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Organometallic Photochemistry in Aqueous Solution. Synthesis, Crystal and Molecular Structure, and Photochemistry of the $(\eta^5\text{-}C_5H_4COOH)_2W_2(CO)_6$ Complex. Generation of 19-Electron Organometallic Complexes in Aqueous Solution and Their Use as Reducing Agents. Photochemical Production of Hydrogen

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The synthesis, crystal structure, and photochemistry of the $(CpCOOH)_2W_2(CO)_6$ ($CpCOOH = \eta^5\text{-}C_5H_4COOH$) complex are described. The pK_a of the molecule is 4.5, and it is soluble in aqueous solutions at pH 6 or higher. The photochemistry of the molecule is similar to the photochemistry of the $Cp_2W_2(CO)_6$ ($Cp = \eta^5\text{-}C_5H_5$) complex: irradiation into the low-energy tail of the lowest energy absorption band ($\lambda_{max} = 488$ nm; $d\pi \rightarrow \sigma^*$) results in homolytic cleavage of the W–W bond to form $(CpCOOH)W(CO)_3$ radicals in nonaqueous solvents or $(CpCOO^-)W(CO)_3$ radicals in aqueous solution. These 17-electron radicals can be trapped with chlorine atom donors (e.g., CCl_4 in nonaqueous solution or CCl_3COO^- in aqueous solution), or they can react with a ligand (e.g., PPh_2R^-; $R^- = C_6H_4SO_3^-$) to form a reactive 19-electron adduct. Like their counterparts in nonaqueous solvents, the 19-electron adducts generated in aqueous solution are good reductants. They were used to reduce a variety of water-soluble substrates, including $Fe(CN)_6^{3-}$, methyl viologen, and cytochrome *c*. Hydrogen is also formed when the dimer is irradiated in aqueous solution in the presence of a ligand. Crystals of the complex $(C_5H_4COOH)_2W_2(CO)_6\cdot 2C_4H_8O$ ($C_{26}H_{26}O_{12}W_2$) are triclinic, space group $P\bar{1}$, with $a = 7.502$ (2) Å, $b = 10.493$ (5) Å, $c = 10.670$ (6) Å, $\alpha = 118.98$ (3)°, $\beta = 100.25$ (3)°, $\gamma = 94.35$ (3)°, $V = 710.2$ (6) Å^3, and $Z = 1$. The complex crystallizes in an anti conformation, with a "trans-like" orientation of the two COOH groups with respect to each other. The W–W bond length of 3.215 (3) Å is nominally shorter than that in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ (3.222 (1) Å).

The synthesis and development of water-soluble complexes for homogeneous catalysis in aqueous solution is an emerging area of organometallic chemistry.[1] In this regard, one of our long-range goals is to exploit the reducing ability[2-5] of 19-electron organometallic complexes[6] for use as electron-transfer initiators and electron-transfer relays in aqueous catalytic redox cycles (for example, in photochemical water-splitting schemes for solar energy conversion). A scheme summarizing how 19-electron complexes are generated from metal–metal-bonded dimers and their subsequent electron-transfer chemistry is shown in eq 1 for the case of the $Cp_2W_2(CO)_6$ dimer.[5,6,10] Other metal carbonyl dimers react analogously.[7]

$$Cp_2W_2(CO)_6 \xrightarrow{h\nu} \underset{17e^-}{2Cp\dot{W}(CO)_3} \underset{}{\overset{L}{\rightleftharpoons}} \underset{19e^-}{CpW(CO)_3L} \xrightarrow{S} S^- + CpW(CO)_3L^+ \quad (1)$$

$$L = \text{ligand};\ S = \text{reducible substrate}$$

The generation of 19-electron complexes in aqueous solution by this method is unfortunately hampered by the fact that all previously studied dimer complexes are soluble only in nonaqueous solvents. In order to overcome this

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[1] For early references dealing with aqueous-soluble organometallic complexes with sulfonated triphenylphosphine ligands, see: (a) Ahrland, S.; Chatt, J.; Davies, N. R. Williams, A. A. *J. Chem. Soc.* 1958, 276. (b) Ahrland, S.; Chatt, J.; Davies, N. R. Williams, A. A. *J. Chem. Soc.* 1958, 1403. (c) Pettit, L. D.; Irving, H. *J. Chem. Soc.* 1964, 5336. The following lead references and the references therein should be consulted for the application of water-soluble complexes to catalysis: (d) Dror, Y.; Manassen, J. *J. Mol. Catal.* 1977, *2*, 219. (e) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nov. J. Chem.* 1978, *2*, 145. (f) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* 1983, *2*, 1138. (g) Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* 1982, *62*, 135. (h) Sinou, D.; Amrani, Y. *J. Mol. Catal.* 1986, *36*, 319 and references therein. (i) Horvath, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* 1989, *2*, 85. (j) Escaffre, P.; Thorex, A.; Kalck, P. *J. Chem. Soc., Chem. Commun.* 1987, 146. (k) Whitesides, G. M. *J. Am. Chem. Soc.* 1979, *101*, 3683 and references therein. (l) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* 1989, *8*, 542–547. (m) Fache, E.; Senocq, F.; Santini, C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* 1990, 1776–1778. (n) Herrmann, W.; Thiel, W. R.; Huchler, J. G.; Behm, J.; Herdtweck, E. *Chem. Ber.* 1990, *123*, 1963–1970. (o) Benyei, A.; Joo, F. *J. Mol. Catal.* 1990, *58*, 151–163. (p) Kullberg, M. L.; Kubiak, C. P. *Organometallics* 1984, *3*, 623–634. (q) Bruce, M. I.; Skelton, B. W.; Wallic, R. C.; Walton, J. K.; White, A. H.; Williams, M. L. *J. Chem. Soc. Chem. Commun.* 1981, 428–430.

[2] MacKenzie, V.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* 1987, 1783–1784.

[3] Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* 1987, *26*, 253–258.

[4] Stiegman, A. E.; Goldman, A. S.; Leslie, D. B.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* 1984, 632–633.

[5] Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. *Inorg. Chem.* 1989, *28*, 1231–1236.

[6] The adducts that form in the reactions of 17-electron species with ligands are known in the literature as "19-electron adducts" (or "19-electron complexes") simply because the sum of 17 valence electrons from the metal radical and the 2 electrons from the ligand is 19. Note, however, that no implication about the electronic or geometric structures of these complexes is necessarily implied by this name. See refs 7–9 for a complete discussion of the possibility that the adducts need not necessarily have a "19-electron" configuration; slipped Cp rings, bent CO ligands, (i.e., CO acting as a 1-electron donor), and phosphoranyl radical-type structures are all possible and would result in an 18- or 17-electron configuration at the metal center.

[7] Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* 1986, *5*, 215–245.

[8] Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; pp 338–364.

[9] Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* 1990, *97*, 199–140.

[10] The 19-electron adducts have three notable properties that make them outstanding choices as photogenerated reducing agents: (1) They are powerful reductants; their potentials are estimated as $\simeq -1.5$ V vs SCE.[2-5,7] Although electron back-transfer is a problem with many photogenerated reducing agents and sensitizers, this very negative potential effectively inhibits electron back-transfer from the reduced substrate to the 18-electron complex. (2) The 19-electron complexes are easy to generate. As the scheme shows, visible light irradiation of a metal–metal-bonded dimer in the presence of a suitable ligand is all that is required to generate these species. (The dimers and ligands are commercially available.) Because the dimers absorb light throughout the visible region, irradiation at wavelengths even longer than 500 nm is possible. Most substrates for reduction do not absorb at such long wavelengths, so concurrent irradiation of the substrate is not a problem. (3) The 19-electron complexes are versatile reductants. Our work has demonstrated that a wide variety of organic, inorganic, and organometallic complexes can be reduced with the 19-electron complexes in nonaqueous solvents.[2-5] Their versatility is attributed to their outer-sphere electron-transfer mechanism.

