Table I. High Cram Selectivity of Imine Reactions[a]

entry	imine, $RCH{=}NR'$: R	R'	allylorganometal M	Cram (3): anti-Cram (4)
1	$PhCH(CH_3)$	*n*-Pr	9-BBN	96:4
2	$PhCH(CH_3)$	*i*-Pr	9-BBN	100:0
3	$PhCH(CH_3)$	*n*-Pr	MgCl	84:16
4	$PhCH(CH_3)$	*i*-Pr	MgCl	70:30
entry	aldehyde		allylorganometal	Cram (1): anti-Cram (2)
5	$PhCH(CH_3)CHO$		9-BBN	55:45
6			MgCl	60:40
7			$SiMe_3$[b]	70:30

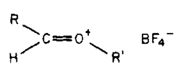
[a] All reactions were carried out on a 1-mmol scale at -78 °C under N_2 and quenched at 0 °C. Total isolated yields were in a range of 88-98%. The Cram:anti-Cram ratio was determined by ^1H NMR analysis and/or GLPC (THEED, 10%, 2 m). [b] $TiCl_4$ was used as a Lewis acid.

The present findings suggest that the Cram/anti-Cram problem of carbonyl groups might be solved by a similar approach.[13] Further work along this line is now under active investigation.

(11) There may be a question that the bad interactions depicted in **9** and **16** can be avoided by rotating the carbon so that the hydrogen is in the position of the methyl in **9** and the phenyl in **16**. Inspection with a Dreiding model clearly indicates that such conformations are destabilized by the steric repulsion between the 9-BBN ring and the phenyl group in **9** and between the 9-BBN ring and the methyl group in **16**.

(12) (a) For addition of allylboronates to Schiff bases, see: Hoffmann, R. W.; Eichler, G.; Endesfelder, A. *Liebigs Ann. Chem.* **1983**, 2000. (b) When alkylorganometallics, such as $BuCu{\cdot}BF_3$ and $Bu_2CuLi{\cdot}BF_3$, were utilized, the Cram/anti-Cram selectivity was low (~4:1). This is reasonable since the six-membered cyclic transition state is not involved in this reaction. For the reaction of imines with $RCu{\cdot}BF_3$, see: Wada, M.; Sakurai, Y.; Akiba, K. *Tetrahedron Lett.* **1984**, *25*, 1079.

(13) An oxonium salt of aldehydes may take a trans geometry (**17**). If



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so, the R group may go to the axial position as described above. In fact, the reaction of α-phenylpropionaldehyde with allyl-9-BBN in the presence of $Et_3O^+BF_4^-$ produced **1** and **2** in a ratio of 7:3 (cv. entry 5). We are also investigating the Lewis acid mediated reaction of acetals bearing an α-chiral center, the results of which will be published soon.

Catalytic Reduction of CO_2 at Carbon Electrodes Modified with Cobalt Phthalocyanine

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We report the electrocatalytic reduction of aqueous solutions of $CO_2(g)$ to $CO(g)$. The reaction occurs on carbon electrodes modified by adsorption of cobalt phthalocyanine, Co(Pc). The CO_2 reduction can be achieved within 300 mV of the thermodynamic CO_2/CO redox potential, and essentially the only carbon-containing product is CO(g). In contrast, Co(Pc) dissolved in homogeneous solution yields poor stability and low catalytic efficiency for CO_2 activation. Thus, in addition to an energy-efficient activation of $CO_2(g)$, this system demonstrates the effectiveness of chemical modification of electrodes in suppressing deleterious decomposition pathways during electrocatalysis.

The abundance of CO_2 as a one-carbon precursor has evoked considerable interest in its catalytic transformations.[1] Direct electrochemical reduction of CO_2 proceeds with large overpotentials[2] and generally yields formate. Electrocatalytic reductions of CO_2 to yield formate have been observed with supported Pd, as well as through the coupling of formate dehydrogenase with methylviologen.[3] Our efforts have focussed upon utilizing transition-metal complexes to promote reduction of CO_2 to CO via (1).

$$CO_2(g) + 2e^- + 2H^+(aq) \rightarrow CO(g) + H_2O(l) \qquad (1)$$

Co(Pc)[4] was deposited onto pyrolytic graphite or carbon cloth surfaces either by adsorption from THF/Co(Pc) solutions or by droplet evaporation of THF/Co(Pc) solutions. Controlled potential electrolysis of such modified carbon cloth electrodes at -1.0 V vs. SSCE in aqueous solution (pH 5.0, 0.05 M citrate buffer, $E^{\circ\prime}(CO_2/CO) = -0.65$ V vs. SCE[5]) under 1 atm of $CO_2(g)$ produced CO(g) as the major carbon-containing species. The catalytic nature of the reaction has been confirmed by formation of over 10^5 molar equiv of CO per molar equiv of electroactive catalyst (Table I).

Typical coulometric experiments (Table I) for potentials from -0.95 to -1.2 V vs. SCE indicate that 55-60% of the charge passed can be accounted for as CO formation and 35-30% detected as H_2, implying overall coulometric efficiencies of 90-95% for the catalytic reaction of Co(Pc) with CO_2/H_2O solutions. Although spot tests indicate the presence of oxalate and formate, as previously reported for a similar Co(Pc)/graphite system at more cathodic operating potentials,[6] we observe that these species are present in only trace amounts, and that the major carbon-containing product is gaseous CO.

Neither of the first two reported reduction potentials for Co(Pc) in DMF solution,[7] -0.40 and -1.40 V vs. SCE, correspond with the potentials at which we detect the onset of CO(g) production in aqueous media (-0.9 V vs. SCE). Furthermore, cyclic voltammograms for the $Co(Pc)^{0/-}$ couple are found to be identical under 1 atm of CO_2 or 1 atm of Ar for THF/Co(Pc) solutions as well as for C/Co(Pc) surfaces in aqueous media. This evidence seems to preclude initial binding of CO_2 to $Co(Pc)^-$ as a viable pathway unless there is only an extremely weak $Co(Pc){-}CO_2$ interaction.

The aqueous reduction of Co(Pc)/graphite surfaces in the absence of CO_2 yields two proton-coupled reductions which appear at -0.58 and -0.95 V vs. SCE at pH 5.0. Over a range of pH 1.5-5.5 we observe a positive shift of $E^{\circ\prime}$ for the first reduction wave of 59 mV/pH unit. The second reduction wave is quasi-reversible, and scan rates of 5 V/s yield reversible behavior for this couple. Interestingly, association of the first electrochemical wave with the one-electron $Co(Pc)^{0/-}$ couple implies that the

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(4) Co(Pc) was obtained from Eastman Kodak Co. and was purified by sublimation. $CO_2(g)$ concentrations were monitored with an Orion Model 95-02 electrode; CO(g) and $H_2(g)$ analyses were performed using a Carle Model 197-B gas chromatograph in the standard factory configuration (columns and thermistor at 60 °C, hydrogen-transfer catalyst at 570 °C; retention times, H_2, 1.5 min, CO, 10.7 min). Oxalate and formate were detected using standard qualitative spot test reagents,[6a] and quantitative determination of oxalate was performed polarographically by determination of Eu^{3+}. Cyclic voltammetric data (100-500 mV/s) were used to determine the coverage of electroactive catalyst on the electrode surface; such coverages ranged from 4×10^{-11} to 40×10^{-11} mol/cm^2 and were generally somewhat less than the total amount of catalyst deposited by the droplet evaporation technique.

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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.

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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(η^1-bis(diphenylphosphino)methane)triosmium

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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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