Photoreduction of Carbon Dioxide to Its Radical Anion by $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$: Formation of Two Carbon–Carbon Bonds via Addition of $CO_2^{\bullet-}$ to Cyclohexene

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The activation and reduction of carbon dioxide has been an active and important area of research.[1-3] Numerous chemical,[4-15] electrochemical,[16-23] and photoelectrochemical[24] systems have now been developed for the reduction of CO_2 to a variety of products. However, *direct* photochemical reduction of CO_2,[25-29] by molecular excited states in homogeneous solution, has proven more difficult to achieve. We now report that CO_2 is reduced directly to its radical anion, $CO_2^{\bullet-}$,[30-32] by $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$, **1** {dppm = bis(diphenylphosphino)methane}, in THF when irradiated at $\lambda > 290$ nm. Significantly, we find that the radical anion, $CO_2^{\bullet-}$, is trapped by cyclohexene, leading to the formation of two new carbon–carbon bonds and the products *cis*- and *trans*-1,2-cyclohexanedicarboxylate.

The new cluster **1** is synthesized by conproportionation of $Ni(COD)_2$[33] (COD = 1,5-cyclooctadiene) and NiI_2 in the presence of dppm[34] Cluster **1** absorbs strongly in the visible region (λ_{max} = 648 nm, ϵ = 5500 (toluene)) but does not emit. It is oxidized cleanly to its radical cation, $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]^{\bullet+}$, **2**, at a potential $E_{1/2}(\mathbf{2}/\mathbf{1}) = -0.69$ V *vs* SCE in 1,1,1-trichloroethane. The oxidation is accompanied by a striking color change from green to purple.

X-ray diffraction studies of **1** and **2** show them to be structurally similar.[35,36] Cluster **2** has slightly longer Ni–Ni and shorter Ni–I bond lengths and reveals an apparent Jahn–Teller distortion of the geometry of the metal core.[37,38]

The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a singlet, δ −14.2 ppm, in toluene or benzene. However, in more polar solvents like THF or CH_2Cl_2 the $^{31}P\{^1H\}$ NMR spectrum is broadened by self-exchange with traces of the radical cation **2**, photogenerated by room light, to line widths of 5000 Hz or greater. When sodium naphthalenide is added to a THF solution of the cluster to suppress formation of the radical cation **2**, the spectrum collapses to a narrow singlet, δ −14.2 ppm. This rapid self-exchange, a signature of facile electron transfer, is not surprising since **1** is structurally very similar its radical cation, **2**. These clusters are also closely related to a recently reported electrocatalyst for CO_2 reduction, $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNMe)(dppm)_3]^+$.[39,40] It is remarkable that cluster **1** is photooxidized by room light in solvents as difficult to reduce as dichloromethane.

Upon broad-band photolysis (500-W Hg lamp, $\lambda > 300$ nm) of a 0.07 mM solution of **1** in dichloromethane for 4 min, complete oxidation occurs, to give the radical cation, **2**. Photolysis is accompanied by an isosbestic transformation in the UV/vis electronic spectrum. Our studies suggest that dichloromethane is reduced to chloromethyl radical and chloride ion. After photolysis of a saturated solution of **1** in CH_2Cl_2 under an atmosphere of CO_2, the solvent was removed *in vacuo*, leaving **2** as a purple solid along with a new material exhibiting IR absorptions at 1730 and 1280 cm^{-1}. Extraction of the solid with water followed by HPLC analysis (C_{18} column, isocratic water/methanol mobile phase, UV absorbance detector) confirmed the presence of chloroacetic acid, the apparent result of addition of CO_2 to $CH_2Cl^\bullet$, followed by reduction to chloroacetate. The quantum yield for photooxidation of **1** was measured using monochromatic irradiation (7-nm bandpass) and potassium ferrioxalate actinometry.[41,42] For a 2% (v/v) solution of CH_2Cl_2 in THF, $\Phi_{254nm} = 2.5 \times 10^{-2}$, $\Phi_{302nm} = 5.6 \times 10^{-3}$, $\Phi_{313nm} = 3.9 \times 10^{-3}$, and $\Phi_{334nm} = 3.5 \times 10^{-3}$.