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Table I. Electronic Spectral Data

complex[a]	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
$(CpCOO^-)_2W_2(CO)_6$[b]	485 (2200), 365 (19 000)	this work
$(CpCOOH)_2W_2(CO)_6$[c]	488 (2100), 359 (16 000)	this work
$Cp_2W_2(CO)_6$[d]	484 (2500), 356 (21 000)	this work
$(MeCp)_2W_2(CO)_6$[c]	488 (2100), 364 (15 000)	this work, 13
cytochrome c^{II}[e]	550, 521, 415	17
cytochrome c^{III}[e]	530, 408	17
methyl viologen radical cation[e]	396 (42 100), 606 (13 700)	18
methyl viologen dication[e]	275 (20 700)	18

[a] Cp = η^5-C_5H_5; CpCOOH = η^5-C_5H_4COOH. [b] H_2O, pH 10. [c] THF. [d] Benzene. [e] H_2O, pH 7.

Scheme I

$$\mathrm{Na^+[C_5H_5^-]} \xrightarrow[\text{2. W(CO)}_6]{\text{1. CO(OCH}_3)_2} \mathrm{(C_5H_4C(O)OCH_3)W(CO)_3^-}$$

$$\mathrm{(C_5H_4C(O)OCH_3)W(CO)_3^-} \xrightarrow{\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O, HOAc, H}_2\text{O}} \underset{\text{I}}{\mathrm{(C_5H_4C(O)OCH_3)_2W_2(CO)_6}}$$

$$\mathrm{(C_5H_4C(O)OCH_3)_2W_2(CO)_6} \xrightarrow[\text{2. CH}_3\text{COOH/H}_2\text{O}]{\text{1. 2-propanol/H}_2\text{O/KOH}} \underset{\text{II}}{\mathrm{(CpCOOH)_2W_2(CO)_6}}$$

insolubility problem, we have prepared several water-soluble derivatives of the metal–metal-bonded dimers.[11] In this paper we report the synthesis of the aqueous-soluble $(CpCOOH)_2W_2(CO)_6$ complex (CpCOOH = η^5-C_5H_4COOH) and its use as a precursor for the photochemical generation of 19-electron complexes in aqueous solution. We also report the reduction of various substrates in aqueous solution using the photogenerated 19-electron complexes.

Results and Discussion

Synthesis and Solubility of the $(CpCOOH)_2W_2(CO)_6$ Complex. The $(CpCOOH)_2W_2(CO)_6$ complex was synthesized by the route in Scheme I, which is a combination of the methods reported by Rausch[12] for the substitution of a Cp ring and by Birdwhistell[13] for the synthesis of the $Cp_2M_2(CO)_6$ dimers.

The pK_a of the $(CpCOOH)_2W_2(CO)_6$ complex is 4.5,[14] and the molecule is soluble in buffered aqueous solutions at pH 6 or higher. Measurements showed that the solubility of the dimer was at *least*[15] 20 g/L (3×10^{-2} M) in buffered aqueous solution at pH 10 and 25 °C. Note that the dimer will be deprotonated in the basic, buffered aqueous solvents employed in this study. ($(CpCOO^-)_2W_2(CO)_6$ will be used to represent the deprotonated dimer in this paper.[16])

Table II. Selected Infrared Spectral Data

complex[a]	$\nu(C{\equiv}O)$, cm^{-1} (ϵ, M^{-1} cm^{-1})	ref
$Cp_2W_2(CO)_6$[b]	2012 (w), 1952 (6000), 1905 (6000)	22
$(CpCOOH)_2W_2(CO)_6$[c]	2018 (m), 1961 (s), 1901 (s)	this work
$(CpCOOH)_2W_2(CO)_6$[d]	2015 (m), 1965 (s), 1914 (s), 1727 (w)[e]	this work
$(CpCOO^-)_2W_2(CO)_6$[f]	2011 (w), 1961 (s), 1910 (m)	this work
$[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^-$[f]	2058 (s), 1990 (w), 1950	this work
$CpW(CO)_3(PPh_3)^+$[g]	2040 (s), 1985 (m), 1945 (s)	23
$[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$[f]	1964 (s), 1888 (s)	this work
$CpW(CO)_2(PPh_2)_2^+$[g]	1965 (s), 1882 (vs)	23
$(CpCOO^-)W(CO)_3Cl$[f]	2054 (s), 1962 (s), 1950 (sh)	this work
$CpW(CO)_3Cl$[h]	2052 (3000), 1969 (5300), 1950 (2450)	19
$(CpCOOH)W(CO)_3H$[d]	2025 (m), 1938 (s), 1879 (m)	this work
$CpW(CO)_3H$[i]	2020 (vs), 1929 (vs), 1880 (w)	24
$[(CpCOO^-)W^0(CO)_3]^{2-}$[f]	1897 (s), 1791 (s, br)[j]	this work
$CpW(CO)_3^-$[d]	1894 (s), 1790 (s), 1740 (s)	22
$K_3Fe(CN)_6$[f]	2116[k]	25
$K_4Fe(CN)_6\cdot 3H_2O$[f]	2039[k]	25

[a] Cp = η^5-C_5H_5; CpCOOH = η^5-C_5H_4COOH. [b] Benzene. [c] KBr. [d] THF. [e] $\nu(C{=}O)$ in COOH. [f] H_2O, pH 10. [g] Nujol. [h] CCl_4. [i] CS_2. [j] Lower frequencies are not seen due to the high absorbance of H_2O in the region below 1800 cm^{-1}. [k] $\nu(C{\equiv}N)$.

Table III. Disappearance Quantum Yields[a] for the Reactions of $(CpCOOH)_2W_2(CO)_6$ with Various Substrates

substrate	eq in text	Φ[b]
CCl_4 in THF[c]	2	0.53
CCl_3COO^- in H_2O[d]	3	0.31
$Na[PPh_2R]$ in THF	4	0.94, 1.2
$Na[PPh_2R]$ in H_2O[d]	5	1.6

[a] *a* $\lambda = 504$ nm; $I \approx 1 \times 10^{-10}$ einstein/s. [b] Errors estimated at ±10%. [c] 1/4 CCl_4/THF. [d] pH 10.

Electronic Spectrum of $(CpCOOH)_2W_2(CO)_6$. In both aqueous and nonaqueous solvents, the electronic absorption spectrum of $(CpCOOH)_2W_2(CO)_6$ exhibits two bands in the visible/near-UV region (Table I). In aqueous solution at pH 10, there is a weak band at 485 nm (2200 M^{-1} cm^{-1}) and an intense band at 365 nm (19 000 M^{-1} cm^{-1}). This spectrum is essentially identical with the spectra of the $(\eta^5$-$C_5H_5)_2W_2(CO)_6$ and $(\eta^5$-$C_5H_4CH_3)_2W_2(CO)_6$ complexes[19–21] in nonaqueous solvents (Table I), and similar

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(11) We were able to reduce water-soluble substrates by generating the 19-electron complexes in micellar solutions.[2] Unfortunately, the concentration of the substrate had to be kept low in order to keep the system homogeneous. The technique was thus impractical because only small quantities of substrate could be reduced.

