**Table I.** Data for Electrocatalytic Reduction of $CO_2(g)$ at Co(Pc)/C Electrodes

| entry | exptl conditions[a] | Coulombs passed | turnover no.[b] | current density, mA/cm$^2$ [c] | product ratio ($CO/H_2$) | Coulometric efficiency for all gaseous products, % |
|---|---|---|---|---|---|---|
| 1 | pH 5/$CO_2$ atm/Co(Pc)/−1.15 V/1.3 × $10^{-11}$ mol cm$^{-2}$ | 16.8 | 3.7 × $10^5$ | 0.98 | 1.5/1 | 87 |
| 2 | pH 5/Ar atm/Co(Pc)/−1.15 V/8.2 × $10^{-11}$ mol cm$^{-2}$ | 20.7 | | 1.22 | only $H_2$ | 86 |
| 3 | pH 5/$CO_2$ atm/naked electrode/−1.15 V | 9.04 | | 0.079 | only $H_2$ | 78 |
| 4 | pH 10/$HCO_3^-$ + $CO_3^{2-}$ = 0.1 M/Ar atm/Co(Pc)/−1.30 V/7.2 × $10^{-10}$ mol cm$^{-2}$ | 11.1 | | 0.073 | only $H_2$ | 88 |
| 5 | 3.1 mM Co(Pc)/THF/3.6 mM TFAA[d]/1 M $H_2O/CO_2$ atm/−1.06 V | 21.5 | 4 | 0.062 | 0.26/1 | 63[e] |
| 6 | pH 5/$CO_2$ atm/$H_2Pc$[f]/−1.10 V/4.5 × $10^{-11}$ mol cm$^{-2}$ | 8.40 | | 0.032 | only $H_2$ | 79 |
| 7 | 3 mM $Co(ClO_4)_2$/pH 5/$CO_2$ atm/−1.10 V | 8.68 | 0.14 | 0.029 | 0.49/1 | 82 |

[a] V vs. SSCE [b] Calculated assuming 2e$^-$/Co(Pc)/CO. [c] Geometric area of carbon cloth. [d] TFAA = trifluoroacetic acid. [e] 80% of Co(Pc) was lost; determined from vis spectra. [f] $H_2Pc$ = metal-free phthalocyanine.

second reduction corresponds to a two-electron process from the Co(Pc)$^-$ state. The agreement between the position of the second reduction wave at −0.95 V (pH 5.0) and the onset of CO(g) production strongly suggests that reduction of Co(Pc)/C at this potential leads to the active form of the catalyst.

The pH dependence of the Co(Pc)$^{0/-}$ reduction implies an initial protonation step in the reaction sequence, which is followed subsequently by further reduction of the complex and attack by $CO_2$. Precedent for the reaction steps involved in such catalysis can be found in proposed mechanisms for catalysis of the water–gas shift reaction, which is essentially the reverse of (1) (with $H_2 = 2H^+ + 2e^-$).[8] A similar reaction sequence has been invoked previously by Eisenberg to explain redox catalysis in the $CO_2$/CO transformation by homogeneous Co and Ni macrocyclic complexes, where a one-electron reduction to a metal hydride species is implicated.[9] Our product distribution is similar to that obtained with these macrocyclic ligands, but an important difference in our system is that the "hydride" (either ligand or metal centered)[10] is not reactive enough to reduce $CO_2$ and must itself be reduced further (by two electrons in this case) to yield the observed catalysis.