The quantum yield for photooxidation of **1** in CH_2Cl_2 is negligibly small at wavelengths near the lowest energy electronic

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(1) Grätzel, M. E. *Energy Resources Through Photochemistry and Catalysis*; Academic Press: New York, 1983.
(2) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(3) Ulman, M.; Aurian-Blajeni, B.; Halmann, M. *Chemtech* **1984**, *14*, 235.
(4) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.
(5) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Meyer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.
(6) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914.
(7) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.
(8) DeLaet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754.
(9) Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* **1979**, *28*, 79.
(10) Evans, G. O.; Walter, W. F.; Mills, D. R.; Streit, C. A. *J. Organomet. Chem.* **1978**, *144*, C34.
(11) Lundquist, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1986**, *108*, 8309.
(12) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.
(13) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *6*, 1805.
(14) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467.
(15) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291.
(16) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics* **1988**, *7*, 238 and references therein.
(17) Breikss, A. I.; Abruña, H. D. *J. Electroanal. Chem.* **1986**, *201*, 347.
(18) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753.
(19) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.
(20) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328.
(21) Ogura, K.; Migita, C. T.; Wadaka, K. *J. Mol. Catal.* **1991**, *67*, 161.
(22) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem.* **1992**, *322*, 325.
(23) Hammouche, M.; Lexa, D.; Momenteau, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *113*, 8455.
(24) Memming, R. In *Topics in Current Chemistry*; Steckhan, E., Ed.; Springer-Verlag: Berlin, 1988; Vol. 143, p 79 and references therein.
(25) Lemke, F. R.; DeLaet, D. L.; Gao, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1988**, *110*, 6904.
(26) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56.
(27) Lehn, J.-M.; Ziessel, R. *J. Organomet. Chem.* **1990**, *382*, 157.
(28) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1987**, 536.
(29) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109.
(30) Solymosi, F. *J. Mol. Catal.* **1991**, *65*, 337.
(31) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1975**, *63*, 3821.
(32) Beckwith, A. L. J.; Norman, R. O. C. *J. Chem. Soc. B* **1969**, 400.
(33) Guerrieri, F.; Salerno, G. *J. Organomet. Chem.* **1976**, *114*, 339.
(34) The preparation of the cluster can be found in the supplementary material.
(35) Crystals of **1** were grown by pentane diffusion into toluene. Cluster **1** crystallizes in the space group $P\bar{1}$ with a = 15.116(2) Å, b = 16.016(3) Å, c = 19.957(2) Å, α = 74.32(1)°, β = 70.38(1)°, γ = 73.40(1)°, V = 4279.1 Å^3. Z = 2, and there are six toluenes of crystallization in the unit cell. Least squares refinement of 6494 reflections with $F^2 > 3\sigma(F^2)$ gave convergence to R_1 = 0.042 and R_2 = 0.051.
(36) Crystals of **2** as a triflate salt were grown by pentane diffusion into a dichloromethane solution. **2** crystallizes in the space group *Pnma* with a = 29.852(3) Å, b = 22.190(2) Å, c = 10.656(1) Å, V = 7059.1 Å^3, and Z = 4. Least squares refinement of 4000 reflections with $F^2 > 3\sigma(F^2)$ gave convergence to R_1 = 0.060 and R_2 = 0.080. Relevant bond distances (Å) and angles (deg): Ni(1)–Ni(1), 2.503(2); Ni(1)–Ni(2), 2.526(2); Ni(1)–I_{av}, 2.641(1); Ni(2)–I_{av}, 2.676(2); Ni(1)–P(12), 2.225(3); Ni(2)–P(21), 2.221(3); Ni(1)–Ni(2)–Ni(1), 59.40(3).
(37) Rives, A. B.; You, X.-G.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286.
(38) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 493.
(39) Ratliff, K. S.; Fanwick, P. E.; Kubiak, C. P. *Polyhedron* **1990**, *9*, 1487.
(40) Ratliff, K. S.; Lentz, R. E.; Kubiak, C. P. *Organometallics* **1992**, *11*, 1986.
(41) Calvert, J. G.; Pitts, J. N. J. In *Photochemistry*; Wiley: New York, 1966; p 783.
(42) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *A235*, 518.

