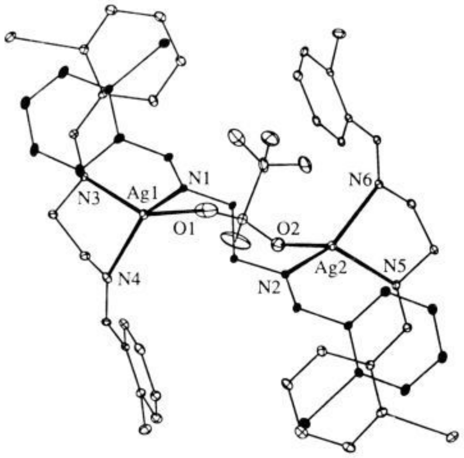

Figure 2. ORTEP representation of $[Ag_2(\mathbf{1c})_3OTf]^+$ with atoms of the bridging ligand as solid elipsoids.

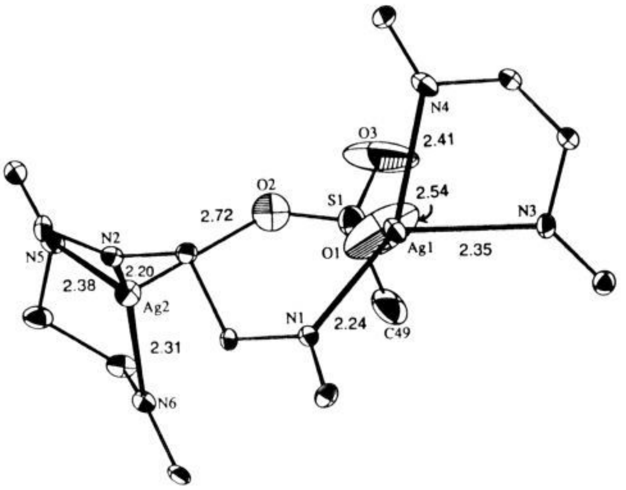

Figure 3. Inner coordination sphere of $[Ag_2(\mathbf{1c})_3OTf]^+$ with selected bond distances (±0.015 Å). Selected bond angles (deg) are as follows: N1–Ag–N3, 131.0 (4); N1–Ag1–N4, 148.1 (4); N3–Ag1–N4, 76.3 (6); N1–Ag1–O1, 102.5 (9); N2–Ag2–N5, 127.9 (4); N2–Ag2–N6, 148.0 (5); N5–Ag2–N6, 76.8 (5); N2–Ag2–O2, 104.3 (7).

The remaining coordination sites on silver are occupied by a chelating bidentate ligand; the THF solvate and noncoordinating triflate do not interact with the metal centers. Each silver ion is coordinated (Figure 3) in an approximate trigonal planar[12] fashion by three imine nitrogens, and the relatively long[13] Ag–O bonds to the bridging trifluoromethanesulfonate[14] serve to pull the silver ions out of these planes by 0.253 (2) Å (Ag1) and 0.314 (2) Å (Ag2). These planes are orthogonal (dihedral angle = 91.6 (4)°), and the Ag1–Ag2 distance is 5.38 Å.

Note that the average Ag–N distance of the chelating ligands is long (2.36 (4) Å) and similar to that observed in $[Ag(\mathbf{1b})_2]OTf$. The 2.22 (3) Å average Ag–N distance of the bridging ligand approaches that of the polymeric species. The pseudotrigonal planar silver environment in $[Ag_2(\mathbf{1c})_3OTf]^+$ is intermediate between that in $[Ag(\mathbf{1b})_2]^+$ and the linear coordination geometry observed in the polymer. Thus net chain growth would be expected upon addition of AgOTf and subsequent replacement of the long Ag–N bonds with the shorter and presumably stronger Ag–N bonds in the polymer.[3] Polymer formation is *observed* upon addition of 1 equiv of AgOTf to a CH_2Cl_2 solution of $[Ag_2(\mathbf{1c})_3OTf]OTf$ to afford $[Ag(\mathbf{1c})]OTf$.[15] These results suggest that $[Ag_2(\mathbf{1c})_3OTf]OTf$ is indeed a reasonable model for the chain-growth process required in the formation of this class of coordination polymers.

