functionalities. As indicated in Figure 4, the pyridyl rings for unprotonated dpp are probably rotated out of the pyrazyl plane due to steric hindrance. This is inferred[17] from the ultraviolet spectrum, which shows a single strong band at 282 nm and only a weak band at 240 nm. For the diprotonated form only a single band at 293 nm is seen, indicating an even more nonplanar conformation. Nevertheless, in Figure 4 we indicate some electrostatic attraction of the pyrazyl nitrogens for the protons at the pyridyl nitrogens.

For the complexed dpp we were unable to detect the protonation of the single pyridyl nitrogen using absorption spectroscopy. But because it is somewhat remote from the $Ru(bpy)_2^{2+}$ chelation site, we would assume its pK_a is close to that of the free-ligand value, or perhaps somewhat more basic ($pK_a > 2.0$). The spectrally detected protonation with $H_0 = -4.9$ in concentrated sulfuric acid is therefore assigned as protonation of the pyrazyl nitrogen para to the ruthenium(II) and is probably hindered by the attraction of this site to the previously protonated pyridyl group. Once protonation takes place, electrostatic repulsion would force rotation of the positive charge away from the pyrazyl plane, as illustrated. The marked color change and shifts in charge-transfer spectra also argue for the correctness of this assignment by analogy to the dimeric complexes. The extremely low pK_a value for protonation of the pyrazyl nitrogens in the complexed dpp, which may be considerably more basic than the uncomplexed ligand sites, would lead to the conclusion that these protonations might not be observable for the free ligand. In fact, the ultraviolet spectrum of dpp shows no further changes from below 1 M acid to 96% sulfuric acid.

For the ppz monomeric complex as well as the ligand, one would expect the protonation at the pyrazyl sites to be even more difficult than that for dpp, since the fused aromatic ring system will not allow any alleviation of the steric repulsion of two adjacent positive charges and in addition increases electron-withdrawal effects. The measured value of $H_0 = -6.8$ is consistent with this. (Note: the successive pK_a's for 1,10-phenanthroline[18] are 4.9 and -0.2.)

Increased Basicity of Coordinated Diimines in Excited States. For the excited-state complexes involving coordinated dpp and ppz, the lower limit of pK is -1.75. Thus, in the MLCT excited states, the coordinated ligands are better bases, with pK values at least 3 (dpp) and 5 (ppz) units higher than those of the ground states. Resonance-enhanced Raman spectra have confirmed[11,12] that the lowest energy charge-transfer state for both the dpp and ppz monomeric complexes involves transfer of electron density to these ligands and not bpy. Further interpretation of the nature of the most enhanced normal modes in these spectra suggests that the pyrazyl ring is the site of more electron density in the excited state and that charge is not transferred symmetrically, as would be the case for bpy or bpz. This would be consistent with increased basicity of the imino nitrogen para to the ruthenium(II). Also, consider that for the radical anion of 2,2'-bipyridine, which is analogous to the charge-transfer excited state, the reported[18] pK_a's are ~24 and 8 (cf. neutral bpy values of 4.45 and 0.45).

The juxtaposition of an already protonated pyridyl nitrogen with a pK_a near 2.0 suggests that, in the excited state, protonation of the now much more basic pyrazyl nitrogen is perhaps unusually facile because it can be accomplished by simply rearranging the proton between two already electrostatically attracted (and favorably oriented) sites that transiently possess imino nitrogens with similar pK_a's. This should occur at an unusually fast (picoseconds) rate and may explain why no emission is detected from the protonated form, since this kind of high-speed dynamic process may provide an especially favorable route to nonradiative deexcitation, if one considers the additional involvement of solvent water in such an H-bonding network.

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Reduction of CO_2 and Other Substrates Using Photochemical Reactions of the $W_2(CO)_{10}^{2-}$ Complex

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The photochemistry of the $W_2(CO)_{10}^{2-}$ complex was investigated with the goal of determining if irradiation of this dimer generates a powerful reducing agent, presumably a 19-electron species. In general, the photochemistry of the $W_2(CO)_{10}^{2-}$ complex is comparable to that of other metal-metal-bonded carbonyl dimers. Irradiation into the low-energy tail of the $d\pi \rightarrow \sigma^*$ electronic transition of the $W_2(CO)_{10}^{2-}$ complex led to W-W bond homolysis. The resulting 17-electron $W(CO)_5^-$ radicals could be trapped with suitable ligands such as 4-cyanopyridine to give "19-electron adducts". (See ref 3 for an important definition of the phrase "19-electron adduct".) Evidence is presented that the ligands PPh_3 and PBu_3 also react with photogenerated $W(CO)_5^-$ to form adducts: $W(CO)_5^- + PR_3 \rightarrow W(CO)_5PR_3^-$. These adducts are powerful reducing agents, and they were used to reduce CO_2 to formate and CO. The only organometallic product formed in the reaction was $W(CO)_5PPh_3$, the oxidized form of the 19-electron complex. In a similar manner, $Mn_2(CO)_{10}$ was reduced to $Mn(CO)_5^-$, Cp_2Co^+ to Cp_2Co, benzophenone to the radical anion, and methylviologen (MV^{2+}) to MV^+. Alternative reduction mechanisms involving the $W(CO)_5^-$ radical, $W(CO)_5^{2-}$, or $HW_2(CO)_{10}^-$ as reductants were shown not to be operating. Nineteen-electron complexes generated by irradiation of $Cp_2Mo_2(CO)_6$ proved incapable of reducing CO_2.

In several recent papers, we demonstrated that 19-electron organometallic complexes[3] can be used as photogenerated reducing agents.[4-6] Nineteen-electron complexes form transiently when metal-metal-bonded carbonyl dimers are irradiated in the presence of selected ligands, e.g.[5-8]

$$Cp_2Fe_2(CO)_4 + 2dppe \xrightarrow{h\nu} \underset{19e^-}{2CpFe(CO)dppe} + 2CO \quad (1)$$

dppe = 1,2-bis(diphenylphosphino)ethane

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(3) The phrase "19-electron complex" or "19-electron adduct" is used to describe the *adducts* that form when 17-electron radicals react with 2-electron ligands. No implication of geometric or electronic structure is implied by this definition. A more complete discussion of the electronic and geometric structures of the 19-electron complexes is found in: Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215-245.

