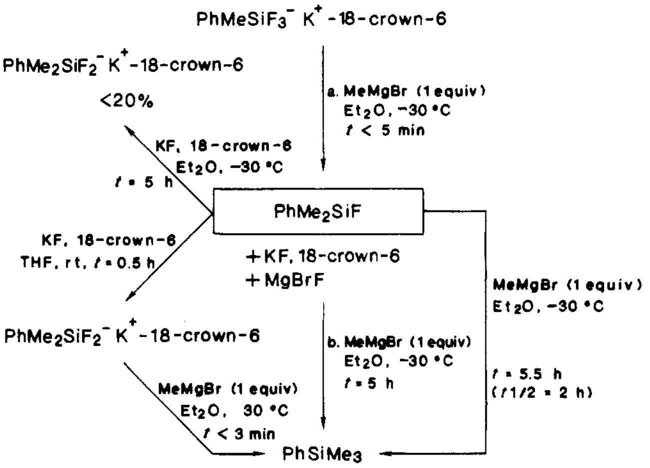
Scheme III



The chemical behavior of 1 and 2 has been compared with that of the corresponding fluorosilanes 3 and 4 using Grignard reagents as nucleophiles; results are summarized in Table I.

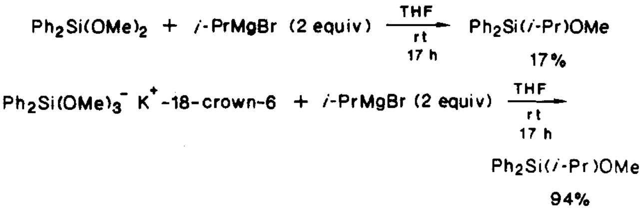
Apparently the pentacoordinated silicon species are more reactive than the tetracoordinated ones, as observed previously.[7,9] Compounds 1 and 2 always react faster than their tetravalent analogues. The larger rate accelerations, i.e., 10–10^2 times faster, are observed with the most hindered nucleophiles. When hydrides ($LiAlH_4$, $LiAlH(OMe)_3$, $LiAlH(O$-t-$Bu)_3$, $(i$-$Bu)_2AlH$) are used instead of Grignard reagents, the rates are very fast with both anionic and neutral compounds. A direct comparison is made impossible because of the insolubility of the potassium salts at lower temperatures.

When the reaction was carried out between Ph_3SiF and i-PrMgBr (2 equiv) in THF at room temperature in the presence of 18-crown-6 (Table I, run 7) or of MgF_2 (Table I, run 8), the corresponding half-reaction times are of the same order of magnitude as that measured in run 6; it clearly indicates that the complexing agent or MgF_2 does not alter significantly the reactivity of the Grignard reagent.

Treatment of 1 with 1 equiv of MeMgBr at −30 °C leads to a mixture of the monofunctional $PhMe_2SiF$, MgBrF, and KF,18-crown-6 within 5 min (Scheme III, step a). The subsequent addition of 1 equiv of MeMgBr at −30 °C leads to $PhSiMe_3$ (reaction time 5 h) (Scheme III, step b). Reaction between $PhMe_2SiF$ and KF,18-crown-6 at −30 °C in ether is quite slow (Scheme III, <20% of $PhMe_2SiF_2^-$ K^+-18-crown-6 determined by ^1H NMR after 5 h), indicating that under our experimental conditions (Scheme III, step b), the concentration of the pentavalent species will be always quite low. Reaction between pure $PhMe_2SiF$ and 1 equiv of MeMgBr is also slow and complete only after 5.5 h. In contrast, the reaction of the preformed $PhMe_2SiF_2^-K^+$-18-crown-6 with MeMgBr (1 equiv) in ether at −30 °C leads quantitatively to $PhSiMe_3$ within 3 min. Thus, the above data clearly indicate that the rate enhancement observed either with $PhMe_2SiF_2^-$ and $Ph_3SiF_2^-$ only results from a coordination of the fluoride anion at silicon.

Such an activation is general. For instance, $Ph_2Si(OMe)_3K^+$-18-crown-6[10] is also quite reactive (Scheme IV) and reacts with i-PrMgBr (2 equiv) in THF at room temperature to completion within 2 h; in contrast, 17% of $Ph_2Si(OMe)_2$ is only converted after 17 h under identical conditions.