The ease of reduction of the Co(Pc) complex allows the $CO_2$ transformation to proceed at a much lower overpotential, yet with faster rates, than in previous catalytic systems for CO production.[9] A comparison of the current density to the amount of electroactive catalyst on Co(Pc)/C electrodes (Table I) indicates that turnover numbers for $CO_2$ reduction can exceed 100 s$^{-1}$, which is over 3 orders of magnitude greater than the values of 2–7 turnovers/h reported for catalysis in homogeneous systems.[9]

Finally, we have obtained evidence which supports the notion that unfavorable decomposition reactions can be suppressed by immobilization of the Co(Pc) catalyst onto the electrode surface. Cyclic voltammetry of Co(Pc) dissolved in aqueous acid/THF or in dry $HBF_4 \cdot Et_2O$/THF solutions indicates that addition of protons produces a quasi-reversible second reduction wave for Co(Pc) similar to that observed in aqueous solutions. However, a controlled-potential electrolysis yielded much lower coulometric efficiencies for CO production, and the electrolysis resulted in a large loss of catalyst after only a few turnovers (Table I). In contrast, Co(Pc)/C electrodes yield an initial decay in the catalytic current to a steady-state value and then proceed at the sustained rates reflected in Table I. Thus, despite the similar transient electrochemical behavior of the adsorbed and homogeneous Co(Pc) species, sustained activity for $CO_2$ reduction appears to be favored on modified electrode surfaces, where site–site interactions leading to catalyst deactivation can be minimized. Applications of these principles to other substrates, as well as a more detailed investigation of the reaction products of Co(Pc)$^-$ with aqueous solutions, are under investigation at present.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge support through the NIH Biomedical Fund at Stanford University, and N.S.L. acknowledges support from an IBM Corp. Young Faculty Development Award.

**Registry No.** Co(Pc), 3317-67-7; $CO_2$, 124-38-9; CO, 630-08-0; C, 7440-44-0.

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## Intramolecular $S_N2$ Bridge Formation Kinetics of Undecacarbonyl($\eta^1$-bis(diphenylphosphino)methane)triosmium

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*Received March 22, 1984*

The rate of chelate complex formation is generally governed by the rate at which the first donor atom of the multidentate ligand enters the coordination sphere,[1] entry of the remaining donor atoms usually being very much more rapid owing to their very high effective concentration.[2] It has proved possible, however, to study the kinetics of chelate ring closure reactions by rapid generation of complexes containing the monodentate form of potentially bidentate ligands.[3]

We report here a kinetic study of reaction 1 in which the

$$Os_3(CO)_{11}(\eta^1\text{-dppm}) \rightarrow Os_3(CO)_{10}(\mu\text{-dppm}) + CO \quad (1)$$

monodentate dppm[4a] is converted slowly at 50–70 °C into the bidentate *bridging* form via an intramolecular process that can be shown to be clearly associative in nature. Although the corresponding reaction of $Ru_3(CO)_{11}(\eta^1\text{-dppe})$[4b] has been observed,[5] no kinetic measurements were reported and the kinetics of reaction 1 are the first of their type.[6] The new complex $Os_3(CO)_{11}(\eta^1\text{-dppm})$ was prepared by the very facile reaction of $Os_3(CO)_{11}(NCMe)$[8] with dppm in cyclohexane at room temperature.

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(6) The bridge-closing reaction $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm}) \rightarrow Ru_3(CO_8)(\mu\text{-dppm})_2 + CO$ has also been studied.[7]

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**Table I.** Kinetic Data[a] for Reaction 1 in Cyclohexane

| $T$, °C | $10^5 k_{obsd}$, $s^{-1}$ | | | |
|---|---|---|---|---|
| 50.0 | 4.76[b] | 4.90[c] | 4.83[d] | 4.85[e] |
| 50.2 | 5.05 | 5.19[f] | 5.22[g] | |
| 61.6 | 15.9 | 16.2 | 17.2 | |
| 70.0 | 40.0 | 42.2 | 39.9 | |

[a] $\Delta H^{\ddagger} = 22.22 \pm 0.44$[h] kcal mol$^{-1}$, $\Delta S^{\ddagger} = -9.6 \pm 1.3$ cal K$^{-1}$ mol$^{-1}$, $\sigma(k_{obsd}) = \pm 5.0\%$.[i] $10^4$[complex] = 2.2–4.4 M; $10^4$[dppm] = 5.6 M unless otherwise indicated. [b-e] $10^4$[dppm] = 0, 14.5, 28.9, and 30.1 M, respectively. [f] Solution equilibrated with 40% CO–$N_2$ gas mixture. [g] Solution equilibrated with pure CO. [h] Uncertainties are estimates of standard deviations adjusted for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them. [i] Standard deviation of an individual measurement of $k_{obsd}$.