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The 19-electron adducts are versatile and powerful reductants, and they can be used to reduce a variety of inorganic, organic, and organometallic substrates, e.g.[4-6,9]

$$\mathrm{CpFe(CO)dppe} + \mathrm{Cp_2Co^+} \rightarrow \mathrm{Cp_2Co} + \mathrm{CpFe(CO)dppe^+} \quad (2)$$

$$\mathrm{CpFe(CO)dppe} + \mathrm{MV^{2+}} \rightarrow \mathrm{MV^+} + \mathrm{CpFe(CO)dppe^+} \quad (3)$$

$$\mathrm{MV^{2+}} = \text{methylviologen}$$

$$\mathrm{CpFe(CO)dppe} + \tfrac{1}{2}\mathrm{Mn_2(CO)_{10}} \rightarrow \mathrm{Mn(CO)_5^-} + \mathrm{CpFe(CO)dppe^+} \quad (4)$$

If no substrate is present, the reducing power of the 19-electron complex is such that it transfers an electron to an unreacted dimer molecule, and the result is disproportionation of the dimer (eq 5) via an electron-transfer-catalyzed chain mechanism.[5-8,10]

$$\mathrm{Cp_2Fe_2(CO)_4} + \mathrm{dppe} \xrightarrow{h\nu} \mathrm{CpFe(CO)dppe^+} + \mathrm{CpFe(CO)_2^-} + \mathrm{CO} \quad (5)$$

Mechanistic studies established that the $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$, and $Co_2(CO)_8$ complexes all disproportionate by the same electron-transfer-catalyzed chain mechanism, and the key step in each pathway is the reaction of a 17-electron metal radical with a ligand to form a 19-electron adduct.[3,10]

In a recent paper, we reported that $W_2(CO)_{10}^{2-}$ also disproportionates when irradiated in the presence of appropriate ligands:[11]

$$\mathrm{W_2(CO)_{10}^{2-}} + \mathrm{PR_3} \xrightarrow{h\nu} \mathrm{W(CO)_5PR_3} + \mathrm{W(CO)_5^{2-}} \quad (6)$$

Although the mechanism of the disproportionation was not studied, a chain pathway involving the formation of 19-electron complexes is suggested by analogy to the mechanism followed in the other dimer disproportionation reactions. Nineteen-electron complexes formed by irradiation of the $W_2(CO)_{10}^{2-}$ dimer should be very powerful reductants, and for that reason we studied the photochemistry of the $W_2(CO)_{10}^{2-}$ complex. In this paper we report the results of our study on the reduction of CO_2 and other substrates using this system.

Experimental Section

Materials. All manipulations were done under an inert atmosphere of argon or nitrogen gas by using a combination of Schlenk techniques, a Vacuum Atmospheres Co. drybox, or a glovebag. Reagent grade solvents were distilled from appropriate drying agents according to literature procedures:[12] acetonitrile, hexane, diethyl ether, 2-propanol, and diglyme were refluxed and then distilled over CaH_2; tetrahydrofuran was dried over either $LiAlH_4$ or sodium metal and then distilled.

$Na_2W_2(CO)_{10}$[13] and $Na[HW_2(CO)_{10}]$[14] were prepared according to literature procedures and recrystallized from THF/hexane solvent mixtures. Triphenylphosphine was obtained from Aldrich and recrystallized from an ethanol/benzene solvent mixture. Tungsten hexacarbonyl, anhydrous oxalic acid, formic acid (reagent grade), and methanolic 1 M tetrabutylammonium hydroxide were also obtained from Aldrich and used as received. Sodium carbonate hydrate, sodium formate, and sodium acetate were Baker Analyzed reagents and were used as received. Barium hydroxide was obtained from Fisher. Three grades of carbon dioxide were used: the first was 99.95% compressed gas from Matheson; the second was 99.99% (Coleman Instrument grade), which was in liquid form, also from Matheson; the third was from Airco and was in liquid form.

Table I. Quantum Yields for the Photochemical Reactions of $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ (4.3×10^{-4} M) in CH_3CN in the Presence of Different Substrates (λ = 436 nm)

substrate(s)	products	quantum yield
none	$W(CO)_6$	0.01
CO_2	$W(CO)_6$	0.01
PPh_3	disproportionation[a]	0.06
PPh_3/CO_2	CO_2 redn products[a]	0.15

[a] See text.

The tetrabutylammonium salt of $W_2(CO)_{10}^{2-}$ was obtained by adding 2 equiv of $(n\text{-}Bu_4N)I$ in a minimum amount of 2-propanol to $Na_2W_2(CO)_{10}$, also in a minimum amount of 2-propanol. The $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ salt, which precipitated as an orange powder, was then collected, rinsed with 2-propanol, and dried.

Irradiation Procedures. All irradiations were done with an Oriel 200-W high-pressure Hg-arc lamp fitted with appropriate glass filters (Corning 3-73, $\lambda > 420$ nm; Corning 3-71, $\lambda > 480$ nm). Unless otherwise stated, all irradiations of the $W_2(CO)_{10}^{2-}$ complex were with light $\lambda > 420$ nm. Use of radiation with wavelengths shorter than 400 nm made reactions more complex (as indicated by IR spectroscopy), possibly due to metal–CO bond dissociation.[14] Samples were irradiated in CaF_2 infrared solution cells (pathlength 0.5 mm), quartz cuvettes, or Schlenk flasks. Infrared spectra were recorded with a Perkin-Elmer 983 spectrometer.