Scheme IV



In conclusion, we have evidence that nucleophilic attack at pentacoordinated silicon species is a general process. These species may be regarded as possible intermediates in nucleophilic activated substitutions at silicon. Morever, the present data point out the enhanced reactivity of these species that might arise from a greater electropositive character of the pentavalent silicon atom, as suggested also by calculations.[11]

Registry No. 1·k-18-crown-6, 102307-92-6; 2·k-18-crown-6, 47102-67-0; 3, 328-57-4; 4, 379-50-0; $PhMeSiH_2$, 766-08-5; PhMe(F)Si(i-Pr), 111268-12-3; PhMe(F)Si(t-Bu), 111268-13-4; $PhMeSi(n$-$Bu)_2$, 17903-10-5; $PhMeSi(C{\equiv}CPh)_2$, 23024-19-3; $PhC{\equiv}CLi$, 4440-01-1; Ph_3SiH, 789-25-3; Ph_3SiEt, 18666-24-5; Ph_3Si-i-Pr, 111268-14-5; $PhSiMe_3$, 768-32-1; $PhMe_2SiF$, 454-57-9; PhMeSi(OMe), 3027-21-2; $Ph_3Si(n$-$Bu)$, 2117-32-0; $Ph_3Si(O$-i-$Pr)$, 1829-43-2; 18-crown-6, 17455-13-9; MgF_2, 7783-40-6; Si, 7440-21-3.

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(10) $Ph_2Si(OMe)_3^-$ K^+-18-crown-6: mp 89–92 °C; ^1H NMR (δ, CD_3COCD_3) 3.25 (s, 6 H, OCH_3), 3.53 (s, 27 H, OCH_3 + OCH_2), 6.93–7.25 (m, 6 H, Ph), 7.47–7.85 (m, 4 H, Ph). Anal. Calcd for $C_{27}H_{43}O_9SiK$: C, 56.03; H, 7.49. Found: C, 55.53; H, 7.62.

(11) Sogah, D. Y., private communication.

Electrocatalytic Reduction of CO_2 by Associative Activation

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Summary: The complex *cis*-$[Os(bpy)_2(CO)H][PF_6]$ (bpy is 2,2′-bipyridine) has been found to be an electrocatalyst for CO_2 reduction in CH_3CN/0.1 M tetra-*n*-butylammonium hexafluorophosphate solution at a Pt working electrode. Under anhydrous conditions CO is the dominant product, but addition of water results in up to 25% formate. Kinetic parameters derived by digital simulation of the cyclic voltammograms under electrocatalytic conditions are consistent with an associative step (k_1) where CO_2 reacts with the di-reduced complex $[Os(bpy)_2(CO)H]^-$ to form an intermediate that leads directly to CO or formate. When extended to a series of related complexes, the kinetic data provide the first example of a significant steric effect on CO_2 reduction as demonstrated by a linear correlation between ln k_1 and the cone angle of the cis ligand in the series *cis*-$[M(bpy)_2(CO)R]^-$ (M = Os, R = H, Me, or Ph; M = Ru, R = CH_2Ph) where k_1 is the rate constant for the initial second-order reaction between the di-reduced complex and CO_2.