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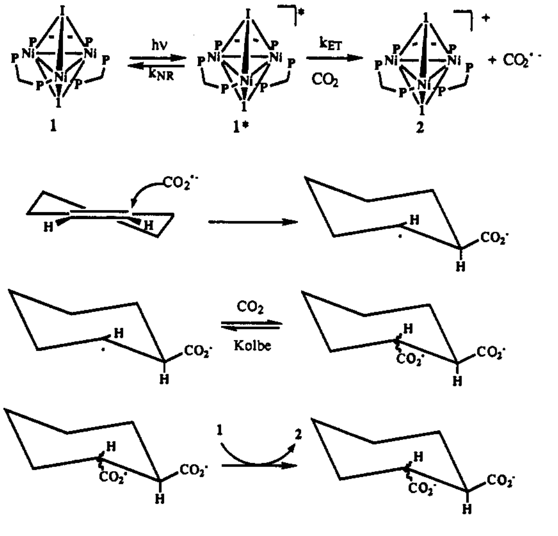
transition (λ_{max} = 648 nm). This indicates that electron transfer does not occur from the lowest excited state, as is the case for the photooxidation of $[(\eta^5\text{-}C_5H_5)(P(OMe)_3)_2Mo{\equiv}CPh]$[43] or $[M(CNPh)_6]$ (M = Mo, W).[44] Importantly, the reduction of methylene chloride by **1** does not proceed by halogen abstraction, as is common.[45] The radical cation **2** is the only nickel-containing product of photolysis. Charge transfer to solvent (CTTS) is another common process leading to photochemical halocarbon reductions;[46–50] however, it is not observed in this case, as net photochemistry of similar efficiencies occurs in both solvents. The production of chloroacetic acid from CH_2Cl_2 and CO_2 likely is initiated via photochemical reduction of CH_2Cl_2.

In order to probe for the intermediacy of $CO_2^{\bullet-}$, a series of photolyses of **1** under CO_2 were performed. Photolysis ($\lambda > 290$ nm) of **1** in THF under 1 atm of CO_2 led to the appearance of CO in the atmosphere above the solution as monitored by GC and the conversion of **1** to **2**. Upon evaporation of the solvent, a new IR absorption at 1435 cm^{-1} was assigned to carbonate. Carbonate was confirmed by HPLC. These results are consistent with the disproportionation of $CO_2^{\bullet-}$ to CO and CO_3^{2-}.

The photolysis experiment was repeated using a 10:1 mixture of THF and toluene. Photolysis was restricted to $\lambda > 350$ nm to forestall complications from toluene triplet photochemistry. No CO was observed by GC. The purple solid remaining after evaporation consisted of **2**, but also showed carboxylate ν(CO) bands in the IR at 1728 and 1185 cm^{-1}. Formate was identified as the only carboxylate present in the water extract by HPLC. These results are consistent with H-atom abstraction from toluene by $CO_2^{\bullet-}$ to give formate.

Since carbonate,[51] formate,[52] and CO[19] all may be formed from CO_2 by inner-sphere mechanisms (although no electrocatalyst is known to produce all three), more definitive evidence for the formation of $CO_2^{\bullet-}$ was obtained by using cyclohexene as a quencher. Photolysis of **1** in a 4:1 v/v THF/cyclohexene solution under 1 atm of CO_2 led to the oxidation of **1** to **2** as evidenced by a change in the color of the solution from green to purple. Evaporation of the solution to dryness followed by derivatization with bis(trimethylsilyl)trifluoroacetamide (BSTFA) in DMF[53–57] and analysis by capillary GC and GC/MS allowed the reduction products to be identified as *cis-meso-* and *trans-*DL-1,2-cyclohexanedicarboxylic acid.[53] These results can be accommodated by a one photon/two electron mechanism involving one photoinduced and one thermal electron transfer. Equations 1–4 summarize the photochemical reduction of CO_2 to $CO_2^{\bullet-}$, followed by addition of $CO_2^{\bullet-}$ and CO_2 to cyclohexene. The *cis:trans* ratio is not 1:1 as would be expected if eq 3 were irreversible; rather, an excess of the thermodynamically more stable *trans* isomer was found (63% *trans*, 37% *cis*).