Analysis for HCO_2^-, CO_3^{2-}, and HCO_3^- Generated by Irradiation of $Na_2W(CO)_{10}$ in the Presence of Ph_3P and CO_2.[15-17] Samples of $Na_2W_2(CO)_{10}$ (0.46 g, 0.7 mmol) and Ph_3P (0.48 g, 1.8 mmol) were added to dry oxygen-free acetonitrile (15 mL) in a Pyrex test tube equipped with a magnetic stirbar. The test tube was stoppered with a rubber septum and then saturated with CO_2 gas. The solution was then immersed in a water bath (~20 °C) and irradiated ($\lambda > 420$ nm) until almost all the tungsten dimer had disappeared, as indicated by infrared spectroscopy. The average time was about 12 h. Throughout the irradiation the reaction mixture was kept under a positive CO_2 pressure. After irradiation, a white precipitate was separated from the supernatant solution by centrifugation. The infrared spectrum of the supernatant solution indicated the presence of $W(CO)_5PPh_3$ (70–90%). The precipitate was rinsed with acetonitrile (4×15 mL) and placed in a desiccator containing P_2O_5, followed by drying under vacuum. The ^1H NMR spectrum of the precipitate (in D_2O) showed the presence of $NaHCO_2$ (8.23 ppm), which was identified by comparison with an authentic sample. The yield was estimated to be 20% (by NMR) based on the tungsten dimer.

To analyze for carbonates, the precipitate from the reaction above was transferred to a 50-mL volumetric flask and diluted to the mark with distilled water. Analysis by titration [with a standard HCl solution (~0.1 N) and phenolphthalein and bromocresol green as indicators] indicated the following yields: Na_2CO_3 39%; $NaHCO_3$, 18%. The hydrochloric acid used for titration was standardized with a standard sample of sodium carbonate hydrate that had initially been dried at 120 °C for 24 h.

Analysis for HCO_2^-, CO_3^{2-}, and HCO_3^- from Irradiation of $Na[HW_2(CO)_{10}]$ in the Presence of Ph_3P and CO_2. A mixture consisting of $Na[HW_2(CO)_{10}]$ (0.31 g, 0.4 mmol) and Ph_3P (0.32 g, 1.2 mmol) in acetonitrile saturated with CO_2 gas was photolyzed ($\lambda > 420$ nm) in the same manner as described above. Analysis of the precipitate showed the presence of $NaHCO_2$ (30%), Na_2CO_3 (27%), and $NaHCO_3$ (29%). The infrared spectrum of the supernatant solution showed the presence of *trans*-$W(CO)_4(PPh_3)_2$ and $W(CO)_5PPh_3$ as major products. There were also two infrared bands at 1852 and 1800 cm^{-1} that could not be assigned.

Qualitative Analysis for CO_3^{2-} and/or HCO_3^- in Samples from the Irradiation of $Na_2W_2(CO)_{10}$ in the Presence of PPh_3 and CO_2. The dry white precipitate obtained from irradiation of $Na_2W_2(CO)_{10}$ with CO_2 as described above was dissolved in about 2 mL of CO_2-free water in a test tube (A). In a second test tube (B) was placed about 4 mL of a clear saturated aqueous solution of $Ba(OH)_2$. Each of the two test tubes was stoppered with a septum and then connected to the other one with a cannula. With use of a syringe, 2 mL of 6 M H_2SO_4 was added to test tube A. Effervescence was immediate, and gas bubbles could be seen going through the solution in test tube B. Gradually solution B became

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Table II. Infrared Bands Due to $\nu(CO)$ of Carbon Oxoanions

compd	$\nu(CO)$, cm^{-1} [a]	ref
Na_2CO_3	1440 vs [Nujol]	20
$NaHCO_3$	1660 s, 1630 s, 1440 m [Nujol]	20
NH_4HCO_3	1655 s, 1620 s, 1400 vs [Nujol]	20
$Bu_4N^+HCO_3^-$	1673 vs [CH_3CN]	this work
$NaHCO_2$	1567 s [Nujol]; 1585 s [aq soln]	21
$C_2O_4H_2$	1573 vs, 1781 vs [CH_3CN]	this work
$(Bu_4N)_2C_2O_4$	1563 vs, 1625 w [CH_3CN]	this work
$[Pt(PPh_3)_2CO_3]$	1680 vs, 1180 w (bidentate)	22
$[Pd(PPh_3)_2CO_3]$	1660, 1635 (bidentate)	22
$[Pt(PMePh_2)_2CO_3]$	1670 vs, 1630 m (bidentate)	23
$[Pt(diphos)_2CO_3]$	1665 w, 1185 s	24
$CuCO_3$	1460 s, 1420 s (bidentate)	25
$[Co(NH_3)_5CO_3]Br$	1373 s, 1070 s (monodentate)	26
$Rh(OAc)(CO)(PPh_3)_2$	1604, 1376 (monodentate)	27
$[Pd(OAc)_2(PPh_3)]_2$	1580, 1411 (bridging)	28

[a] The medium or solvent used in the measurement is given in brackets.

cloudy and a white precipitate was deposited. A control experiment gave no precipitate.

Determination of the Quantum Yields for the Disappearance of $W_2(CO)_{10}^{2-}$. In the presence of CO_2, the sodium salt of $W_2(CO)_{10}^{2-}$ was unsuitable for monitoring the disappearance of the tungsten dimer by electronic absorption spectroscopy because of the formation of insoluble inorganic salts such as Na_2CO_3 and $NaHCO_3$. Hence, it was necessary to use the $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ complex because no insoluble precipitates formed when this species was irradiated. The procedure was as follows. $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ (24.3 mg, 0.2 mmol) was dissolved and diluted to 50 mL with dry oxygen-free acetonitrile to give a 4.3×10^{-4} M solution of the solute. Quantum yields were determined under four different conditions: (i) the above solution was used as it was; (ii) the above solution was saturated with CO_2 gas; (iii) 43 mg (0.16 mmol) of PPh_3 was dissolved and the solution diluted to 25 mL with the stock solution to give a solution about 6.4×10^{-3} M in PPh_3; (iv) the solution from (iii) was saturated with CO_2 gas. In each case about 5 mL of the solution was irradiated at intervals of about 1–5 min. The disappearance of $W_2(CO)_{10}^{2-}$ was monitored at 400 and/or 436 nm by using a Beckman DU-7 spectrophotometer. Quantum yields (Table I) were calculated by using slopes obtained from the linear plots of absorbance vs time. Aberchrome 540 was used as an actinometer according to the method of Heller and Langan.[18]