Two factors appear to be important in the formation of extended polymers by this pathway. The metal ion must have several accessible coordination numbers and geometries to stabilize soluble precursors and allow for chain elongation. In addition the flexible backbone of the ligand is crucial in enabling transformation from chelating to bridging modes of coordination. We are continuing to pursue the solution and solid-state characterization of these materials with related ligand systems and metal ions.

Acknowledgment. T.G.R. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry Dreyfus Foundation, Inc. We are grateful for support from the Petroleum Research Fund administered by the American Chemical Society. E.P.K. was supported by the NSF URP program. We thank Professor G. E. Keck and his research group for useful synthetic advice.

Supplementary Material Available: NMR spectroscopic data along with crystallographic data including tables of bond distances and angles and final positional and thermal parameters for $[Ag(\mathbf{1b})_2]OTf{\cdot}MeOH$ and $[Ag_2(\mathbf{1c})_3OTf]OTf{\cdot}THF$ (28 pages); tables of observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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[11] Crystal data for $[Ag_2(\mathbf{1c})_3OTf]OTf{\cdot}THF$: $I_6Ag_2SO_7N_6F_6C_{54}H_{50}$, colorless, triclinic, $P\bar{1}$, $a = 13.245$ (5) Å, $b = 13.207$ (5) Å, $c = 20.496$ (5) Å, $\alpha = 89.35$ (3)°, $\beta = 100.64$ (3)°, $\gamma = 108.20$ (3)°, $V = 3342.9$ Å^3, $Z = 2$, Mo Kα. Of 9530 reflections collected (syntex $P\bar{1}$, ambient temperature), 7292 were unique and 5835 with $I > 2\sigma(I)$ were used in the solution and refinement (SPD package). Final refinement included all non-hydrogen atoms as anisotropic contributions. For 744 parameters, $R = 0.066$ and $R_w = 0.074$, GOF = 2.35.

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[15] Analytical data for $[Ag(\mathbf{1c})]OTf$. Anal. Calcd for $C_{17}H_{14}N_2AgF_3I_2O_3S$: C, 27.41; H, 1.89; N, 3.76. Found: C, 27.69; H, 1.84; N, 3.52.

A Model for the Unsaturated Intermediate in Dissociative Electron-Transfer-Catalyzed Substitution Reactions of Organometallic Compounds

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Reductively induced electron transfer catalysis (ETC) has rapidly become an important reaction in organometallic substitution chemistry.[1-8] Virtually all papers on this subject agree

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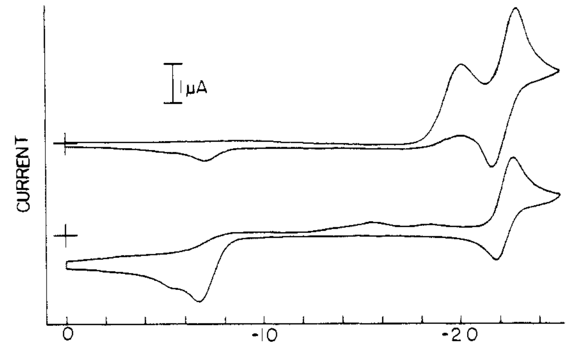


Figure 1. Cyclic voltammetry scans of 5.2×10^{-4} **1** at 273 K in THF/0.1 M Bu_4NPF_6 at a Pt electrode, $v = 0.2$ V/s: top, prior to exhaustive electrolysis; bottom, after electrolysis at −2 V. The lower CV is that of $\mathbf{2}^-$.

that the initially formed 19-electron species responsible for catalytic initiation must undergo a structural change to generate a coordinatively unsaturated species, which may then interact with the substituting ligand. Postulated structural changes include dissociation of a two-electron ligand (usually CO)[6a,7-9] breaking or stretching of a M–M bond,[1,2,9-11] or rearrangement of a cluster bridging ligand from a capping to an edge-bridging position.[3b] Direct evidence for the unsaturated intermediate has been difficult to obtain[8] and only Ohst and Kochi[3b] have been successful in confirmation of it by spectroscopy (ESR).