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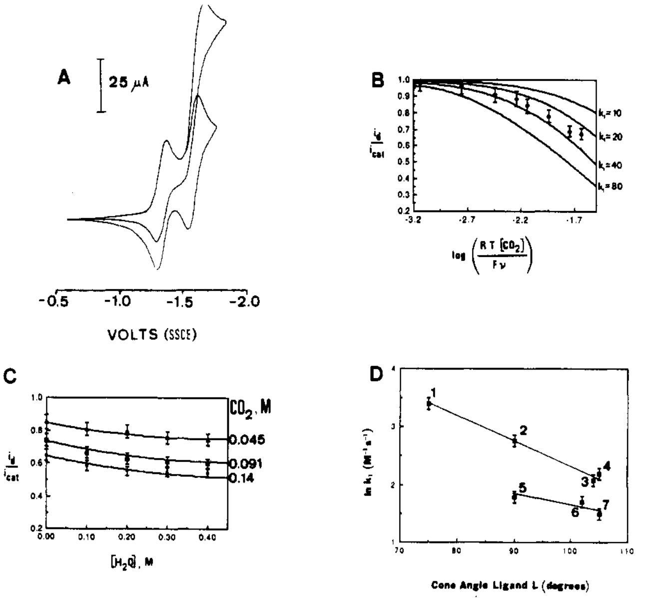
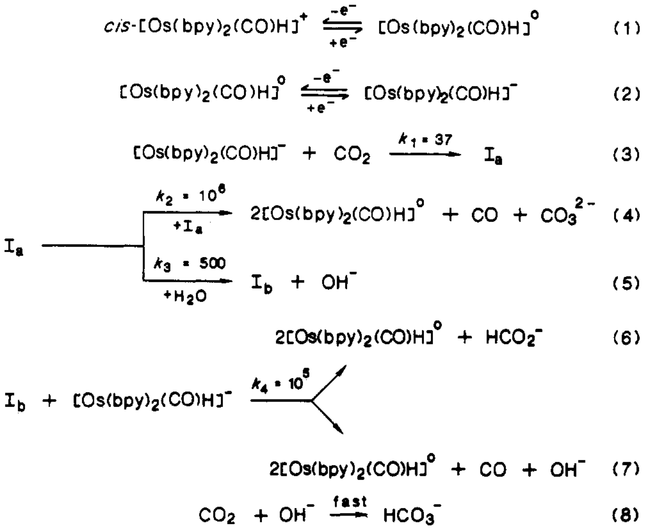


Figure 1. (A) Cyclic voltammograms of 0.1 M TBAH–CH_3CN solutions containing *cis*-$[(bpy)_2Os(CO)H][PF_6]$ (~4.2 mM) using a Pt button electrode (~0.125 cm^2) and a scan rate of 100 mV s^{-1} in the absence of CO_2 in an argon-saturated solution and in a CO_2-saturated solution ($[CO_2] \approx 0.14$ M). (B) The ratio of the diffusional and catalytic currents $i_d/i_{cat.}$ measured at the peak of the second reductive wave vs log ($RT[CO_2]/F\nu$) in 0.1 M TBAH–CH_3CN at room temperature at various assumed values of k_1, where R = gas constant, T = temperature, F = Faraday's constant, and ν = scan rate. The data shown are average values obtained from two to five CV experiments with ν = 0.02–0.5 V/s and $[CO_2]$ = 0.0014–0.14 M under anhydrous conditions with no added water. (c) The ratio $i_d/i_{cat.}$ vs $[H_2O]$ with $[CO_2]$ = 0.045, 0.091, and 0.14 M as indicated. (d) A plot of ln k_1 vs the cone angle of the ligand cis to CO in 0.1 M TBAH–CH_3CN at room temperature for the complexes *cis*-$[(bpy)_2Os(CO)H]^+$ (1), *cis*-$[(bpy)_2Os(CO)CH_3]^+$ (2), *cis*-$[(bpy)_2Ru(CO)CH_2C_6H_5]^+$ (3), *cis*-$[(bpy)_2Os(CO)C_6H_5]^+$ (4), *trans*-$[(bpy)_2Os(CO)CH_3]^+$ (5), *trans*-$[(bpy)_2Os(CO)CH_2CH_3]^+$ (6), and *trans*-$[(bpy)_2Os(CO)C_6H_5]^+$ (7).

A number of electrocatalysts for the reduction of CO_2 are known,[1] and, although some information exists concerning the key redox steps,[2,3] the detailed mechanistic insight necessary for the rational design of catalysts and the control of product selectivity is, in general, not yet available. We report here the results of electrochemical kinetic and mechanistic studies that reveal a heretofore unidentified pathway for the electrocatalytic reduction of CO_2. The key feature of the new pathway appears to be an associative step in which CO_2 reacts with highly reduced polypyridyl complexes of Ru and Os by coordination sphere expansion to give a reactive intermediate. The intermediate, in turn, leads to CO or formate in a ratio which depends upon the water content of the electrolysis solution.

