

Reduction of CO₂ by the 19 Electron Complexes Fe^I(cp)L₃ [cp = η⁵-cyclopentadienyl; L₃ = C₆H₆, C₆Me₆, or (PMe₃)₃]

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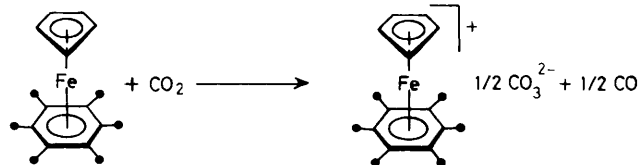
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The 19 electron complexes [Fe^I(cp)(C₆R₆)], R = H (**1**) or Me (**2**), cp = η⁵-C₅H₅, reduce CO₂ in tetrahydrofuran to give [Fe^{II}(cp)(C₆R₆)]⁺, ½ CO₃²⁻, and ½ CO; in the presence of PMe₃ and Na⁺PF₆⁻, reduction of CO₂ yields Na₂CO₃, [Fe^{II}(cp)(PMe₃)₃]⁺[PF₆]⁻ (**3**⁺), and [Fe^{II}(cp)(PMe₃)₂CO]⁺[PF₆]⁻ (**4**⁺) resulting from the reactions of the very electron-rich 19 electron species [Fe^I(cp)(PMe₃)₃] (**3**).

The catalytic reduction of CO₂ has recently attracted considerable attention¹ in view of the possibilities of using this abundant, low-cost source of chemicals.² The thermodynamic potential *E*^o of the redox system CO₂/CO₂^{-•} is difficult to determine because of the high rates of reactions of CO₂^{-•}, 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 CO₂ 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 states⁵ of redox catalysts, as for instance in Lehn's rhenium system.^{1k} Thus we have investigated CO₂ reduction by the well characterized 19 electron complexes [Fe^I(cp)(C₆R₆)], R = H (**1**)⁶ or Me (**2**),⁷ cp = η⁵-C₅H₅, which have *E*^o values (vs. S.C.E.) in DMF of -1.36 V (**1**^{+/•}) and -1.55 V (**2**^{+/•}).⁵ We have also used CO₂ reduction to trap the new transient 19 electron species [Fe^I(cp)(PMe₃)₃] (**3**).

The 19 electron complex (**2**) rapidly reacts with CO₂ in tetrahydrofuran (THF) under ambient conditions (20 °C, 1 atm) or at 0 °C to give cleanly a yellow precipitate of (**2**⁺), ½ CO₃²⁻ (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 CO₂ reduction products. After reduction using ¹³CO₂, the ¹³C n.m.r. spectrum indicates that the anion is ¹³CO₃²⁻ (δ 171, CD₂Cl₂)⁹ together with traces of ¹³C₂O₄²⁻ and H¹³CO₂⁻. The 19 electron complex (**1**) reacts similarly at 0 °C (Scheme 1). In the presence of 1 equiv. of Na⁺PF₆⁻, the reactions of (**1**) and (**2**) with CO₂ directly give (**1**⁺)PF₆⁻ or (**2**⁺)PF₆⁻, CO, and Na₂CO₃.

When (**1**) is treated with 1 atm of CO₂ at 0 °C in the absence of Na⁺PF₆⁻ but in the presence of excess of PMe₃, the course of the reaction is still unchanged and only (**1**⁺), ½ CO₃²⁻ is obtained. However when this latter reaction is carried out in the presence of 1 equiv. of Na⁺PF₆⁻, (**1**⁺) is no longer obtained and the reaction now yields 66% of [Fe^{II}(cp)(PMe₃)₃]⁺[PF₆]⁻ (**3**⁺),¹⁰ 33% of [Fe^{II}(cp)(PMe₃)₂CO]⁺[PF₆]⁻ (**4**⁺),¹⁰ and Na₂CO₃. These known complexes (**3**⁺) and (**4**⁺) result from exchange of the labile benzene ligand in (**1**) by 3 PMe₃ groups giving the 19 electron species

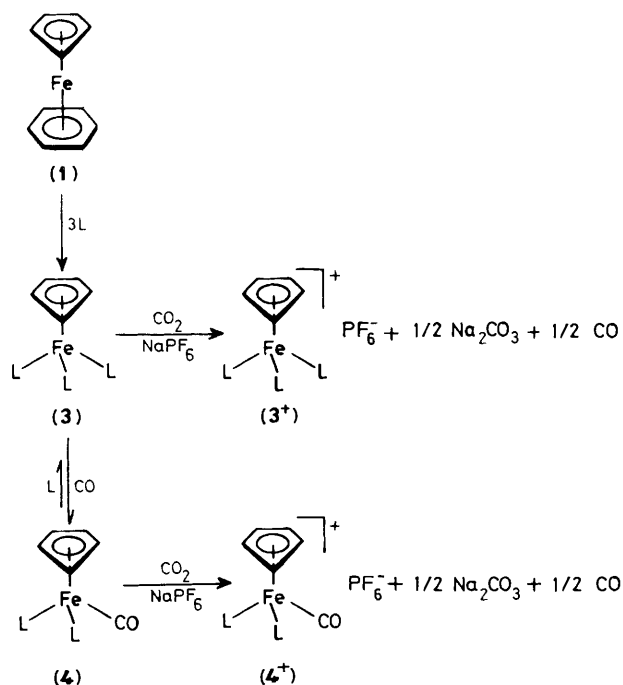


(1) → = H
(2) → = Me

Scheme 1

(**3**). The species (**3**) can either reduce CO₂ or exchange one PMe₃ by CO (Scheme 2). The *E*^o value of (**3**^{+/•}) is 2.05 V vs. S.C.E. in CH₂Cl₂ (-50 °C) and the reduction of CO₂ 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 CO₂ reduction is incorporated into the product (**4**⁺). This indicates that the transient 19 electron species (**3**) is substitution labile and that substitution of one PMe₃ by CO is complete at this 19 electron level and faster than CO₂ 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 CO₂ (ref. 11) (Scheme 2).

