Reduction of CO_2 by the 19 Electron Complexes $Fe^I(cp)L_3$ [cp = η5-cyclopentadienyl; $L_3 = C_6H_6$, C_6Me_6, or $(PMe_3)_3$]

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The 19 electron complexes $[Fe^I(cp)(C_6R_6)]$, R = H (1) or Me (2), cp = η5-C_5H_5, reduce CO_2 in tetrahydrofuran to give $[Fe^{II}(cp)(C_6R_6)]^+$, $\frac{1}{2}$ CO_3^{2-}, and $\frac{1}{2}$ CO; in the presence of PMe_3 and $Na^+PF_6^-$, reduction of CO_2 yields Na_2CO_3, $[Fe^{II}(cp)(PMe_3)_3]^+[PF_6]^-$ (3+), and $[Fe^{II}(cp)(PMe_3)_2CO]^+[PF_6]^-$ (4+) resulting from the reactions of the very electron-rich 19 electron species $[Fe^I(cp)(PMe_3)_3]$ (3).

The catalytic reduction of CO_2 has recently attracted considerable attention[1] in view of the possibilities of using this abundant, low-cost source of chemicals.[2] The thermodynamic potential $E°$ of the redox system $CO_2/CO_2^{-•}$ is difficult to determine because of the high rates of reactions of $CO_2^{-•}$, but it can be calculated as -2.21 V vs. standard calomel electrode (S.C.E.) in dimethylformamide (DMF).[3] Thus the search for redox catalysts able to mediate CO_2 reduction at lower potentials is intense but the mechanisms for mediated reduction are not yet clear. It is probable that a key feature is the requirement of inner-sphere mechanisms able to increase electron-transfer rates significantly.[4] Such mechanisms should involve 19 electron states[5] of redox catalysts, as for instance in Lehn's rhenium system.[1k] Thus we have investigated CO_2 reduction by the well characterized 19 electron complexes $[Fe^I(cp)(C_6R_6)]$, R = H (1)[6] or Me (2),[7] cp = η5-C_5H_5, which have $E°$ values (vs. S.C.E.) in DMF of -1.36 V (1+/1) and -1.55 V (2+/2).[5] We have also used CO_2 reduction to trap the new transient 19 electron species $[Fe^I(cp)(PMe_3)_3]$ (3).

The 19 electron complex (2) rapidly reacts with CO_2 in tetrahydrofuran (THF) under ambient conditions (20 °C, 1 atm) or at 0 °C to give cleanly a yellow precipitate of (2+), $\frac{1}{2}$ CO_3^{2-} (Scheme 1). The cation (2+) is easily characterized by comparison of its 1H n.m.r. spectrum with that of an authentic sample.[8] The crude reaction mixture was also studied by 13C n.m.r. spectroscopy to detect the nature of the anionic CO_2 reduction products. After reduction using 13CO_2, the 13C n.m.r. spectrum indicates that the anion is 13CO_3^{2-} (δ 171, CD_2Cl_2)[9] together with traces of 13$C_2O_4^{2-}$ and H13CO_2^-. The 19 electron complex (1) reacts similarly at 0 °C (Scheme 1). In the presence of 1 equiv. of $Na^+PF_6^-$, the reactions of (1) and (2) with CO_2 directly give (1+)PF_6^- or (2+)PF_6^-, CO, and Na_2CO_3.

When (1) is treated with 1 atm of CO_2 at 0 °C in the absence of $Na^+PF_6^-$ but in the presence of excess of PMe_3, the course of the reaction is still unchanged and only (1+), $\frac{1}{2}CO_3^{2-}$ is obtained. However when this latter reaction is carried out in the presence of 1 equiv. of $Na^+PF_6^-$, (1+) is no longer obtained and the reaction now yields 66% of $[Fe^{II}-(cp)(PMe_3)_3]^+$ $[PF_6]^-$ (3+),[10] 33% of $[Fe^{II}(cp)(PMe_3)_2-CO]^+$ $[PF_6]^-$ (4+),[10] and Na_2CO_3. These known complexes (3+) and (4+) result from exchange of the labile benzene ligand in (1) by 3 PMe_3 groups giving the 19 electron species
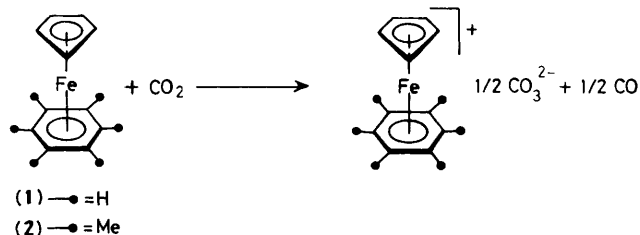
(3). The species (3) can either reduce CO_2 or exchange one PMe_3 by CO (Scheme 2). The $E°$ value of (3+/3) is 2.05 V vs. S.C.E. in CH_2Cl_2 (-50 °C) and the reduction of CO_2 by (3) must thus presumably be much faster than reduction by (1); the reaction products are consistent with this. Another noteworthy feature of the reaction is that all the CO produced by CO_2 reduction is incorporated into the product (4+). This indicates that the transient 19 electron species (3) is substitution labile and that substitution of one PMe_3 by CO is complete at this 19 electron level and faster than CO_2 reduction. We also learn from this that the 19 electron species (4) is thermodynamically downhill as compared to (3) and that it can also reduce CO_2 (ref. 11) (Scheme 2).