Scheme I



Cyclic voltammograms (CV) of *cis*-$[Os(bpy)_2(CO)H][PF_6]$[4] in argon deoxygenated CH_3CN solution that contains 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte show two one-electron, bpy-based, reversible reductions at $E_{1/2}$ = −1.34 and −1.60 V versus the NaCl-saturated calomel electrode (SSCE). As shown in Figure 1A, the second wave is greatly enhanced in a solution saturated in CO_2. Sustained electrolysis (20 electron equivalents per complex) of solutions that contains 1–2 mM of complex in dry,[5a] CO_2-saturated CH_3CN at potentials of −1.4 to −1.6 V at a Pt mesh working electrode gives CO with Faradaic current efficiencies of up to 90% as shown by gas chromatography. In addition, <5% formate and traces of oxalate and glycolate are found after analysis of the electrozylate by ion chromatography.[5b] With added water the amount of formate increases until its appearance reaches a maximum Faradaic current efficiency of 25% at $[H_2O]$ ~ 0.3 M past which H_2 becomes a major product. Under our conditions the net reactions are

$$3CO_2 + 2e^- + H_2O \rightarrow CO + 2HCO_3^-$$

$$2CO_2 + 2e^- + H_2O \rightarrow HCO_2^- + HCO_3^-$$

where the proton requirement in "dry" acetonitrile is met

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[2] (a) See, for example: Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604. (b) Keene, F. R.; Creutz, C.; Sutin, N. *Coord. Chem. Rev.* **1985**, *64*, 247. (c) Darensbourg, D. J.; Kudarowski, R. *J. Am. Chem. Soc.* **1984**, *106*. (d) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *Ibid.* **1985**, *107*, 7463. (e) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500.

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[4] Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241.

[5] (a) For the purpose of the experiments described here "dry" conditions refer to a water content of <0.01 M. (b) At longer electrolysis times complications arise, apparently from air leakage into the cell used. (c) Past the initial stages of the electrolysis where HCO_3^- becomes a significant product, the availability of protons will presumably be dictated at least in part, by the buffer ratio $[CO_2][H_2O]/[HCO_3^-]$ even in dry acetonitrile. In that this ratio varies during the electrolysis and there is a proton demand in both the appearance of CO and CO_2, the product distribution could vary during the course of the electrolyses.

by the trace water in the medium.[5c] UV–vis and FTIR spectra at the end of the electrolysis period show that the catalyst remains unchanged during the electrolysis experiments.

The kinetics of CO_2 reduction were studied by computer simulation of the scan rate dependence of cyclic voltammetric wave shapes under conditions where the concentrations of *cis*-$[Os(bpy)_2(CO)H][PF_6]$, CO_2, and H_2O could be systematically varied.[6] Of a variety of possible mechanistic cases that were considered, the data were most satisfactorily fit by a mechanism that involves an initial, irreversible reaction between $[Os(bpy)_2(CO)H]^-$ and CO_2 with a rate constant, k_1, to give an intermediate which subsequently undergoes either a self-reaction or an irreversible reaction with H_2O as shown in eq 1–8 (Scheme I). In one alternate mechanism, which gives a similar variation in $i_d/i_{cat.}$ with concentration, see below, but with a less satisfactory fit, parallel pathways exist which are first order in *cis*-$[(bpy)_2Os(CO)H][PF_6]$ and CO_2 with one of the two pathways involving a following step which is first order in added H_2O. As shown, the mechanism does not include the H_2 production pathway which appears at high $[H_2O]$. In principle, it should have been possible to use product ratio studies at high added $[H_2O]$ to evaluate k_6 and k_7. However, there are large uncertainties in the analyses, and we have insufficient data to justify using the results in this way.

In Figure 1B is shown a plot of the ratio of the diffusion and catalytic currents measured at the second wave ($i_d/i_{cat.}$) vs the function log ($RT[CO_2]/F\nu$) at various assumed values of k_1 where ν is the scan rate and F the Faraday constant. This concentration–scan rate function is appropriate for the mechanism in eq 1–4 in the absence of added H_2O. The variation of $i_d/i_{cat.}$ with added water is consistent with the additional steps proposed in the mechanism (see Figure 1C). The combination of results from the kinetic and product studies suggests that formate arises from the H_2O branch (reaction 5 followed by reaction 6) and CO from both branches.

When the isotopically labeled complex *cis*-$[Os(bpy)_2(CO)D][PF_6]$ was used as a catalyst under conditions where formate production is nearly maximized (0.3 M added H_2O), there was no proton incorporation after 1.8 turnovers of formate. Likewise, in experiments using $^{13}CO_2$ there was no incorporation of ^{13}CO into the catalyst after 5.5 turnovers in terms of the production of CO. The labeling studies are consistent with the mechanism in eq 1–8 and rule out pathways like insertion of CO_2 into the Os–H bond. They show that the –CO and –H groups in the proposed intermediates I_a and I_b are inert and are not involved in the net reductions.