This trend is taken into account by the better back-bonding with the CO ligand than with PMe₃, 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⁺PF₆⁻. Since electron-transfer from (**1**) to CO₂ is not expected to be slowed down by Na⁺PF₆⁻, we believe that the latter increases the rate of ligand exchange.† Binding of Na⁺



Scheme 2. L = PMe₃.

† In the absence of CO₂, (**1**) [or (**2**)] reacts in THF with PMe₃ and Na⁺PF₆⁻ to give (**3**⁺) and Fe(PMe₃)₄ whereas [Fe(cp)(PMe₃)₂H] is obtained in the absence of Na⁺PF₆⁻ (ref. 12a) [these products do not react with CO₂ 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 CO₂ is selective for CO and CO₃²⁻ 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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References

- 1 (a) S. Meshitsuka, M. Ichikawa, and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1974, 158; (b) K. Hiratsuka, K. Takahashi, H. Sasaki, and S. Toshima, *Chem. Lett.*, 1977, 158; (c) K. Takahashi, K. Hiratsuka, H. Sasaki, and S. Toshima, *ibid.*, 1979, 305; (d) B. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 7361; (e) M. Tesuka, T. Yajima, A. Tsuchiya, Y. Matsumoto, Y. Uchida, and M. Hidai, *ibid.*, 1982, **104**, 6834; (f) C. M. Lieber and N. S. Lewis, *ibid.*, 1984, **106**, 5033; (g) C. J. Stadler, S. Chao, D. P. Summers, and M. S. Wrighton, *ibid.*, 1983, **105**, 6318; 1984, **106**, 2723; 1984, **106**, 3673; (h) S. Slater and J. H. Wagenknecht, *ibid.*, 1984, **106**, 5367; (i) M. G. Bradley, T. Tysak, D. J. Graves, and N. A. Vlachopoulos, *J. Chem. Soc., Chem. Commun.*, 1983, 349; (j) C. M. Bolinger, B. P. Sullivan, D. Conrad, J. A. Gilbert, N. Story, and T. J. Meyer, *ibid.*, 1985, 796, 1414; (k) J. Hawecker, J. M. Lehn, and R. Ziessel, *ibid.*, 1984, 328; redox mediator Re(bipy)(CO)₃Cl, bipy = 2,2'-bipyridyl; (l) M. Beley, J. P. Colin, R. Ruppert, and J. P. Sauvage, *ibid.*, 1984, 1315; (m) T. R. O'Toole, L. D. Margerum, T. D. Wesmoreland, W. J. Vining, R. W. Murray, and T. J. Meyer, *ibid.*, 1985, 1416; (n) J. Y. Becker, B. Vainas, R. Eger, and L. Kaufman, *ibid.*, 1985, 1471; (o) H. Ishida, H. Tanaka, K. Tanaka, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1987, 131; (p) D.-L. DuBois and A. Miedaner, *J. Am. Chem. Soc.*, 1987, **109**, 113.
- 2 S. Inoue, N. Y. Yamazaki, 'Organic and Bioinorganic Chemistry of Carbon Dioxide,' Wiley, New York, 1982.
- 3 (a) J. C. Gressin, D. Michelet, L. Nadjo, and J.-M. Savéant, *Nouv. J. Chem.*, 1979, 545; (b) C. A. Amatore and J.-M. Savéant, *J. Am. Chem. Soc.*, 1981, **103**, 5021; (c) E. Lamy, L. Nadjo, and J.-M. Savéant, *J. Electroanal. Chem.*, 1977, **78**, 403; (d) Y. Hori, A. Murata, K. Kikuchi, and S. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1987, 728.
- 4 T. Meyer and H. Taube, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Oxford, 1987, vol. I, ch. 7.2.
- 5 D. Astruc, *Chem. Rev.*, 1988, **88**, 1189.
- 6 A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovtseva, and V. A. Petrakova, *J. Organomet. Chem.*, 1973, **61**, 329.
- 7 D. Astruc, J.-R. Hamon, G. Althoff, E. Roman, P. Batail, P. Michaud, J.-P. Mariot, F. Varret, and D. Cozak, *J. Am. Chem. Soc.*, 1979, **101**, 5445.
- 8 (a) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989; (b) I. U. Khand, P. L. Pauson, and W. E. Watts, *ibid.*, 1968, 2257.
- 9 (a) C. J. Stalder, S. Chao, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1984, **106**, 3673; (b) J. B. Stothers, ¹³C N.M.R. Spectroscopy, Academic Press, London, 1972, p. 295.
- 10 (a) P. M. Treichel and D. C. Molzahn, *Synth. React. Met. Org. Chem.*, 1979, **9**, 21; (b) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177; (c) D. Catheline and D. Astruc, *J. Organomet. Chem.*, 1984, **272**, 417.
- 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.
- 12 (a) J. Ruiz, M. Lacoste, and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1989, 813; (b) J. Ruiz and D. Astruc, *ibid.*, 1989, 815.