(12) Macomber, D. W.; Rausch, M. D. *J. Organomet. Chem.* 1983, *258*, 331–341.

(13) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* 1978, *157*, 239–241.

(14) The pK_a values of various organometallic carboxylic acid substituted Cp complexes are generally about 4.5. See ref 12 for further examples.

(15) We abandoned the quantitative determination of the solubility (using 1 mL of solution) in order to save material. The material is clearly much more soluble than 20 g/L (3×10^{-2} M).

(16) Nomenclature. Because the dimer complex is charged in basic solution and because the PPh_2R^- ligand used in the disproportionation reactions is charged, the reactants and products in this paper can be confusing when compared to the regular Cp (η^5-C_5H_5) analogues. For example, the photochemical disproportionation of $(\eta^5$-$C_5H_5)_2W_2(CO)_6$ with a neutral phosphine ligand yields the anionic $CpW(CO)_3^-$ and cationic $CpW(CO)_3(PR_3)^+$ and $CpW(CO)_2(PR_3)_2^+$ products. However, the same reaction using $(CpCOOH)_2W_2(CO)_6$ and $Na[PPh_2R]$ in aqueous solution at pH 10 yields "$(CpCOO)W(CO)_3(PPh_2R)^-$" and "$(CpCOO)W(CO)_2(PPh_2R)_2^{2-}$" (the analogues of the W(II) cations) and "$(CpCOO)W(CO)_3^{2-}$" (the analogue of the W(0) anion). In order to facilitate comparison to the disproportionation reactions of the neutral dimer complex, the oxidation state of the W will be indicated in all disproportionation reactions. For further clarity and to remind the reader that the PPh_2R ligand is charged and that the CpCOOH ligand has additional charge when it is deprotonated, a minus charge will be shown on the PPh_2R ligand and the deprotonated form of the CpCOOH ligand will be written as $CpCOO^-$. Thus, $(CpCOO)W(CO)_3^{2-}$ will be written as $[(CpCOO^-)W^0(CO)_3]^{2-}$, $(CpCOO)W(CO)_3(PPh_2R)^-$ will be written as $[(CpCOO)^-)W^{II}(CO)_3(PPh_2R^-)]^-$, and $(CpCOO)W(CO)_2(PPh_2R)_2^{2-}$ will be written as $[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$. In complexes such as these written with brackets, the charge of the complex is indicated by the superscript number following the last bracket. In complexes written without brackets (e.g., $(CpCOO^-)_2W_2(CO)_6$), the charge on the complex is not indicated and it must be calculated in the usual way by adding up the charges on the ligands and the metals.

(17) Smith, D. W.; Williams, J. P. *Struct. Bonding* 1970, *7*, 8–39.

(18) Watanabe, T.; Honda, K. *J. Phys. Chem.* 1982, *86*, 2617–2619.

band assignments are therefore proposed: The band at 365 nm is assigned to the $\sigma \rightarrow \sigma^*$ transition and the band at 485 nm to a $d\pi \rightarrow \sigma^*$ transition. All of the photochemical irradiations in this paper were carried out into the low-energy tail of the $d\pi \rightarrow \sigma^*$ band ($\lambda > 525$ nm for general irradiations or $\lambda = 504$ nm for quantum yields).

Photolysis of the W–W Bond. In order to use $(CpCOOH)_2W_2(CO)_6$ as a source of 17-electron radicals for the generation of 19-electron complexes (eq 1), it was first necessary to establish that irradiation of the complex resulted in cleavage of the W–W bond.[7] This was accomplished by using standard metal radical trapping experiments[21] in both aqueous and nonaqueous solution. Thus, irradiation ($\lambda > 525$ nm) of the dimer in CCl_4/THF solution led to the quantitative formation of $(CpCOOH)W(CO)_3Cl$ (eq 2), a product that is now taken as standard

$$(CpCOOH)_2W_2(CO)_6 \xrightarrow[CCl_4/THF]{h\nu} 2(CpCOOH)W(CO)_3Cl \quad (2)$$

evidence of metal–metal bond homolysis.[21] Similarly, irradiation ($\lambda > 525$ nm) of $(CpCOO^-)_2W_2(CO)_6$ and CCl_3COO^- in aqueous solution buffered at pH 10 led to the quantitative formation of $(CpCOO^-)W(CO)_3Cl$ (eq 3), as detected by infrared spectroscopy (Table II).

$$(CpCOO^-)W_2(CO)_6 \xrightarrow[H_2O\ (pH\ 10)/CCl_3COO^-]{h\nu} 2(CpCOO^-)W(CO)_3Cl \quad (3)$$

The quantum yield for disappearance of the dimer in the CCl_4/THF (1/4, v/v) solvent system is considerably larger than the quantum yield in aqueous solution (0.53 vs 0.31; Table III). This result may be attributable to the increased viscosity of the aqueous solvent compared to the nonaqueous solvent system. Our measurements gave a value of 0.667 cP for the viscosity of the CCl_4/THF (1/4, v/v) mixture and a value of 1.09 cP for the buffered aqueous solution. The increased viscosity will favor geminate pair recombination in the aqueous solvent system and thus a smaller quantum yield for cage escape (trapped radical) products.

M–CO Dissociation. The section above is not meant to imply that W–W photolysis is the only primary photoprocess. Abrahamson showed that W–W homolysis and W–CO bond dissociation both occurred as primary photoprocesses when the $Cp_2W_2(CO)_6$ complex (Cp = η^5-C_5H_5) is irradiated with visible light;[26] it is logical to assume that W–CO bond dissociation also occurs when the $(CpCOOH)W_2(CO)_6$ complex is irradiated. One ostensible outcome of W–CO dissociation would be the formation of substitution products; e.g., $(CpCOOH)_2W_2(CO)_5(PPh_2R^-)$ would form when $(CpCOOH)_2W_2(CO)_6$ is irradiated in the presence of $Na[PPh_2R]$ ($R^- = C_6H_4SO_3^-$; this phosphine is water soluble; see the Experimental Section). However, this product would not be detected, because it would photochemically disproportionate (see below).[27,28] As W–CO dissociation is not relevant to 19-electron complex formation, our investigation did not pursue this photoprocess further.

Formation of 19-Electron Complexes. Our previous studies showed that 19-electron species are key intermediates in the photochemical disproportionation reactions of the metal–metal-bonded carbonyl dimers.[28] Thus, if disproportionation of the $(CpCOOH)_2W_2(CO)_6$ complex occurred, it would strongly suggest the intermediate formation of 19-electron complexes. In fact, disproportionation occurred in both nonaqueous and aqueous solvents: irradiation of $(CpCOOH)_2W_2(CO)_6$ and $Na[PPh_2R]$ in dioxane or THF gave the disproportionation products shown in eq 4.[16] The formation of the hydride complex,

$$(CpCOOH)_2W_2(CO)_6 \xrightarrow[PPh_2R^-/dioxane\ or\ THF]{h\nu} [(CpCOO')W^{II}(CO)_3(PPh_2R^-)]^n + [(CpCOO')W^{II}(CO)_2(PPh_2R^-)_2]^m + [(CpCOO')W^0(CO)_3H]^n \quad (4)$$

$$R^- = C_6H_4SO_3^-;\ CpCOO' = CpCOOH\ (n = 0;\ m = -1)\ \text{or}\ CpCOO^-\ (n = -1;\ m = -2)$$

rather than the $(CpCOOH)W(CO)_3^-$ species, was expected. The latter complex is a strong base,[29] and it will deprotonate a carboxylic acid group. Deprotonation of the carboxylic acid group is evidenced by the loss of the 1730-cm^{-1} band (of the COOH group) and the appearance of a band at 1637 cm^{-1} (attributed to the COO^- group) during the course of the reaction.[30] Also, note in reaction 4 (and 5) that $[(CpCOO')W^{II}(CO)_3(PPh_2R^-)]^n$ and $[(CpCOO')W^{II}(CO)_2(PPh_2R^-)_2]^m$ both form. Both products also form in the disproportionation reactions of the $Cp_2M_2(CO)_6$ complexes in nonaqueous solvents, so the formation of both products in eqs 4 and 5 should not be construed as unusual. The disproportionation chain mechanism readily accounts for the formation of both complexes. See ref 3 for further discussion.

