 after allowing for the persistence of some $Li[Fp(CO_2)]$.

We conclude that the reaction of $Li_2[W(CO)_5(CO_2)]$ with $[Fp(CO)]BF_4$ to give $[Fp_2]$ probably involves initial oxide ion transfer, and this suggests that oxide ion transfer to electrophilic substrates may indeed be a characteristic reaction of carbon dioxide when activated by coordination to an anionic transition-metal complex.

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**Registry No.** $Li_2[W(CO)_5(CO_2)]$, 96807-09-9; $[Fp(CO)]BF_4$, 12244-69-8; $[W(CO)_6]$, 14040-11-0; $[Fp_2]$, 38117-54-3; $Li_2[W_2(CO)_{10}]$, 96807-10-2; $Li[Fp(CO_2)]$, 96807-11-3; oxide, 16833-27-5.

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[16] The presence of a small quantity of *bis*-labeled complex is indicative of some scrambling within the labeled $Li_2[W(CO)_5(CO_2)]$.[2]

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# Synthesis and Reactions of the First Heterodinuclear Methoxycarbyne Complex $(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}COCH_3)(\mu\text{-}CO)Mn(CO)(\eta^5\text{-}CH_3C_5H_4)$

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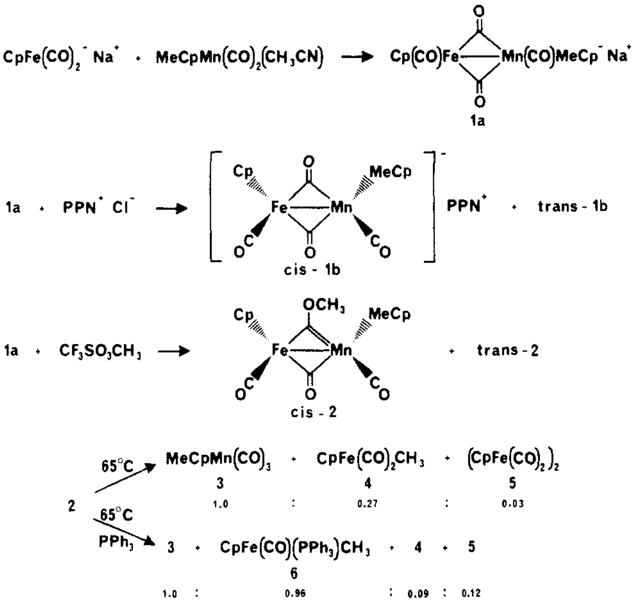
*Summary:* **Alkylation of the new anion $Cp(CO)Fe(\mu\text{-}CO)_2Mn(CO)MeCp^-$ (1) with methyl triflate gives the novel heterodinuclear methoxycarbyne complex $Cp(CO)Fe(\mu\text{-}COMe)(\mu\text{-}CO)Mn(CO)MeCp$ (2). Thermal decomposition of 2 in the presence of triphenylphosphine gives $MeCpMn(CO)_3$ and $CpFe(CO)(PPh_3)CH_3$. Kinetic and isotopic labeling studies of this methyl migration are described.**

Recent work on the Fischer–Tropsch reaction[1] has led to wide acceptance[2] of a carbon–carbon bond-forming mechanism involving surface-bound methylene polymerization. The key proposed intermediate might most simply be modelled by a dinuclear $\eta^1$-alkyl, $\mu$-methylene complex. While many dinuclear $\mu$-methylene compounds are known,[3] only a single type of system is known that also contains an additional $\eta^1$-alkyl group.[4,5] A stepwise approach to the synthesis of such compounds might reasonably involve alkylation of a dinuclear anion. We report here the synthesis of a new heterodinuclear anion, its alkylation to give not an alkyl complex but rather a novel heterodinuclear methoxycarbyne complex, and its decomposition to give a mononuclear alkyl complex. This final

**Scheme I**



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