(1)

(2)

(3)

(4)

While the addition of $CO_2^{\bullet-}$ to a double bond, eq 2, has not been previously reported, such additions are common in free radical chemistry.[58] The CO_2 addition in eq 3 is a reverse Kolbe reaction and is likely to be reversible.[59] The electron transfer in the final step may occur either from the ground state of **1** or from $CO_2^{\bullet-}$.

The proposed mechanism is consistent with the known chemistry of $CO_2^{\bullet-}$ and with the work of Muzyka and Fox on the photochemical *oxidation* of 1,2-cyclohexanedicarboxylic acid.[60,61] Muzyka and Fox oxidized both *cis-* and *trans-*1,2-cyclohexanedicarboxylic acid in aqueous nitric acid by photolysis in the presence of platinized TiO_2. Monodecarboxylation to form cyclohexanecarboxylic acid was the major reaction pathway. The mechanism is simply the reverse of eqs 3 and 4 followed by hydrogen abstraction before a second oxidation/decarboxylation can occur. Significantly, Muzyka and Fox also find differences in the reactivity of the *cis* and *trans* isomers, although the authors attribute this to differences in orientation and the two isomers when adsorbed.

We have demonstrated that the nature of the products obtained subsequent to photogeneration of $CO_2^{\bullet-}$ can be controlled quite selectively by variation of reaction conditions. Most significantly, carbon–carbon bond forming reactions can be accomplished by Michael-type addition of $CO_2^{\bullet-}$ to the double bond of cyclohexene. We are currently attempting to broaden the range of compounds which may be prepared from photogenerated $CO_2^{\bullet-}$.[62]

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Supplementary Material Available: Tables of general temperature factors β_{ij}, bond distances, bond angles, and torsional angles for **1** and **2**, additional information on the synthesis of **1** and on the derivatization of the photolysis products, and an ORTEP drawing of **2** (64 pages); observed and calculated structure factors for **1** and **2** (46 pages). Ordering information is given on any current masthead page.

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(43) Leep, C. J.; Kingsbury, K. B.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 7535.

(44) Weston, C. W.; Verstuyft, A. W.; Nelson, J. H.; Jonassen, H. B. *Inorg. Chem.* **1977**, *16*, 1313.

(45) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; J. Organomet. Chem. Lib.; Elsevier: Amsterdam, 1990; Vol. 22, p 67.

(46) Brand, J. C. D.; Snedden, W. *Trans. Faraday Soc.* **1957**, *53*, 894.

(47) Traverso, O.; Scandola, F. *Inorg. Chim. Acta* **1970**, *4*, 493.

(48) Bock, C. R.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1309.

(49) Miessler, G. L.; Zoebisch, E.; Pignolet, L. H. *Inorg. Chem.* **1978**, *17*, 3636.

(50) Vogler, A.; Kunkely, H. *Inorg. Chem.* **1982**, *21*, 1172.

(51) Reinking, M. K.; Ni, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 6459.

(52) Pugh, R. J.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86.

(53) The details of the addition of BSTFA to the photolysis product can be found in the supplementary material.

(54) Horning, M. G.; Boucher, E. A.; Moss, A. M.; Horning, E. C. *Anal. Lett.* **1968**, *1*, 713.

(55) Butts, W. C. *Anal. Lett.* **1970**, *3*, 29.

(56) Butts, W. C. *J. Chromatogr. Sci.* **1970**, *8*, 474.

(57) Butts, W. C. In *Handbook of Derivatives for Chromatography*; Blau, K., King, G. S., Eds.; Heyden: Philadelphia, 1978; p 411.

(58) Pryor, W. A. In *Introduction to Free Radical Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1966; p 70.

(59) Vijh, A. K.; Conway, B. E. *Chem. Rev.* **1967**, *67*, 623.

(60) Muzyka, J. L.; Fox, M. A. *J. Org. Chem.* **1990**, *55*, 209.

(61) Fox, M. A. In *Electroorganic Synthesis*; Little, R. D., Weinberg, N. L., Eds.; Dekker: New York, 1991; p 181.

(62) Ratliff, K. S.; Kubiak, C. P. *Isr. J. Chem.* **1991**, *31*, 3.