It was identified spectroscopically in situ and after isolation.[9] $Os_3(CO)_{10}(\mu$-dppm) was prepared by the very rapid reaction of $Os_3(CO)_{10}(NCMe)_2$[8] with dppm and characterized spectroscopically[10] and by analysis.[12] It is identical with the product of reaction 1 and the mode of preparation confirms the bridging nature of the dppm ligand.

The progress of reaction 1 is accompanied by a slight increase in intensity of the electronic absorption band at ca. 350 nm and a decrease of absorbance of the maximum at 417 nm, the latter shifting to 410 nm.[14] Isosbestic points are evident at 392 and 330 nm. Rate constants were obtained graphically from the absorbance changes at 410 nm and are shown in Table I together with the activation parameters. The rate constants are not sensitive to the presence of $O_2$ and are independent of [complex], [dppm], and [CO]. Free dppm had no effect on the nature of the product so no competing intermolecular substitution of an additional dppm ligand occurred. The absence of any retardation by CO shows that simple reversible CO dissociation is not rate determining, nor does it precede the rate-determining step.

Since the data in Table I are the first of their type there are no activation parameters for direct comparison and even studies involving intramolecular chelate ring formation have seldom involved determination of temperature dependence of the rates. An exception to this is the extensive study of the reaction shown in eq 2.[3c] When M = Cr and LL = dppm the values of $\Delta H^{\ddagger}$ and

$$M(CO)_5(\eta^1\text{-LL}) \rightarrow M(CO)_4(\eta^2\text{-LL}) + CO \qquad (2)$$

$\Delta S^{\ddagger}$ are 33.7 kcal mol$^{-1}$ and +17.0 cal K$^{-1}$ mol$^{-1}$, respectively. The high value of $\Delta H^{\ddagger}$ and the positive value of $\Delta S^{\ddagger}$ both indicate a high degree of Cr–CO bond breaking in the transition state, the values being very close to those for dissociation of CO from $Cr(CO)_5(PPh_3)$, viz., $\Delta H^{\ddagger} = 35.3$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = +14.4$ cal K$^{-1}$ mol$^{-1}$.[15] This shows that bond making is negligible or small and that the mechanism of chelate ring closure is essentially $I_d$ in nature.

The activation parameters in Table I lead to quite the opposite conclusion for the bridge-formation reaction shown in eq 1. The much lower value of $\Delta H^{\ddagger}$ and the substantially negative value of $\Delta S^{\ddagger}$ both point strongly to an associative mechanism. This conclusion is supported by the activation parameters for the [P-$n$-$Bu_3$]-independent introduction of P-$n$-$Bu_3$ into $Os_3(CO)_{11}$(P-$n$-$Bu_3$) which are $\Delta H^{\ddagger} = 39.6 \pm 1.0$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = +24 \pm 3$ cal K$^{-1}$ mol$^{-1}$ whereas those for the corresponding associative substitution are 15 ± 1 kcal mol$^{-1}$ and −36 ± 3 cal K$^{-1}$ mol$^{-1}$, respectively.[11] While it would be preferable to have data for reaction of $Os_3(CO)_{11}(PPh_2Me)$ with $PPh_2Me$ it is unlikely that they would be substantially different. The activation parameters show, therefore, that the bridge formation reaction involves a high degree of bond making and can be unambiguously classified as $I_a$ or $S_N2$ in nature.