In dry CH_3CN[5a] where the formate pathway is negligible, similar current enhancements at the second bpy wave are observed for the related complexes *cis*-$[M(bpy)_2(CO)R]^+$ (M = Os, R = Me or Ph; M = Ru, R = CH_2Ph) and *trans*-$[Os(bpy)_2(CO)R]^+$ (R = Me, C_2H_5, or Ph). Values for k_1 were obtained for the series by assuming the same mechanism and by using the same kinetic analysis. As shown by the plot of ln k_1 vs the cone angle[7] of the R group in Figure 1D: (1) rate constants for the cis complexes have a remarkable dependence on the steric bulk of the group cis to CO, (2) although the stereochemically more crowded cis isomers are more sensitive to steric effects than are the trans isomers, they are intrinsically more reactive toward CO_2, and (3) if isomeric intermediates exist for the cis and trans series, they are stereochemically rigid under the conditions that lead to CO_2 reduction.

Finally, a comparison between our proposed mechanism of catalysis with that of Amatore and Saveant for the reduction of CO_2 in CH_3CN solution at a Pt electrode[8] is revealing in three ways. First, oxalate formation is the kinetically favored pathway for the uncatalyzed reduction with $k = 10^7$ M^{-1} s^{-1} for the coupling of CO_2^-, but this pathway is suppressed in the Os-catalyzed reaction, apparently as a consequence of CO_2 binding and the subsequent bimolecular reaction of sterically demanding intermediates. Second, for CO production, the dimerization of I_a replaces the reaction between CO_2^- and free CO_2 that occurs in the uncatalyzed system. Lastly, the formate making step is of similar form in both mechanisms, i.e., reaction of a proton with either CO_2^- or reduced, metal-complexed CO_2, followed by a rapid electron transfer from an external reductant, that is, CO_2^- in the uncatalyzed process or a reduced Os complex in the catalyzed process.

Acknowledgment. Financial support by the Gas Research Institute is greatly appreciated. Special thanks are due to Dr. C. Mark Bolinger for the development of the electrolysis techniques.

Registry No. *cis*-$[Os(bpy)_2(CO)H][PF_6]$, 84117-35-1; CO_2, 124-38-9; CO, 630-08-0; HCO_2^-, 71-47-6; *cis*-$[Os(bpy)_2(CO)H]^-$, 111437-23-1; *cis*-$[Os(bpy)_2(CO)CH_3]^-$, 111437-17-3; *cis*-$[Os(bpy)_2(CO)C_6H_5]$-$^-$, 111437-18-4; *cis*-$[Ru(bpy)_2(CO)CH_2C_6H_5]^-$, 111437-19-5; *cis*-$[(bpy)_2Os(CO)H]^+$, 84117-34-0; *cis*-$[(bpy)_2Os(CO)CH_3]^+$, 111437-20-8; *cis*-$[(bpy)_2Ru(CO)CH_2C_6H_5]^+$, 82482-59-5; *cis*-$[(bpy)_2Os(CO)C_6H_5]^+$, 111437-21-9; *trans*-$[(bpy)_2Os(CO)CH_3]^+$, 111554-34-8; *trans*-$[(bpy)_2Os(CO)CH_2CH_3]^+$, 111437-22-0; *trans*-$[(bpy)_2Os(Co)C_6H_5]^+$, 111554-35-9.

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Reaction of a Terminal Phosphinidene Complex with a Carbyne Complex. Synthesis and X-ray Crystal Structure of a Metallaphosphirene

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Summary: The terminal phosphinidene complex $[PhP{=}W(CO)_5]$ as generated from the appropriate 7-phosphanorbornadiene complex reacts with the carbyne complex $PhC{\equiv}W(CO)_2Cp$ to give a three-membered tungstaphosphirene ring via a formal [1 + 2] P + W≡C cycloaddition.

In a previous note,[2] we described the condensation of a terminal phosphinidene[3] with a carbene complex. A η^1-P

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(2) Tran Huy, N. H.; Mathey, F. *Organometallics* 1987, *9*, 207.