Disproportionation in aqueous solution gave the products in eq 5.[16,31]

$$(CpCOO^-)_2W_2(CO)_6 \xrightarrow[PPh_2R^-/H_2O\ (pH\ 10)]{h\nu,\ \phi > 1} [(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^- + [(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-} + [(CpCOO^-)W^0(CO)_3]^{2-} + H_2 \quad (5)$$

Our previous studies showed that the disproportionation reactions in nonaqueous solvents follow a radical chain mechanism and that 19-electron complexes were key intermediates.[3,27,28] The same mechanism appears to be operating in eqs 4 and 5 because the quantum yields (Table III) (1) show the scatter typical of a chain process and (2) are larger than the quantum yield for homolysis. Because 19-electron species are intermediates in the chain reactions, we conclude that irradiation of the $(CpCOOH)_2W_2(CO)_6$ or $(CpCOO^-)_2W_2(CO)_6$ complexes in the presence of PPh_2R^- results in the formation of the $(CpCOO')W^I(CO)_3(PPh_2R^-)$ and $(CpCOO')W^I(CO)_2(PPh_2R^-)_2$ 19-elec-

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(29) Reference 24 reports that $CpW(CO)_3^-$ will deprotonate acetic acid. The pK_a of acetic acid is 4.7 while that of the $(CpCOOH)_2W_2(CO)_6$ complex is 4.5.

(30) Silverstein, R. M.; Bassler, G. C., Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 120.

(31) At pH 7, a small amount of $(CpCOO^-)W(CO)_3H$ also forms in reaction 5.

Table IV. Crystallographic Data

composition	$C_{26}H_{26}O_{12}W_2$
formula wt	898.2
space group	$P\bar{1}$
a	7.502 (2) Å
b	10.493 (5) Å
c	10.670 (6) Å
α	118.98 (3)°
β	100.25 (3)°
γ	94.35 (3)°
V	710.2 (6) Å^3
Z	1
d_{calc}	2.100 g cm^{-3}
T	18 °C
λ	0.71069 Å
μ	83.3 cm^{-1}
rel transmission coeff	0.53–1.00
no. obsd rflcns	1890 [$I \geq 3\sigma(I)$]
$R(F_o)$	0.070
$wR(F_o)$	0.092

tron species (CpCOO′ = CpCOOH or $CpCOO^-$, as appropriate). Note that H_2O can react as a weak ligand to the 17-electron $(CpCOO^-)W(CO)_3$ species to form a 19-electron complex because disproportionation of the $(CpCOO^-)_2W_2(CO)_6$ complex occurred very slowly even in the absence of PPh_2R^-.

In addition to the organometallic products shown in eq 5, H_2 is also formed. One likely pathway for its formation involves the reduction of water by a 19-electron complex.[32] Quantitative measurements showed that the yield of H_2 in reaction 5 was less than or equal to 10%.

Reduction of Water-Soluble Substrates. The 19-electron complexes generated in aqueous solution can be used as photogenerated reducing agents. The substrates reduced in this study were methyl viologen, ferricyanide, and cytochrome *c*. For each of these substrates, 1-electron reduction occurred:

$$(CpCOO^-)_2W_2(CO)_6 + 2PPh_2R^- + 2S \xrightarrow[H_2O]{h\nu} 2S^- + 2[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^- \quad (6)$$

$$S = MV^{2+} \text{ (methyl viologen)}, Fe(CN)_6^{3-}, \text{cytochrome } c^{III}$$

The reactions were not stoichiometric as written in eq 6 because disproportionation products (eq 5) and small amounts of H_2 also formed. The mass balance for the reaction was studied for the case of the MV^{2+} reduction: in the presence of excess MV^{2+}, the reduction of MV^{2+} to $MV^{\bullet+}$ was 83% based on the amount of dimer present; disproportionation products accounted for the remaining 17%. (Complete details are given in the Experimental Section.)

The potential of the 19-electron $(CpCOO^-)W(CO)_3(PPh_2R^-)$ complex can be estimated by its ability to reduce the substrates in the reaction 6. The potential of the $MV^{2+}/MV^{\bullet+}$ couple (the most difficult to reduce substrate in eq 6) is −0.46 vs SCE,[33] so the potential of the 18-/19-electron complex couple is more negative than this value. In fact, the potential is probably much more negative than −0.46 V vs SCE. This conclusion follows because one of the key steps in the disproportionation reaction chain mechanism is the reduction of the metal carbonyl dimer by a 19-electron complex.[3,7,27,28] For example, the reduction of $(CpCOO^-)_2W_2(CO)_6$ by $(CpCOO^-)W^I(CO)_3(PPh_2R^-)$ is a key step in reaction 5. The electrochemical potential of the 18-/19-electron complex couple must, therefore, be more negative than the reduction potential of the dimer complexes. The potentials of the metal carbonyl dimers are less than −1 V vs SCE,[34] and it is likely the $(CpCOO^-)_2W_2(CO)_6$ complex has a similar potential. Thus, the potential of the 18-/19-electron complex couple can be estimated as less than −1 V vs SCE. (Cyclic voltammetry of the $(CpCOO^-)_2W_2(CO)_6$ dimer in aqueous solution at pH 10 showed no current attributable to the reduction of the dimer above the solvent limit (−1.0 V vs SCE).)

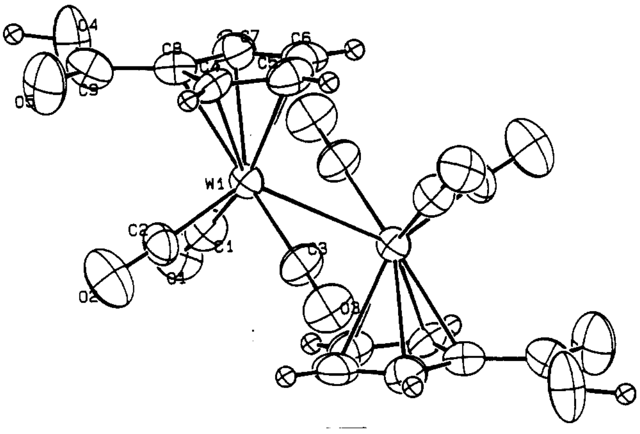

Figure 1. Molecular structure of the $(\eta^5\text{-}C_5H_4COOH)_2W_2(CO)_6$ complex showing the atom-numbering scheme, the anti conformation of the molecule, and the trans-like orientation of the two COOH groups.