The difference between the values $\Delta S^{\ddagger} = -36$ cal K$^{-1}$ mol$^{-1}$ for the intermolecular associative attack of P-$n$-$Bu_3$ on $Os_3(CO)_{11}$(P-$n$-$Bu_3$) and $\Delta S^{\ddagger} = -9.6$ cal K$^{-1}$ mol$^{-1}$ for bridge formation must reflect, to a large degree, the much higher effective concentration of the uncoordinated P atom in $Os_3(CO)_{11}(\eta^1$-dppm). The difference amounts to a factor of ca. $5 \times 10^5$ in rates. This is somewhat lower than the factor of ca. $10^8$ generally expected but it is by no means unusual.[17] This aspect of such reactions can now be investigated further by studying the dependence of the kinetic parameters on the nature of various bridging ligands such as $R_2P(CH_2)_nPR_2$.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council, Ottawa, for support.

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[9] $\nu_{CO}$ in cyclohexane: 2098 (m), 2048 (ms), 2026 (sh), 2010 (s), 2000 (sh), 1988 (w), 1980 (w), 1967 (w), 1953 (w) cm$^{-1}$. Cf. $Os_3(CO)_{11}(PPh_3)$, $\nu_{CO}$: 2108 (ms), 2055 (s), 2035 (s), 2009 (s), 2000 (ms), 1989 (ms), 1978 (m) cm$^{-1}$.[8] Traces of $Os_3(CO)_{10}(\mu$-dppm) were evident[10] in the isolated complex and consequently no elemental analysis was attempted.

[10] $\nu_{CO}$ in cyclohexane: 2088 (s), 2027 (sh), 2006 (vs), 1983 (s), 1965 (m), 1955 (m), 1945 (w) cm$^{-1}$. Cf. $Os_3(CO)_{10}$(P-$n$-$Bu_3)_2$, $\nu_{CO}$ in decalin: 2070 (m), 2012 (s), 1995 (s), 1958 (m), 1950 (w), 1935 (w) cm$^{-1}$.[11]

[11] Poë, A. J.; Sekhar, V. C., unpublished results.

[12] Anal. Calcd for $Os_3(CO)_{10}$(dppm): C, 34.03; H, 1.78. Found:[13] C, 34.69; H, 1.62.

[13] Microanalysis performed by Canadian Microanalytical Service, Ltd., Vancouver.

[14] $Os_3(CO)_{11}(\eta^1$-dppm) shows maxima in cyclohexane at 410 ($\epsilon$ $6.4 \times 10^3$ M$^{-1}$ cm$^{-1}$) and 350 nm ($\epsilon$ $1.14 \times 10^4$ M$^{-1}$ cm$^{-1}$); $Os_3(CO)_{10}(\mu$-dppm) shows maxima at 417 ($\epsilon$, $5.2 \times 10^3$ M$^{-1}$ cm$^{-1}$) and 354 nm ($\epsilon$ $1.2 \times 10^4$ M$^{-1}$ cm$^{-1}$).

[15] These parameters are derived from values of $E_a$ and $k_{obsd}$ at 30 °C. Atwood, J. D.; Cohen, M. A.; Brown, T. L. unpublished results quoted in reference 16.

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## Chiral Vinyllithium Reagents. Carbenoid Reactions[1]

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The reaction of an organic halide that possesses a proton on the halogen-bearing carbon with a lithium reagent can lead to either halogen–lithium exchange[2,3] or hydrogen–lithium exchange (metalation[4]). The latter reaction results in the formation of intermediates known as carbenoids,[5,6] which are capable of undergoing ambiphilic reactions.[7-9] During the course of our study of chiral vinyllithium reagents,[10] prepared by halogen–lithium exchange, we often observed side products which could be rationalized as resulting from nucleophilic substitution on a vinylidene carbenoid. The stereochemical investigation of this reaction is the subject of this communication.

Treatment of ($aS$)-(+)-(4-methylcyclohexylidene)bromomethane (**1**) of known absolute configuration[10] in ether at −90

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