We set out to prepare a mononuclear $17e^-$ anion which could be viewed as a model intermediate for a dissociative ETC substitution reaction. The strategy involved $1e^-$ reduction of a complex ML_1 (eq 1), followed by loss of L_1 to produce the desired $17e^-$

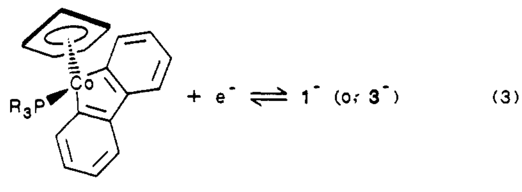
$$ML_1 + e^- \rightleftharpoons ML_1^- \qquad (1)$$

$$ML_1^- \rightarrow M^- + L_1 \qquad (2)$$

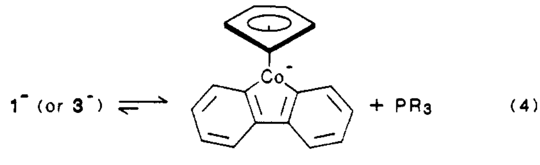
M^- (eq 2). The specific requirements of ML_1 were that its LUMO be antibonding with respect to the $M–L_1$ bond and that the resulting M^- be resistant to the side reactions (e.g., dimerization, protonation, further ligand loss, etc.) which normally decompose these species. This communication reports the first physical evidence for a mononuclear $17e^-$ anion which undergoes ETC substitution reactions.

The cobaltacyclopentadienyl complex $Cp(PPh_3)CoC_4Ph_4$ was shown to lose PPh_3 upon reduction, but the resulting anion formed the π-complex $CpCo(\eta^4\text{-}C_4Ph_4H_2)$ within a few seconds.[12] We anticipated that elimination of the σ-to-π rearrangement pathway for the metallacycle would lead to a stable $17e^-$ anion. Hence the cobaltafluorenyl complex $Cp(PPh_3)CoC_{12}H_8$, **1** (R = Ph)[13] (see idealized structure below) was reduced electrochemically.[14]

Two $1e^-$ waves are encountered in the negative potential scan (Figure 1, top). The first ($E_{pc} = -2.0$ V) is irreversible up to scan rates of 100 V/s and results in formation of the phosphine-free $17e^-$ anion $\mathbf{2}^-$ through eq 3 and 4 (in this note we will label the three differently charged versions of the phosphine-free cobaltacycle as $\mathbf{2}^{n-}$, $n = 0, 1, 2$). The second wave is reversible ($E° = -2.24$ V) and is due to the reduction of $\mathbf{2}^-$ to the $18e^-$ unsaturated dianion $\mathbf{2}^{2-}$. The oxidation wave at $E_{pa} = -0.7$ V is due to the oxidation of $\mathbf{2}^-$ (vide infra).



1 (R = Ph)
3 (R = OMe)



$\mathbf{2}^-$

Exhaustive electrolysis of **1** consumed one electron (1.1 F/eq **1**) and produced an orange solution of $\mathbf{2}^-$ (Figure 1, bottom) which when frozen gave an intense ESR spectrum tentatively assigned to $g = 2.38$ ($A_{Co} = 30$ G) and $g = 2.12$ ($A_{Co} = 41$ G). The radical anion is remarkably stable, with a half-life of over 1 h under nitrogen at 273 K. Back-oxidation of the solution at a potential positive of the anodic wave at −0.7 V regenerates the original cobaltacycle **1** in about 65% yield. It seems likely that reoxidation at $E_{pa} = -0.7$ V gives the $16e^-$ complex $\mathbf{2}^0$ which rapidly adds the PPh_3 lost in the original reduction. Thus, although the reduction of **1** and its oxidative recovery is chemically reversible, the redox couple involves two essentially irreversible EC sequences.[15]

The $17e^-$ anion $\mathbf{2}^-$ supports ETC reactions. Thus, reduction of **1** in the presence of phosphines or phosphites more nucleophilic than PPh_3 leads to catalytic substitution reactions. For example, addition of 20 equiv of $P(OMe)_3$ gave no change in CV scans of 0.5 mM **1**, but exhaustive reduction of the solution required just 0.8 F/equiv and resulted in a mixture of 80% $\mathbf{2}^-$ and 20% of the substituted cobaltacycle, $Cp[P(OMe)_3]CoC_{12}H_8$, **3**. Back-oxidation of this mixture at −0.5 V gave >95% yield of **3**.