Table V. Bond Lengths (Å) for Non-Hydrogen Atoms[a]

W(1)–C(1)	1.94 (3)	O(5)–C(9)	1.19 (3)
W(1)–C(2)	1.97 (2)	O(6)–C(10)	1.46 (4)
W(1)–C(3)	1.98 (3)	O(6)–C(13)	1.42 (5)
W(1)–C(4)	2.30 (2)	C(4)–C(5)	1.36 (3)
W(1)–C(5)	2.32 (2)	C(4)–C(8)	1.48 (3)
W(1)–C(6)	2.35 (2)	C(5)–C(6)	1.38 (4)
W(1)–C(7)	2.35 (2)	C(6)–C(7)	1.39 (4)
W(1)–C(8)	2.31 (2)	C(7)–C(8)	1.43 (3)
O(1)–C(1)	1.18 (3)	C(8)–C(9)	1.48 (3)
O(2)–C(2)	1.12 (3)	C(10)–C(11)	1.40 (5)
O(3)–C(3)	1.16 (3)	C(11)–C(12)	1.49 (6)
O(4)–C(9)	1.31 (3)	C(12)–C(13)	1.46 (6)
W(1)–W(1^i)	3.215 (3)		

[a] Symmetry code: (i) 1 − *x*, −*y*, −*z*. Hydrogen bond: O(4)···O(6) = 2.66 (3) Å.

Crystal Structure. The molecular structure of the $(\eta^5\text{-}C_5H_4COOH)_2W_2(CO)_6$ complex (Figure 1; Table IV) is similar to that of the parent complex, $(\eta^5\text{-}C_5H_5)W_2(CO)_6$,[35] and to the $(\eta^5\text{-}C_5H_4C(O)OCH_3)_2W_2(CO)_6$ complex.[36] The molecule crystallizes in an anti conformation, with a "trans-like" orientation of the two COOH groups with respect to each other. The space group is $P\bar{1}$, and the molecule lies on a crystallographic center of symmetry. The W–W bond length of 3.215 (3) Å is nominally shorter than that in $(\eta^5\text{-}C_5H_5)W_2(CO)_6$ (3.222 (1) Å)[35] but virtually identical with that in $(\eta^5\text{-}C_5H_4C(O)OMe)_2W_2(CO)_6$ (3.216 (1) Å).[36] C_{ring}–C_{ring}, W–C_{ring}, W–C(O), and C≡O distances are all normal and comparable to those in the $(\eta^5\text{-}C_5H_5)W_2(CO)_6$ and $(\eta^5\text{-}C_5H_4C(O)OCH_3)_2W_2(CO)_6$ complexes. Bond length data for the $(\eta^5\text{-}C_5H_4C(O)OCH_3)_2W_2(CO)_6$ complex are given in Table V, and com-

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(32) An alternative mechanism for the formation of hydrogen might involve a binuclear elimination mechanism from the $(CpCOO^-)W(CO)_3H$ complex. We are presently studying the mechanism of H_2 formation.

(33) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632–2635.

(34) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117–5121.

(35) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090.

(36) Weakley, T. J. R.; Avey, A. A., Jr.; Tyler, D. R. *J. Organomet. Chem.*, submitted for publication.

Table VI. Atomic Coordinates and Isotropic or Equivalent Isotropic Thermal Parameters (Å^2) ($B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$)

atom	x	y	z	B_{eq}
W(1)	0.49350 (12)	0.15857 (11)	0.13670 (11)	2.88 (4)
O(1)	0.1088 (23)	0.0557 (21)	−0.0836 (21)	5.0 (7)
O(2)	0.2328 (27)	0.2300 (26)	0.3469 (23)	6.8 (9)
O(3)	0.5554 (25)	−0.0564 (21)	0.2596 (20)	5.2 (7)
O(4)	0.3639 (27)	0.5272 (25)	0.1448 (21)	6.9 (9)
O(5)	0.4014 (30)	0.5668 (24)	0.3726 (21)	6.5 (9)
O(6)	0.1426 (33)	0.7246 (28)	0.2143 (28)	8.1 (6)
C(1)	0.2545 (37)	0.0893 (28)	−0.0020 (27)	4 (1)
C(2)	0.3308 (31)	0.2018 (28)	0.2733 (27)	3.8 (8)
C(3)	0.5269 (34)	0.0131 (29)	0.2029 (28)	4 (1)
C(4)	0.6850 (31)	0.3777 (25)	0.3188 (27)	3.5 (8)
C(5)	0.7948 (34)	0.2896 (29)	0.2406 (31)	4 (1)
C(6)	0.7545 (37)	0.2570 (29)	0.0959 (33)	5 (1)
C(7)	0.6112 (35)	0.3263 (28)	0.0727 (27)	4.0 (9)
C(8)	0.5689 (31)	0.4072 (27)	0.2123 (27)	3.7 (8)
C(9)	0.4302 (33)	0.5045 (30)	0.2527 (27)	4 (1)
C(10)	0.2025 (50)	0.8346 (42)	0.3722 (44)	7.9 (9)
C(11)	0.0853 (61)	0.8025 (49)	0.4457 (51)	10 (1)
C(12)	−0.0925 (62)	0.7369 (53)	0.3302 (56)	10 (1)
C(13)	−0.0412 (64)	0.6578 (51)	0.1892 (54)	10 (1)

parative bond lengths for the three related complexes are found in ref 36. The atomic coordinates are listed in Table VI. All other structural data are found in the supplementary material. There is hydrogen bonding between the COOH group hydrogen atoms and the oxygen atoms of the THF molecules in the lattice (O(4)···O(6) = 2.66 (3) Å). There are no distortions in the C–C bond distances in the C_5 ring that would be indicative of "allyl-ene"- or "diene"-type bonding of the ring.

Conclusions. $(CpCOOH)_2W_2(CO)_6$ is soluble in aqueous solutions at pH 6 or above. The photochemistry of this molecule in aqueous solution is essentially identical with the photochemistry of the $Cp_2W_2(CO)_6$ complex in nonaqueous solvents: Irradiation at wavelengths longer than 500 nm results in homolytic cleavage of the W–W bond. (W–CO bond dissociation probably also occurs, but no evidence for this process was observed.) The resulting $(CpCOO^-)\dot{W}(CO)_3$ radicals can be trapped (by CCl_3COO^-) or they can react with a water-soluble ligand (e.g., Na[PPh_2R]) to form a 19-electron adduct. If no reducible substrates are present, the net reaction is disproportionation of the dimer (and some concomitant reduction of water). If suitable substrates are present, then the photogenerated 19-electron complexes reduce the substrates.

Experimental Section

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere by using standard Schlenk or vacuum line techniques or by handling the materials and solutions in a Vacuum Atmospheres Co. glovebox.

Materials. Sodium (*m*-sulfophenyl)diphenylphosphine (Na[PPh_2R]·$2H_2O$; R = $C_6H_4SO_3$; this phosphine is abbreviated as just Na[PPh_2R]) was synthesized by literature methods[37] and recrystallized from ethanol three times. $K_3Fe(CN)_6$ (Mallinckrodt), methyl viologen dichloride hydrate ([MV^{2+}]Cl_2) (Aldrich), cytochrome *c* (Sigma), trichloroacetic acid (Aldrich), and pH 7 and 10 buffers (Baker) were used a received.