Solution Infrared Spectra of HCO_3^-, $C_2O_4^{2-}$, and HCO_2^- in MeCN. Because the Na^+ salts of HCO_3^-, $C_2O_4^{2-}$, and HCO_2^- are insoluble in acetonitrile, $n\text{-}Bu_4N^+$ salts of these species were generated. A sample, presumably of $n\text{-}Bu_4N^+HCO_3^-$, was prepared by bubbling CO_2 gas through a methanolic solution of $n\text{-}Bu_4NOH$: $Bu_4N^+OH^- + CO_2 \rightarrow Bu_4N^+HCO_3^-$. Filtration, followed by evaporation of the solvent, left a gelatinous residue. An infrared spectrum (in CH_3CN) showed an absorption band at 1673 cm^{-1} attributed to HCO_3^-. There were other bands at 1450–1500 m (broad), 1287 vs, 1181 w, 1154 vs, 1075 s, and 1027 m cm^{-1}. Addition of an increasing amount of water shifted the 1673-cm^{-1} band to lower frequency until it finally settled at 1611 cm^{-1}, by which time it became very broad, extending from 1550 to 1680 cm^{-1}. (HCO_3^- probably decomposes on addition of H_2O, and the band at 1611 cm^{-1} is assigned to water.[19])

Table III. Selected Infrared Spectral Data

complex	solvent	$\nu(CO)$, cm^{-1}	ref
$Na_2W_2(CO)_{10}$	CH_3CN	1941 m, 1891 vs, 1790 s	13
$Na_2W_2(CO)_{10}$	THF	2024 vw, 1945 m, 1903 vs, 1881 m (sh), 1834 vw, 1811 vw, 1753 m	13
$(n\text{-}Bu_4N)_2W_2(CO)_{10}$	CH_3CN	1941 m, 1891 vs, 1790 m	13
$(n\text{-}Bu_4N)_2W_2(CO)_{10}$	THF	1941 m, 1890 vs, 1789 m	11
$W(CO)_6$	CH_3CN	1978	30
$W(CO)_6$	THF	1976	
$W(CO)_5PPh_3$	cyclohexane	2073 w, 1944 s	31
$W(CO)_5PPh_3$	CH_3CN	2074 w, 1981 w, 1940 vs	
$W(CO)_5PPh_3$	THF	2071 w, 1976 w, 1940 s	
$W(CO)_5PPh_3$	acetone	2073 w, 1983 vw (sh), 1940 s	
$W(CO)_5PBu_3$	cyclohexane	2068 w, 1943 w, 1936 s	31
$W(CO)_5PBu_3$	THF	2068 w, 1932 s	
$W(CO)_5THF$	THF	1975 w, 1950 s, 1931 s	32
$W(CO)_5CH_3CN$	*n*-hexane	2083 w, 1948 s, 1931 m	33
$W(CO)_5CH_3CN$	CH_3CN	1934	33
$Na_2W(CO)_5$	DME	1827 s, 1757 s (br)	34
$Na_2W(CO)_5$	HMPA	1755 s, 1731 s	35
$Na_2W(CO)_5$	THF	1827 s, 1757 s (br)	35
$Na_2W(CO)_5$	THF	1829 vs, 1772 s (br)	36
$(n\text{-}Bu_4)_2W(CO)_5$	CH_3CN	1780 s, 1740 s	11
$Na[HW_2(CO)_{10}]$	CH_3CN	2045 w, 1939 vs, 1879 m	14
$Na[HW_2(CO)_9(CH_3CN)]$	CH_3CN	2058 vw, 2000 vw (sh), 1925 m (sh), 1875 m, 1845 w	14
$NEt_4[HW_2(CO)_9PPh_3]$	THF	2060 w, 2000 w, 1928 s (sh), 1923 s, 1878 m-s, 1840 m	14
$Na[W(CO)_5H]$	CH_3CN	2046 vw, 1894 s, 1860 s (sh)	37
$W(CO)_5(O_2CH)^-$	CH_3CN	2064, 1966, 1915, 1851	37
$Mn_2(CO)_{10}$	THF	2046 s, 2010 vs, 1981 m	38
$K[Mn(CO)_5]$	THF	1898, 1863	39
trans-$W(CO)_4(PPh_3)_2$	CH_3CN	2020 w, 1900 s	32
trans-$W(CO)_4(CH_3CN)_2$	CH_3CN	1898	40

A sample of $(n\text{-}Bu_4N)_2(C_2O_4)$ was obtained by reacting $(n\text{-}Bu_4N)OH$ with oxalic acid in the molar ratio 2:1 in methanol. The infrared spectrum (in CH_3CN) showed a band at 1563 cm^{-1}, which is attributed to $\nu(CO)$ of $C_2O_4^{2-}$. There were other bands at 1665 w, 1625 m (assigned to H_2O), and 1290 vs cm^{-1}.

Finally, a sample of $Bu_4N^+HCO_2^-$ was synthesized by mixing equimolar solutions of $(n\text{-}Bu_4N)OH$ and HCO_2H in methanol followed by evaporation of as much solvent (under vacuum) as possible (24 h at 20 °C). The infrared spectrum (in CH_3CN) showed a band at 1606 vs cm^{-1} assigned to $\nu(CO)$ of HCO_2^-. There was also a weak shoulder around 1665 cm^{-1} possibly due to the bending mode of H_2O.

Infrared data for CO_3^{2-}, HCO_3^-, and $C_2O_4^{2-}$ are listed in Table II. Also included in Table II are infrared data for several complexes of CO_3^{2-} and HCO_2^-.