Higher concentrations of **1** or of the substituting phosphite increased the ETC efficiency. Only 0.1 F/equiv was required to completely convert a 4.6 mM solution of **1** and 100 equiv of $P(OMe)_3$ to **3** in a reductive electrolysis. A detailed discussion of the chain mechanism is beyond the scope of this communication, but it is clear that the catalytic reaction requires that eq 4 be reversible (although highly favoring the dissociated species) and that the homogeneous electron-transfer reaction (eq 5) sustain

$$\mathbf{1} + \mathbf{3}^- \rightleftharpoons \mathbf{3} + \mathbf{1}^- \qquad (5)$$

the chain process. The reduction wave of the $P(OMe)_3$ complex **3** is almost 200 mV negative of that of the PPh_3 complex **1** so there appears to be an appreciable driving force for eq 5.[16] However, because $\mathbf{3}^-$ is highly dissociated (eq 4), its low concentration limits the rate of the chain reaction early in the electrolysis. Later in the electrolysis the amount of unelectrolyzed **1** is small, and the progress of eq 5 may also be impeded by the low concentration of **1**. When the electrolysis is complete, the lack of an oxidizing agent (neutral **1**) blocks further conversion of $\mathbf{3}^-$ to **3**. Thus, the final solution after exhaustive electrolysis of **1** in the presence of $P(OMe)_3$ consists of neutral **3** (formed mostly in the early part of the electrolysis), the 17-electron metallacycle $\mathbf{2}^-$, and a very small, unmeasured, amount of the 19-electron species $\mathbf{3}^-$.

It seems likely that the extraordinary stability of $\mathbf{2}^-$ is due in part to its ability to delocalize charge throughout the five-mem-

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(16) E_{pc} for **3** is −2.18 V at $v = 0.1$ V/s. The irreversibility of the couples $\mathbf{1}/\mathbf{1}^-$ and $\mathbf{3}/\mathbf{3}^-$ keeps us from calculations of specific free energy changes. The new complex **3** was isolated by chromatography after electrolytic preparation from **1** and $P(OMe_3)$. ^1H NMR in $CDCl_3$: metallacycle resonances at δ 7.66 (d, 2 H), 7.63 (d, 2 H), 7.00 (t, 2 H), 6.83 (t, 2 H); Cp = 4.97 (s, 5 H); $P(OMe)_3$ = 3.21 (d, 9 H).

bered cobaltacyclic ring, and we will comment later on its electronic structure.[17] The facts of its existence and its ability to take part in catalytic substitution reactions give strong support to the dissociative model for reductively induced electron-transfer catalytic reactions of mononuclear complexes.

Acknowledgment. This research was supported by the National Science Foundation (CHE 86-03728).

Registry No. 1, 51614-82-5; **1**$^-$, 113353-94-9; **2**$^-$, 113353-92-7; **2**$^{2-}$, 113353-95-0; **3**, 113353-93-8; **3**$^-$, 113378-72-6.

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Diastereoselective Reactions of Chiral-at-Iron Carbene Complexes $C_5H_5(CO)(PR_3)Fe{=}CHR^+$. Synclinal Isomers Are More Reactive Than Anticlinal Isomers