Synthesis of $(CpCOOH)_2W_2(CO)_6$. $(CpCOOH)_2W_2(CO)_6$ was synthesized by a modification of literature procedures (Scheme I).[12,13] Sodium sand (0.46 g, 20 mmol) was reacted at room temperature with 1.56 g (23.6 mmol) of freshly cracked cyclopentadiene for 12 h in diglyme. Dimethyl carbonate (3.00 mL, 35.5 mmol) was then added to the solution, and the solution was refluxed for 1 h. $W(CO)_6$ (7.74 g, 22.0 mmol) was added to the solution, and refluxing was continued for an additional 1.5 h. The reaction mixture was then cooled to room temperature. A solution consisting of 12 g of $Fe(NO_3)_3 \cdot 9H_2O$ (29.7 mmol), 10 mL of acetic acid, and 200 mL of water was then cannulated into the reaction flask. The brick red ester (complex I in Scheme I) precipitated from solution, was separated by filtration, and was washed with H_2O (5.6 g; 72% yield). The ester complex (2.00 g) was then saponified in a solution of 30 mL of 2-propanol, 0.5 g of NaOH, and 5.0 mL of H_2O with stirring for 12 h in the dark. The product (complex II) was then precipitated by cannulating the reaction mixture into a solution of 150 mL of H_2O and 3 mL of acetic acid (0.44 g; 22%). The product was recrystallized by two different methods. For X-ray analysis, a mixed-solvent system of THF and diethyl ether gave suitable crystals containing THF and diethyl ether molecules. However, repeated elemental analyses on these crystals always have variable amounts of solvent molecules, a result we attribute to loss of solvent molecules from the crystal with time. NMR spectroscopy confirmed that solvent was lost from the crystals upon storage. For elemental analysis, the product was recrystallized by dissolution in THF, layering in a 3- to 4-fold volume excess of *hexane*, and storing at −20 °C in a freezer. Crystals grown from this solvent system also contained solvent, but after drying in vacuo for 2 days, the loss of solvent was not problematical. Anal. Calcd for $C_{18}H_{10}O_{10}W_2 \cdot 0.25$ hexane·0.10THF: C, 30.54; H, 1.84. Found: C, 30.48; H, 1.45. (For this analysis, the amount of lattice solvent was determined by NMR.) ^1H NMR (DMSO-d_6): δ 5.88 (m, 8.0, Cp protons), 13.09 (s, 1.2, acid proton; this resonance disappears upon treatment of the sample with D_2O). IR (KBr): 3000 (m, br) ν(OH); 2018 (m) ν(C≡O); 1961 (s) ν(C≡O); 1901 (s) ν(C≡O); 1685 (m) cm^{-1} ν(C=O, carboxylic acid group). For comparison, the ν(C≡O) portion of the IR spectrum of $Cp_2W_2(CO)_6$ in benzene shows bands at 2012 (m), 1952 (s), and 1905 (s) cm^{-1}.[22] This and other infrared spectroscopic data are summarized in Table II. EIMS (59 eV), *m/z* [ion, relative intensity]: 378 [$(C_5H_4COOH)W(CO)_3$ + 1, 100], 349 [$(C_5H_4COOH)W(CO)_2$, 10], 321 [$(C_5H_4COOH)W(CO)$, 50], 292 [$(C_5H_4COOH)W$, 90]. (Attempts to obtain a FAB MS using magic bullet, DMSO, 3-nitrobenzyl alcohol, and (*m*-nitrophenoxy)octane matrices were unsuccessful).

Instruments. Photochemical reactions were carried out with an Oriel 200-W high-pressure mercury arc lamp. A Corning CS 3-68 cutoff filter (λ > 525 nm) was used for all of the irradiations except for the quantum yield determinations. For the quantum yields, an Edmund Scientific Co. 504-nm interference fringe filter was used. Aqueous infrared spectra were obtained with a Nicolet 5DXB FT-IR and a 0.025-mm path length calcium fluoride sealed cell. Electronic spectra were obtained with a Beckman DU-7. Proton NMR data were collected on a GE QE-300 spectrometer.

Quantum yield measurements were made with a Backman DU spectrophotometer using matched quartz 1.00-cm cells fitted with rubber septum caps. All solutions were stirred during irradiation, and the disappearance of the $(CpCOOH)_2W_2(CO)_6$ or $(CpCOO^-)_2W_2(CO)_6$ was monitored at 488 or 485 nm, respectively. The lamp intensity was measured with Aberchrome 540 according to the method of Heller and Langan.[38] Lamp intensities at 504 nm were typically 1 × 10^{-10} einstein/s.

Viscostities were measured with a Cannon-Fenske viscometer calibrated with cyclohexane.

Thermal Stability of $(CpCOOH)_2W_2(CO)_6$ in H_2O. Control experiments showed that the $(CpCOOH)_2W_2(CO)_6$ dimer is thermally stable in aqueous solution in the dark: the electronic spectrum of a solution of the dimer (4 × 10^{-6} M) in buffered aqueous solution at pH 10 was unchanged over 10 h at room temperature in the dark. When the same solution was exposed to the overhead fluorescent lights, the solution changed from pink to clear over a period of several hours. A similar experiment was carried out in an IR cell at 55 °C but with the difference that Na[PPh_2R] was added. The infrared cell was kept in the dark (in an oven at 55 °C) for 40 min, and no reaction was detected spectroscopically. Exposure of this solution to light (λ > 525 nm) led to disproportionation of the dimer. (Spectroscopic details are found below in the section on the disproportionation reactions.)

Photochemical Reaction of $(CpCOOH)_2W_2(CO)_6$ with Radical Traps. Irradiation (λ > 525 nm) of $(CpCOOH)_2W_2(CO)_6$

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(37) Ahrland, S.; Chatt, S.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, *264*, 276–288.

(38) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341–343.

(6.6 mM) in CCl_4/THF (1/4, v/v) in an infrared cell led to the disappearance of the dimer bands at 2008 (m), 1963 (s), and 1908 (s) cm^{-1} and the appearance of new bands at 2052 (m), 1969 (s), and 1950 (sh) cm^{-1}. No other products were detected by IR. The product was identified as $(CpCOOH)W(CO)_3Cl$ by comparison to $CpW(CO)_3Cl$[16] (Table II). Infrared experiments using the exinction coefficients reported in ref 22 showed that $(CpCOOH)W(CO)_3Cl$ formed in quantitative yield: 5.8 mM $(CpCOOH)_2W_2(CO)_6$ yielded 12 (±1) mM $(CpCOOH)W(CO)_3Cl$. The disappearance quantum yield for the reaction of $(CpCOOH)_2W_2(CO)_6$ with CCl_4 in the CCl_4/THF solution was 0.53 ± 0.05. (The quantum yields are summarized in Table III.)

A similar experiment was carried out in aqueous solution. A pH 10 buffered aqueous solution of CCl_3COO^- (6.6×10^1 mM) and $(CpCOO^-)_2W_2(CO)_6$ (6.6 mM) was prepared and transferred in the dark to an IR cell. The cell was kept in the dark for 5 min, and no reaction was observed, as monitored by infrared spectroscopy. However, irradiation of the solution for 10 min led to the disappearance of the dimer peaks and the appearance of bands at 2054 (m), 1962 (s), and 1943 (sh) cm^{-1}. Comparison of these infrared bands to the spectrum of the $CpW(CO)_3Cl$ complex in various nonaqueous solvents[19] indicated that the product of the reaction in aqueous solution was $(CpCOO^-)W(CO)_3Cl$. The reaction in aqueous solution was also quantitative: 9.2 mM $(CpCOO^-)_2W_2(CO)_6$ yielded 18 (±1) mM $(CpCOO^-)W(CO)_3Cl$. The disappearance quantum yield for the reaction of $(CpCOO^-)_2W_2(CO)_6$ with CCl_3COO^- in buffered aqueous solution at pH 10 was 0.31 (Table III).