Irradiation of $W(CO)_6$ in the Presence of PPh_3 in CH_3CN. The following control reaction established that $W(CO)_6$ does not react with PPh_3 to give $W(CO)_5PPh_3$ and *trans*-$W(CO)_4(PPh_3)_2$ when irradiated with $\lambda > 420$ nm. Thus, irradiation ($\lambda > 420$ nm) of a solution (3 mL) of $W(CO)_6$ (0.05 M) and Ph_3P (0.8 M) for 14 min gave no reaction. However, when shorter wavelength radiation ($\lambda > 340$ nm) was used, most of the tungsten carbonyl was consumed in about 5 min to give *cis*-$W(CO)_4(PPh_3)_2$ and $W(CO)_3(PPh_3)_3$.

Results

Electronic Spectrum of the $W_2(CO)_{10}^{2-}$ Complex. The $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ complex exhibits absorption features at 347 nm ($\epsilon = 7210$) and 390 nm (shoulder, $\epsilon = 4840$) in CH_3CN solution. This two-peak pattern is typical for metal–metal-bonded carbonyl dimers, and Harris and Gray therefore assigned these bands to $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions, respectively.[29] The irradiations

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of the $W_2(CO)_{10}^{2-}$ complex in this study were all with light $\lambda >$ 420 nm; the irradiations were therefore into the low-energy tail of the $d\pi \rightarrow \sigma^*$ transition.

Irradiation of $W_2(CO)_{10}^{2-}$ in CH_3CN in the Presence of PPh_3 and CO_2. Irradiation of a CH_3CN solution of $Na_2W_2(CO)_{10}$ (5–50 mM) and PPh_3 (usually a 3-fold molar excess) saturated with CO_2 led to the deposition of a white precipitate containing $NaHCO_2$, Na_2CO_3, and $NaHCO_3$. (See the Experimental Section for details of the qualitative and quantitative analysis.) Infrared analysis of the solution showed that $W(CO)_5PPh_3$ (70–90%) was the only organometallic product (Table III). The solution spectrum also showed a very weak broad band extending from around 1600 to 1700 cm^{-1}, probably due to precipitated $NaHCO_3$. No $W(CO)_6$ was observed to form in the reaction if high-purity CO_2 was used and if the reaction solution was kept at room temperature (or lower) during the photolysis. However, substantial amounts of $W(CO)_6$ (~10%) formed if lower purity CO_2 was used or if the reaction cell warmed up above room temperature during the irradiation.

$W(CO)_5PPh_3$ was also the only organometallic product formed if the n-Bu_4N^+ salt of $W_2(CO)_{10}^{2-}$ was used instead of the Na^+ salt. No precipitate formed in this case, however, because the n-Bu_4N^+ salts of the carbon oxoanion products are soluble in CH_3CN; bands at 1680 and 1642 cm^{-1} are assigned to HCO_3^- or bidentate CO_3^{2-} (Table II). In addition, a band at 2143 cm^{-1} was assigned to free CO.

Control experiments showed that irradiation of $Na_2W_2(CO)_{10}$ (3 mM) in CH_3CN in the absence of PPh_3 and CO_2 led only to the very slow ($\phi = 0.01$) formation of $W(CO)_6$, as indicated by the growth of a band at 1978 cm^{-1}. No bands due to other species such as $HW_2(CO)_{10}^-$, $W(CO)_5CH_3CN$, $W(CO)_5^{2-}$, or $W(CO)_5H^-$ were observed. Control experiments also showed that irradiation of $Na_2W_2(CO)_{10}$ (14 mM) in CH_3CN in the presence of PPh_3 (38 mM), but not CO_2, led to disproportionation (eq 6).[11] (The disproportionation reactions of the $W_2(CO)_{10}^{2-}$ complex have been discussed before and will not be discussed further here.[11]) The important point is that the carbon oxoanions are the products of the photochemical reactions of the $W_2(CO)_{10}^{2-}$ complex only when a ligand (in this case PPh_3) and CO_2 are both present.

Reduction of $Mn_2(CO)_{10}$, Cp_2Co^+, and Methylviologen (MV^{2+}) Using the $W_2(CO)_{10}^{2-}/h\nu/PPh_3$ System. Irradiation ($\lambda >$ 420 nm) of $Na_2W_2(CO)_{10}$ (1.6×10^{-3} M), PPh_3 (0.11 M), and $Mn_2(CO)_{10}$ (3.8×10^{-2} M) in THF led to the formation of $Mn(CO)_5^-$ (1863 and 1898 cm^{-1}), $W(CO)_5PPh_3$ (2071, 1976, and 1940 cm^{-1}), and some $W(CO)_6$ (1976 cm^{-1}). In the absence of PPh_3, irradiation of an otherwise identical solution yielded $Mn(CO)_5^-$ as well as $W(CO)_5(THF)$ (1975, 1950, 1931 cm^{-1}) and $W(CO)_6$. A control experiment showed that no $Mn(CO)_5^-$ formed on the time scale of the experiments above when $Mn_2(CO)_{10}$ was irradiated ($\lambda >$ 420 nm) by itself in THF. We conclude, therefore, that photochemical disproportionation of $Mn_2(CO)_{10}$ is not the source of the $Mn(CO)_5^-$ in these experiments.[10]

Cp_2Co^+ and benzophenone could also be reduced by the $W_2(CO)_{10}^{2-}/h\nu/PR_3$ system in a similar fashion. Thus, irradiation of $Na_2W_2(CO)_{10}$ (3.5×10^{-2} M), $(Cp_2Co)PF_6$ (3.7×10^{-2} M), and PPh_3 (4.9×10^{-2} M) in acetone led to the formation of Cp_2Co and $W(CO)_5PPh_3$. The Cp_2Co was detected by the appearance of an NMR peak at −51.3 ppm.[41,42] Irradiation of $(n$-$Bu_4N)_2W_2(CO)_{10}$ (5.9×10^{-3} M), benzophenone (3.7 M), and PBu_3 (1.6×10^{-2} M) in THF led to the disappearance of the $W_2(CO)_{10}^{2-}$ dimer and benzophenone (1662 cm^{-1}) and the formation of $W(CO)_5PBu_3$ (2068 and 1932 cm^{-1}) and the ketyl radical (1556 cm^{-1}).[43] In all of the reduction reactions reported above, overlapping bands in the infrared region prevented the stoichiometries of the reactions from being measured.