This trend is taken into account by the better back-bonding with the CO ligand than with PMe_3, the retrodonation by the Fe^I centre being required by its electron excess. Note that the ligand exchange is totally induced by the presence of $Na^+PF_6^-$. Since electron-transfer from (1) to CO_2 is not expected to be slowed down by $Na^+PF_6^-$, we believe that the latter increases the rate of ligand exchange.† Binding of Na^+

Scheme 2. L = PMe_3.

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(1) —• =H
(2) —• =Me

Scheme 1

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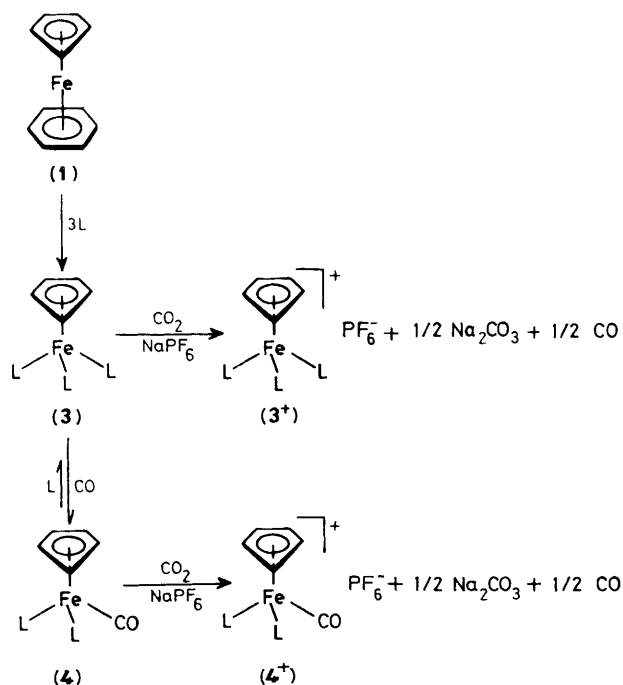
† In the absence of CO_2, (1) [or (2)] reacts in THF with PMe_3 and $Na^+PF_6^-$ to give (3+) and $Fe(PMe_3)_4$ whereas $[Fe(cp)(PMe_3)_2H]$ is obtained in the absence of $Na^+PF_6^-$ (ref. 12a) [these products do not react with CO_2 to form (3+) or (4+)].

to the electron-rich Fe^I centre of (**1**) probably destabilizes the weak Fe^I–benzene bond.

In conclusion reduction of CO_2 is selective for CO and $CO_3{}^{2-}$ formation and rapid at $0\,°C$ in a process which is endergonic by -0.9 V [with (**1**)]; it has been used to trap new 19 electron species and examine their relative stability and oxidation. The rich chemistry of this new series of 19 electron species is now currently under active investigation.

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11 It has been shown that the 19 electron species Fe(cp)L₂(CO) [L₂ = Ph₂PCH₂CH₂PPh₂ or (PBu₃)₂] generated by photolysis of Fe₂(cp)₂(CO)₄ in the presence of the phosphine can behave as a reductant: (a) A. S. Goldman and D. R. Tyler, *Inorg. Chem.*, 1987, **26**, 253; (b) V. MacKenzie and D. R. Tyler, *J. Chem. Soc., Chem. Commun.*, 1987, 1783; (c) A. E. Stiegman, A. S. Goldman, D. B. Leslie, and D. R. Tyler, *ibid.*, 1984, 632.

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