Disproportionation of the Dimer in Nonaqueous and Aqueous Solvents.[16] A dioxane[39] solution of $(CpCOOH)_2W_2(CO)_6$ (6.6 mM) and $Na[PPh_2R]$ (6.6×10^1 mM) was irradiated for 20 min in an IR cell. Disproportionation of the dimer occurred,[27,28] and the products were identified by infrared spectroscopy as $[(CpCOOH)W^{II}(CO)_3(PPh_2R^-)]$, $[(CpCOOH)W^{II}(CO)_2(PPh_2R^-)_2]^-$, and $(CpCOOH)W^0(CO)_3H$ (Table II).[40] (The hydride complex is formed by protonation of the $(CpCOOH)W(CO)_3^-$ complex, an expected product of the disproportionation reaction, with a proton from the carboxylic acid groups of the various species. Thus, some of the carboxylic acid groups on the $[(CpCOOH)W^{II}(CO)_3(PPh_2R^-)]$, $[(CpCOOH)W^{II}(CO)_2(PPh_2R^-)_2]^-$, and $(CpCOOH)W(CO)_3H$ species are deprotonated. Infrared spectroscopic evidence for this assertion is presented in the Results and Discussion.) An analogous disproportionation reaction occurred in THF solution. Quantum yield measurements for the disproportionation reaction in THF displayed the scatter that is typical of radical chain reactions;[27,28] values of 0.94 and 1.2 were found in two separate measurements (Table III).

In a similar experiment, a buffered aqueous solution at pH 10 containing $(CpCOO^-)_2W_2(CO)_6$ (1.32×10^1 mM) and $Na[PPh_2R]$ (9.9×10^1 mM) was irradiated in an IR cell for 15 min. Disproportionation occurred, and the products were identified by infrared spectroscopy as $[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^-$, $[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$, and $[(CpCOO^-)W^0(CO)_3]^{2-}$ (Table II).[41] Quantitative infrared experiments showed that the reaction proceeded in about 80% yield: 9.2 mM $(CpCOO^-)_2W_2(CO)_6$ yielded 7.3 mM $[(CpCOO^-)W^0(CO)_3]^{2-}$. (The extinction coefficients used for this determination are those reported in ref 19.) The quantum yield of disproportionation in aqueous solution was 1.6.

Reduction of Methyl Viologen (MV^{2+}) in Aqueous Solution. An aqueous solution (pH 10) of $(CpCOO^-)_2W_2(CO)_6$ (2.1×10^{-1} mM), $Na[PPh_2R]$ (2.4 mM), and $[MV^{2+}]Cl_2$ (1.1 mM) was degassed by four freeze–pump–thaw cycles and then irradiated with stirring. The progress of the reaction was followed by electronic absorption spectroscopy, which showed the disappearance of the dimer and the growth of the characteristic 606-nm absorption band of reduced methyl viologen ($MV^{\bullet+}$).[18] An analogous reaction was carried out in an IR cell, and the organometallic products were $[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^-$ and $[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$ as well as a small amount of $[(CpCOO^-)W^0(CO)_3]^{2-}$ as detected by infrared spectroscopy (Table II). (The latter product undoubtedly forms in a disproportionation reaction.) Quantitative experiments showed that $(CpCOO^-)_2W_2(CO)_6$ formed $MV^{\bullet+}$ and $[(CpCOO^-)W^0(CO)_3]^{2-}$ quantitatively: $MV^{\bullet+}$ formed in 83% yield (0.078 mM dimer gave 0.13 mM $MV^{\bullet+}$ as detected by electronic spectroscopy), and $[(CpCOO^-)W^0(CO)_3]^{2-}$ formed in 17% yield (6.6 mM dimer gave 1.1 mM $[(CpCOO^-)W^0(CO)_3]^{2-}$ as detected by infrared spectroscopy in an analogous experiment). A control experiment showed that no reduction of MV^{2+} occurred in the dark and that no reduction occurred (with irradiation) in the absence of $(CpCOO^-)_2W_2(CO)_6$.

Reduction of $Fe(CN)_6^{3-}$. In a typical experiment, 5 mg of $(CpCOOH)_2W_2(CO)_6$ (6.6×10^{-6} mol), 22 mg of $Na[PPh_2R]$ (6.6×10^{-5} mol), and 22 mg (6.6×10^{-5} mol) of $K_3Fe(CN)_6$ were mixed in a 10-mL test tube fitted with a rubber septum. Deoxygenated buffer solution (1 mL; at pH 10) was then transferred into the test tube via cannula. The solution was warmed to 55 °C in the dark to facilitate dissolution of the phosphine. The solution was then transferred to an IR cell, and an initial spectrum was taken. The cell was irradiated, and the progress of the reaction was monitored by infrared spectroscopy until completion of the reaction. The loss of $Fe(CN)_6^{3-}$ was monitored by the decrease in intensity of the CN stretching band at 2116 cm^{-1},[25] and the formation of $Fe(CN)_6^{4-}$ was monitored by the growth of the CN stretch at 2039 cm^{-1}.[25] The major products of the reaction were $[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^-$, $[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$, and $Fe(CN)_6^{4-}$. No $[(CpCOO^-)W^0(CO)_3]^{2-}$ was detected. A control reaction in the dark revealed a slow thermal reduction of $Fe(CN)_6^{3-}$ with no loss of $(CpCOO^-)_2W_2(CO)_6$ or formation of $[(CpCOO^-)W^{II}(CO)_3(PPh_2R^-)]^-$, $[(CpCOO^-)W^{II}(CO)_2(PPh_2R^-)_2]^{2-}$, or $[(CpCOO^-)W^0(CO)_3]^{2-}$.[42]

Reduction of Cytochrome *c*. Cytochrome *c* was reduced in a quartz cuvette in buffered aqueous solution at pH 7. The following concentrations of reactants were used: $(CpCOOH)_2W_2(CO)_6$, 4.0×10^{-5} mM; $Na[PPh_2R]$, 3.3×10^{-3} mM; cytochrome *c*, 1.3×10^{-3} mM. The reaction was monitored by electronic absorption spectroscopy, which showed the disappearance of the $(CpCOO^-)_2W_2(CO)_6$ band at 485 nm as well as the growth of the characteristic bands of reduced cytochrome *c* at 550 and 521 nm.[17,43,44] No reduced cytochrome *c* formed in control reactions in the dark or when no $(CpCOOH)_2W_2(CO)_6$ was present.

Generation and Detection of Hydrogen. In the hydrogen evolution experiments, 20 mg (5.3 mmol) of $(CpCOOH)_2W_2(CO)_6$ and 80 mg (40 mmol) of $Na[PPh_2R]$ were placed in a 5-mL glass vial with a magnetic stir bar. The vial was then fitted with a septum and deoxygenated by a nitrogen gas purge. Deoxygenated buffer (5 mL; pH 10) was then transferred to the reaction vial with use of a gas-tight syringe. The vial was warmed in a water bath (at about 50 °C) in the dark to facilitate dissolution of the phosphine. The solution was then irradiated at room temperature. During the irradiation, the solution was stirred magnetically. Fifty microliters of cover gas was extracted every 5 min for GC analysis. The evolved hydrogen was measured by a Varian Aerograph 2700 gas chromatograph with an 18 ft/1/8 in. i.d. stainless steel column packed with 60/80-mesh silica gel from Alltech Co. The injector and detector were maintained at room temperature, and the column was cooled to −78 °C. Argon was used as the carrier gas with a flow rate of 25 mL/min.