Methylviologen was reduced by $W_2(CO)_{10}^{2-}$ in a dark reaction: Reaction of $W_2(CO)_{10}^{2-}$ (1.1×10^{-3} M) with MV^{2+} (2.7×10^{-3} M) in the dark led to the formation of MV^+, as evidenced by the growth of a new peak in the electronic spectrum of the reaction solution at 604 nm.

Irradiation of $W_2(CO)_{10}^{2-}$ in CH_3CN/H_2O. The following experiment was done to determine the photochemical reactivity of the $W_2(CO)_{10}^{2-}$ complex in the presence of water but in the absence of both CO_2 and PPh_3. Irradiation of $Na_2W_2(CO)_{10}$ (10 mM) in CH_3CN/H_2O (9:1) led to the rapid disappearance of the dimer and the formation of substantial amounts of $HW_2(CO)_9(CH_3CN)^-$, $W(CO)_5CH_3CN$, and $W(CO)_6$. There were also peaks at 2046 vw, 1894 s, and 1860 cm^{-1} attributable to $Na[W(CO)_5H]$.

These results are consistent with a previous report that the $W_2(CO)_{10}^{2-}$ complex reacts photochemically with H_2O to form $HW_2(CO)_{10}^-$ (eq 7).[44] In subsequent photochemical steps, this complex then either substitutes (eq 8, L = CH_3CN)[14] or disproportionates (eq 9, L = CH_3CN),[45] two reactions also previously reported.

$$W_2(CO)_{10}^- \xrightarrow[H_2O]{h\nu} HW_2(CO)_{10}^- \qquad (7)$$

$$HW_2(CO)_{10}^- + L \xrightarrow{h\nu} HW_2(CO)_9L^- + CO \qquad (8)$$

$$HW_2(CO)_{10}^- + L \xrightarrow{h\nu} HW(CO)_5^- + W(CO)_5L \qquad (9)$$

Photochemical Reactions of $HW_2(CO)_{10}^-$. Irradiation ($\lambda >$ 420 nm) of $Na[HW_2(CO)_{10}]$ (7 mM) in the presence of PPh_3 (30 mM) initially led to the formation of $HW_2(CO)_9PPh_3^-$ (eq 8, L = PPh_3) and small amounts of $W(CO)_5PPh_3$ and *trans*-$W(CO)_4(PPh_3)_2$. Prolonged irradiation (≥6 min) gave rise to higher yields of $W(CO)_5PPh_3$ and *trans*-$W(CO)_4(PPh_3)_2$ while the amount of $HW_2(CO)_9PPh_3^-$ gradually decreased. Irradiation of an identical reaction solution saturated with CO_2 gave identical metal-containing products and a white precipitate containing HCO_2^-, HCO_3^-, and CO_3^{2-}. (See the Experimental Section for details about the quantitative analysis of the precipitate.) Note that no $W(CO)_5(O_2CH)^-$ was detected in this reaction.

In the absence of CO_2, reactions 8 and 9 account for the formation of the organometallic products obtained in the reaction. In addition, we propose that the $HW_2(CO)_9PPh_3^-$ complex can disproportionate (eq 10) in a reaction analogous to the disproportionation of $HW_2(CO)_{10}^-$ (eq 9). We have no explanation why $HW(CO)_5^-$ was not spectroscopically observed.

$$HW_2(CO)_9PPh_3^- + PPh_3 \xrightarrow{h\nu} trans\text{-}W(CO)_4(PPh_3)_2 + HW(CO)_5^- \qquad (10)$$

Attempted Reduction of CO_2 Using $(MeCp)_2Mo_2(CO)_6$ and $(MeCo)_2Fe_2(CO)_4$. Addition of dppe ($Ph_2PCH_2CH_2PPh_2$, 28 mM) to a CO_2-saturated solution containing $(MeCp)_2Mo_2(CO)_6$ (15 mM; MeCp = η^5-$C_5H_4CH_3$) and Bu_4NPF_6 (40 mM) in CH_3CN led to the immediate formation of $(MeCp)Mo(CO)_2(dppe)^+$ and $(MeCp)Mo(CO)_3^-$.[7] No other product (in particular, HCO_3^- or coordinated CO_3^{2-}) was detected. It is concluded that neither $(MeCp)Mo(CO)_2(dppe)$ nor $(MeCp)Mo(CO)_3^-$ has the potential to reduce CO_2. Because the disproportionation reaction is a chain process that can be initiated by room lights, the reaction was complete even before irradiation with the lamp.[7]

A similar reaction was carried out by using $(MeCp)_2Fe_2(CO)_4$ instead of $(MeCp)_2Mo_2(CO)_6$. In this case there was virtually no reaction before irradiation. Irradiation ($\lambda >$ 420 nm) led to

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a slow disappearance of the dimer and growth of new bands at 1680 and 1736 cm^{-1}. The former band is probably due to HCO_3^-. Note that $CpFe(CO)_2^-$, a product of the disproportionation of $Cp_2Fe_2(CO)_4$, will reduce CO_2.[46] Consequently, the reaction of $Cp_2Fe_2(CO)_4$/dppe with CO_2 was not pursued further.

Discussion

Reductions Using $W_2(CO)_{10}^{2-}$ and PR_3. Irradiation of the $W_2(CO)_{10}^{2-}$ complex and PPh_3 or PBu_3 in the presence of a substrate led to reduction of the substrate. Thus, irradiation of a CO_2-saturated acetonitrile solution containing $W_2(CO)_{10}^{2-}$ and PPh_3 gave formate, CO, carbonate, and bicarbonate (eq 11), the

$$CO_2 \xrightarrow[W_2(CO)_{10}^{2-}/PPh_3]{h\nu\ (\lambda > 420\text{ nm})} HCO_2^-\ (20\%) + CO_3^{2-}\ (39\%) + HCO_3^-\ (18\%) + CO + W(CO)_5PPh_3\ (70\text{–}90\%) \quad (11)$$

typical products of CO_2 reduction.[47] (Residual water is thought to be the source of the hydrogen in formate.[47a]) With high-purity CO_2, the only organometallic product formed in the reaction was $W(CO)_5PPh_3$; no $W(CO)_6$ or $W(CO)_5^{2-}$ was observed.