Crystal Structure Analysis. Crystals were grown from a mixture of diethyl ether and tetrahydrofuran. Complete details of the analysis are given in the supplementary material.

Acknowledgment is made to the National Science

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[39] Dioxane was chosen as the solvent to help stabilize the products and prevent back-reactions. See: Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434–4436. A discussion of the back-reaction problem and ways to prevent it is given.

[40] Discussions of the disproportionation mechanism can be found in refs 3, 7, 27, and 28.

[41] The anion is formed instead of the hydride in basic aqueous solutions.

[42] The reduction of $Fe(CN)_6^{3-}$ might be accompanied by the slow thermal oxidation of $Na[PPh_2R]$. Note, however, that no reduction of $Fe(CN)_6^{3-}$ occurs when $(CpCOOH)_2W_2(CO)_6$ is not in the solution. The photochemical reduction of $Fe(CN)_6^{3-}$ was 5 times faster than the thermal reduction under the conditions of our experiment.

[43] Butler, J.; Davies, D. M.; Sykes, A. G. *J. Inorg. Biochem.* **1981**, *15*, 41–53.

[44] Adar, F. *The Porphyrins*; Academic: New York, 1978.

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Supplementary Material Available: Experimental section for the crystal structure analysis and tables of atomic coordinates and isotropic or equivalent isotropic thermal parameters, bond angles, crystallographic information, nonbonded contact distances, calculated coordinates and thermal parameters for hydrogen atoms, anisotropic thermal parameters, torsion angles, and least-squares planes (14 pages); tables of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

Electronic Origin for the Geometric Preferences of HM$_3$(CO)$_{10}$(μ-CR) Compounds

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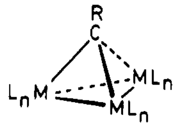
The electronic factors that control the variation of the bridging carbyne unit in HM$_3$(CO)$_{10}$(μ-CR) from μ_2 to μ_3 have been studied by extended Huckel calculations on the models HFe$_3$(CO)$_{10}$(μ-CR) (**3a**, R = H; **3b**, R = NH$_2$) and HFe$_3$(CO)$_{10}$(μ-COMe) (III). The HOMO-1 of **3a** (and of **3b** and III) has antibonding character between the p orbital of carbyne and all the three metals. Substituents on the carbynyl carbon influence the metal–carbon antibonding interaction, but not equally with all metals. This delicate balance of antibonding interactions leads to a variation in the dihedral angle θ between the M–M–M plane and the M–C–M plane as a function of R. Molecular orbital patterns indicate only the μ_2 arrangement for carbyne in all HM$_3$(CO)$_{10}$(μ-CR) compounds. In HOs$_3$(CO)$_{10}$(μ-CH) (XXI) the C–H bond is η^2-μ_2 bridging but not μ_3 bridging. The μ_3 arrangement of carbyne in HM$_2$M'(CO)$_7$Cp(μ-CR) is due to the directionality of the MOs of the M(CO)Cp unit.

Introduction

Carbyne (CR) ligands appear in organometallic chemistry with metal attachments ranging from one to four (μ_1–μ_4).[1] μ_1, μ_2, and μ_3 bridging carbyne arrangements are in principle possible with a trinuclear carbyne complex. There has been no characterized example of a monohapto (μ_1) carbyne ligand attached to a trinuclear cluster. The μ_3 carbyne bridging mode is well-known in the trinuclear complexes 1,[1c] isolobal to tetrahedrane. μ_2-CR on trimetallic templates presents a different story.[2-25] A perusal of available structures (Table I) indicates that the μ_2-CR attachment is a very delicate one. With changes in the substituent R, the CR group can shift gradually from a μ_2 to a μ_3 position. The electronic factors that control such a gradation are discussed in this contribution.



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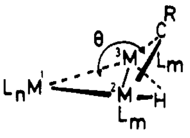
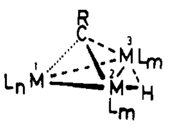


2a



2b

All structures of type **2** (listed in Table I) have 48 valence electrons, same as that in **1**. However, their geometries are very different. At one extreme these could be described as the bicyclobutane-like structure **2a** where the

Table I. Structures of Trinuclear Carbyne Complexes (I–XXVIII) along with the M(1)–C Distance (Å) and Dihedral Angle θ (deg)

compd	no.	M(1)–C	θ	ref
HFe$_3$(CO)$_{10}$(μ-CO)$^-$	I	3.00	102.0	2a
HFe$_3$(CO)$_{10}$(μ-CNMe$_2$)	II	2.89	96.8	3e
HFe$_3$(CO)$_{10}$(μ-COMe)	III	2.70	91.0	2a
HFe$_3$(CO)$_{10}$(μ-COH)	IV			4
HFe$_3$(CO)$_{10}$(μ-CCH$_3$)	V			5
HFe$_3$(CO)$_{10}$(μ-CH)	VI			6
HRu$_3$(CO)$_{10}$(μ-CO)$^-$	VII	3.17	102.4	7
HRu$_3$(CO)$_{10}$(μ-CNMe$_2$)	VIII	3.08	100.4	8
HRu$_3$(CO)$_{10}$(μ-COMe)	IX	2.90	94.4	9
HRu$_3$(CO)$_{10}$(μ-COH)	X			10
HRu$_3$(CO)$_9$Py(μ-CNBz$_2$)	XI			11b
HRu$_3$(CO)$_9$PPh$_3$(μ-CNBz$_2$)	XII			11b
HRu$_3$(CO)$_{10}$(μ-COBH$_2$NMe$_3$)	XIII	2.96	95.8	12
HRu$_3$(CO)$_{10}$(μ-CH)	XIV			13
HOs$_3$(CO)$_{10}$(μ-COMe)	XV			14
HOs$_3$(CO)$_{10}$(μ-CNMe$_2$)	XVI			15
HOs$_3$(CO)$_{10}$(μ-CPh)	XVII	2.59	78.2	16
HOs$_3$(CO)$_{10}$(μ-CCH=CH$_2$)	XVIII			17
HOs$_3$(CO)$_{10}$(μ-CCH$_3$)	XIX			18
HOs$_3$(CO)$_{10}$(μ-CCH$_2$CHMe$_2$)	XX	2.64	82.1	17
HOs$_3$(CO)$_{10}$(μ-CH)	XXI	2.35	69.7	19
HRhFe$_2$Cp(CO)$_7$(μ-COMe)	XXII	2.21	69.2	20
HCoFe$_2$Cp(CO)$_7$(μ-COMe)	XXIII	2.00	64.7	21
NiFe$_2$Cp(CO)$_7$(μ-COMe)	XXIV	1.96		21
(AuPPh$_3$)M$_3$(CO)$_{10}$(μ-COMe)^a	XXV			22
(AuPPh$_3$)Fe$_2$CoCp(CO)$_7$(μ-COMe)	XXVI	1.93		21
HOs$_3$(CO)$_9$(μ-CPh)[=C(OMe)$_2$]	XXVII	2.29	66.6	14b
HOs$_3$(CO)$_{10}$(μ-C[PhC=C=C(Ph)-Re(CO)$_4$PMe$_2$Ph])	XXVIII	3.09	99.1	23

[a] M = Fe, Ru.

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