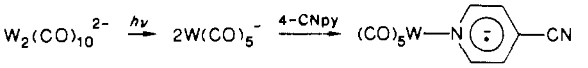
In conceptually similar reactions, the $W_2(CO)_{10}^{2-}/h\nu/PPh_3$ system was used to reduce other substrates. For example, $Mn_2(CO)_{10}$ was reduced to $Mn(CO)_5^-$ and Cp_2Co^+ was reduced to Cp_2Co. The tungsten-containing product in these reactions was $W(CO)_5PPh_3$ (and a small amount of $W(CO)_6$). Although the stoichiometries of these reactions could not be measured, the following reactions are suggested:

$$W_2(CO)_{10}^{2-} + Mn_2(CO)_{10} + 2PPh_3 \rightarrow 2Mn(CO)_5^- + 2W(CO)_5PPh_3 \quad (12)$$

$$W_2(CO)_{10}^{2-} + 2Cp_2Co^+ + 2PPh_3 \rightarrow 2Cp_2Co + 2W(CO)_5PPh_3 \quad (13)$$

Similarly, irradiation of $W_2(CO)_{10}^{2-}$, PBu_3, and benzophenone in THF led to the formation of the ketyl radical anion and $W(CO)_5PBu_3$.

Mechanistic Conjectures. The $W_2(CO)_{10}^{2-}$ complex is a typical metal–metal-bonded carbonyl dimer in that irradiation into the lowest energy electronic absorption bands leads to homolysis of the metal–metal bond.[48] The results of several experiments support this conclusion: (1) Kaim,[49] and later we,[11] demonstrated that irradiation of this dimer in the presence of 4-cyanopyridine (4-CNpy) led to the $W(CO)_5(4\text{-CNpy})^-$ adduct. It is logical to propose that this species is formed by reaction of a photogenerated $W(CO)_5^-$ radical with 4-cyanopyridine:



(14)

(2) Irradiation of the $W_2(CO)_{10}^{2-}$ complex and a ligand led to disproportionation (eq 6).[11] This reactivity suggests metal–metal bond photolysis because the disproportionation reactions of the other metal–metal-bonded dimers are chain pathways initiated by homolysis of the metal–metal bond.[10] (3) Finally, the electronic spectrum of the $W_2(CO)_{10}^{2-}$ complex is similar to those of the other metal–metal-bonded dimers in having $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions at lowest energy.[29] It is well established that irradiation into these bands in the other dimers leads to homolysis of the metal–metal bond, and similar reactivity is therefore expected with the $W_2(CO)_{10}^{2-}$ complex.

Homolysis of the W–W bond in $W_2(CO)_{10}^{2-}$ gives the $W(CO)_5^-$ radical. This species is one possibility for the reducing agent generated when $W_2(CO)_{10}^{2-}$ is irradiated. However, if this were the reducing agent, then reductions should occur in the absence of phosphines (Scheme I). The $W(CO)_5$ formed by this pathway would presumably decompose and release CO. The CO would be scavenged by other $W(CO)_5$ molecules, and substantial $W(CO)_6$ would be formed. Our results show, however, that, with the exception of $Mn_2(CO)_{10}$, no reductions occur in the absence of ligand,[50] and the mechanism in Scheme I is therefore unlikely.

Scheme I

$$W_2(CO)_{10}^{2-} \xrightarrow{h\nu} 2W(CO)_5^-$$

$$W(CO)_5^- + S \rightarrow W(CO)_5 + S^-$$

S = reducible substrate

Another possible mechanism for reduction of the substrates involves the initial disproportionation of the $W_2(CO)_{10}^{2-}$ complex (eq 6) followed by the reaction of $W(CO)_5^{2-}$ with the substrate, e.g.[47a]

$$W(CO)_5^{2-} + 2CO_2 \rightarrow W(CO)_6 + CO_3^{2-} \quad (15)$$

However, if this were the mechanism of CO_2 reduction, then one of the products of the reaction would be $W(CO)_6$. Recall that no $W(CO)_6$ was observed when high-purity CO_2 was used. In addition, control experiments showed that $W(CO)_6$ did not react photochemically to form $W(CO)_5PR_3$ under the conditions of our experiments ($\lambda > 420$ nm). Thus, the absence of $W(CO)_6$ must be taken as evidence that the pathway in eq 15 is not operating. Also, recall that HCO_2^- was obtained in our experiments. Reaction 9 cannot account for this product. Finally, note in Table I that the quantum yield for reduction of CO_2 is considerably higher than the quantum yield for disproportionation (0.15 vs 0.06). If $W(CO)_5^{2-}$, formed by disproportionation of $W_2(CO)_{10}^{2-}$, were the reducing agent, then the (maximum) quantum yield for reduction of CO_2 would be the quantum yield of disproportionation. Clearly, this is not the case, and we conclude that $W(CO)_5^{2-}$ is not the reducing agent.

A third possible mechanism for CO_2 reduction is shown in eq 16–18. Each of these reactions has been reported to occur

$$W_2(CO)_{10}^{2-} \xrightarrow[h\nu]{H_2O} HW_2(CO)_{10}^- \quad (16)^{45}$$

$$HW_2(CO)_{10}^- \xrightarrow[h\nu]{PR_3} W(CO)_5H^- + W(CO)_5PR_3 \quad (17)^{46}$$

$$W(CO)_5H^- \xrightarrow{CO_2} W(CO)_5(O_2CH)^- \quad (18)^{44}$$

separately, but not as part of the sequence as shown. Our results confirmed that the photochemical reactivity of the $W_2(CO)_{10}^{2-}$ complex in the presence of H_2O is as described by reaction 16. However, four results are inconsistent with the proposed reaction sequence. First, control experiments showed that irradiation of $W_2(CO)_{10}^{2-}$ in the CH_3CN used in our experiments did not yield $HW_2(CO)_{10}^-$. Thus, the water content of the CH_3CN is not sufficient to promote reaction 16. Second, $W(CO)_5(O_2CH)^-$ was not observed as a product of any of the CO_2 reduction reactions. (This species may be reacting photochemically at $\lambda > 420$ nm, however.) Third, reactions 16–18 cannot account for the formation of carbonates in the CO_2 reduction reactions. Finally, it is not obvious how reactions 16–18 account for the reduction of $Mn_2(CO)_{10}$, Cp_2Co^+, and benzophenone by the $W_2(CO)_{10}^{2-}/PR_3/h\nu$ system.

We suggest the most plausible mechanism for the reduction of CO_2 and the other substrates is one involving the 19-electron $W(CO)_5PR_3^-$ complex (Scheme II). This scheme is consistent

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Scheme II

$$W_2(CO)_{10}^{2-} \underset{}{\overset{h\nu}{\rightleftharpoons}} 2W(CO)_5^-$$

$$W(CO)_5^- + PR_3 \rightleftharpoons \underset{19e^-}{W(CO)_5PR_3^-}$$

$$W(CO)_5PR_3^- + S \rightarrow W(CO)_5PR_3 + S^-$$

$$S = \text{reducible substrate}$$

with the facts that other 17-electron radicals react with ligands to form 19-electron complexes[4-8] and that the only organometallic product formed in the reduction reactions is $W(CO)_5PR_3$. The mechanism in Scheme II is also reasonable on thermodynamic grounds because the 19-electron $W(CO)_5PR_3^-$ complexes will be very powerful reductants. Although the exact oxidation potentials are not known, values around 2.6 V vs SCE can be approximated.[51] This potential is sufficient to reduce CO_2.

Summary. In general, the photochemistry of the $W_2(CO)_{10}^{2-}$ complex is comparable to that of other metal-metal-bonded carbonyl dimers. Irradiation into the low-energy tail ($\lambda > 420$ nm) of the $d\pi \rightarrow \sigma^*$ electronic transition of the $W_2(CO)_{10}^{2-}$ complex leads to W-W bond homolysis. The resulting 17-electron $W(CO)_5^-$ radicals can be trapped with suitable ligands such as 4-cyanopyridine to give 19-electron adducts. It is proposed that ligands such as PPh_3 and PBu_3 also react with photogenerated $W(CO)_5^-$ to form adducts, $W(CO)_5PR_3^-$. These latter adducts are powerful reducing agents, and we demonstrated the reduction of several substrates, including CO_2, using these species. The reducing agents generated by irradiation of the $W_2(CO)_{10}^{2-}$ complex are better reductants than those generated from other metal-metal-bonded dimers such as $Cp_2Mo_2(CO)_6$.

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Interactions of Nickel and Manganese Carbonyls with Oxide Surfaces: Formation of Reduced, Oxidized, and Zerovalent Metal Species

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Reactions of the metal carbonyls $Ni(CO)_4$ and $Mn_2(CO)_{10}$ on the oxide supports γ-Al_2O_3 and MgO (pretreated by evacuation at 400 °C) were investigated by infrared spectroscopy and other methods. An array of oxidized, neutral, and reduced species was formed in each case as evidenced by ν(CO) IR bands. Supported $Ni(CO)_4$ gave rise to an anionic tricarbonyl species on γ-Al_2O_3 and the high-nuclearity cluster anions $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, and $[Ni_9(CO)_{18}]^{2-}$ on MgO. Addition of $Mn_2(CO)_{10}$ to γ-Al_2O_3 produced few spectral changes, while $[Mn(CO)_5]^-$ and other surface-substituted manganese carbonyl species resulted on MgO. $[Mn(CO)_5]^-$ on MgO exists as an ion pair with Mg^{2+} unless these sites are blocked. A mechanism, involving a common type of intermediate formed via attack on a CO ligand by a surface oxide, is proposed to explain the variety of surface species observed. This can be used to explain both decarbonylation and redox reactions. Scission of metal-oxygen bonds in the intermediate and subsequent formation of metal-metal bonds also occur to yield metal particles and cluster anions. These processes are particularly favored with the supported nickel carbonyls, consistent with the solution chemistry of these Ni complexes.

Introduction

Investigations of the chemistry of metal carbonyls at oxide surfaces have disclosed, not surprisingly, that first-row transition-metal carbonyls are more reactive and produce a much more complex array of supported surface carbonyl species than do their second- and third-row congeners.[1-3] Studies of cobalt and iron carbonyls found evidence for valence disproportionation of the parent complexes into cationic and anionic supported metal species. On Al_2O_3, MgO, and zeolites, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ reacted with surface oxides (O_s^-)[4] to form species proposed to be $Co(CO)_m(O_s)_w$ and $Co(CO)_4^-$.[5-8] Similarly, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ on Al_2O_3 yielded $HFe_3(CO)_{11}^-$ as well as zerovalent and oxidized iron centers.[9] Since these observed surface reactions are analogous to those described between the parent complexes and Lewis bases in solution, the possibility arises for similar observations with other supported first-row-metal carbonyl complexes.

In an effort to establish and define trends in the surface reactivities of supported first-row-metal carbonyls, a study of γ-Al_2O_3- and MgO-supported $Ni(CO)_4$ and $Mn_2(CO)_{10}$ was undertaken. Generally, $Ni(CO)_4$ reacts with oxide surfaces to lead to supported zerovalent metal. Parkyns found $Ni(CO)_4$ to be unreactive toward SiO_2 but proposed the formation of small metal crystallites upon room-temperature reaction with Al_2O_3.[10] Later, the alumina reaction was further characterized and mononuclear subcarbonyl species were proposed as intermediates in the crystallite formation.[11] Nickel metal particles also have been discussed with regard to samples of $Ni(CO)_4$ on MgO.[12]

In the present study, $Ni(CO)_4$ and $Mn_2(CO)_{10}$ on the oxide surfaces were found to undergo reactions analogous to those with

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