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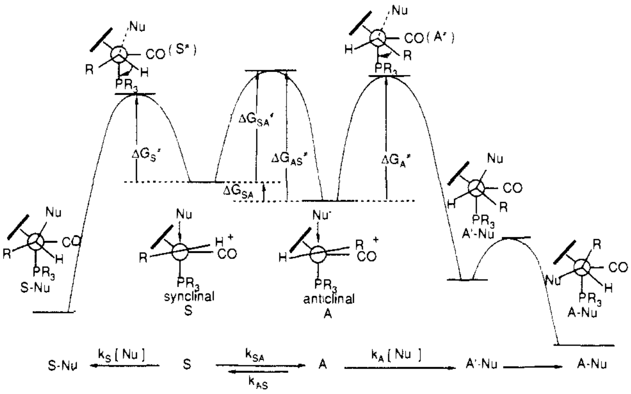
The $C_5H_5(NO)(PPh_3)Re$– and $C_5H_5(CO)(PPh_3)Fe$– groups have been used extensively as chiral auxiliaries to carry out diastereo- and enantioselective reactions.[1-4] Nucleophilic addition at C_α in carbene complexes of the type $C_5H_5(NO)(PPh_3)Re{=}CHR^+$ normally shows high diastereoselection since one face of the carbene ligand is shielded by PPh_3 and barriers to $Re{=}C_\alpha$ bond rotation are high; consequently, preparation and addition of nucleophiles to a single carbene isomer can be achieved.[1a-c,5]

We report here a study of addition of simple nucleophiles to chiral-at-iron carbene complexes of the type $Cp(CO)(PR_3)Fe{=}CHR^+$. These studies show that the factors controlling diastereoselectivity are surprisingly complex and involve not only anticlinal:synclinal isomer ratios but also the intrinsic differences in reactivity of these isomers, the nature and concentration of the nucleophile, and the ionic strength of the medium.

Iron–carbene complexes **1–5** were prepared by treatment of the α-ether complexes $Cp(CO)(L)FeCH(OCH_3)R$ with TMSOTf at −78 °C in CH_2Cl_2.[4] ^1H NMR analysis of CD_2Cl_2 solutions confirmed quantitative generation of **1–5**. For ethylidene systems **1–3**, the synclinal and anticlinal isomers (Scheme I) could be observed by low-temperature ^1H NMR (ca. −114 °C).[6,7] Equilibrium isomer ratios and $\Delta G^{\ddagger}$'s (from line shape analysis) for interconversions are listed in Scheme I. Benzylidene complexes exhibited a single set of resonances which showed no temperature dependence, and we assume a high anticlinal:synclinal ratio (>30) based on $Cp(NO)(PR_3)Re{=}CHC_6H_5^+$ as a model.[1b] The anticlinal:synclinal ratio has been independently established as >30:1 for **5**.[8]

Scheme I. Free Energy Diagram for the Reactions of $Cp(CO)PR_3Fe{=}CHR^+$ with Nucleophiles



	L	R	K_{eq} = A/S (°C)	$\Delta G_{AS}^{\ddagger}$ (kcal/mol)	$\Delta G_{SA}^{\ddagger}$ (kcal/mol)
1-S, 1-A	PMe_3	CH_3	4.6 (−104)	9.3	8.8
2-S, 2-A	PEt_3	CH_3	10.9 (−104)	9.6	8.8
3-S, 3-A	PPh_3	CH_3	4.6 (−104)	7.8	7.3
4-S, 4-A	PPh_3	Ph	est >30 (−125)	est <7	est <7
5-S, 5-A	PEt_3	Ph	est >30 (−125)	est <7	est <7

Reactions of carbene complexes **1–5** with nucleophiles were carried out by quenching into stirred methanol solutions. Large molar excesses (>6 equiv) of nucleophile were present so concentrations changed little during the quench. Two diastereomers were formed in each quench. Results of Gladysz,[1] Davies[2] and Liebeskind[3] clearly establish that the phosphine ligand shields one face of the carbene moiety.[9] Thus, one diastereomer (S–Nu) should arise from attack on the Si face of the synclinal isomer, while the other (A–Nu) presumably comes from attack on the Re face of the anticlinal isomer (Scheme I).

Diastereomer ratios from quenching **1–5** were determined by ^1H NMR analysis of crude products. Complexes **1-A-Nu**:**1-S-Nu**, **2-A-Nu**:**2-S-Nu**, and **3-A-Nu**:**3-S-Nu** were separated by chromatography and structures assigned by ^1H and ^{13}C NMR.[7] In each pair only one diastereomer exhibited a $^4J_{P-H}$ (1.3–1.7 Hz); it was assigned the A-Nu configuration based on the P-Fe-C_α-CH_3 "W" geometry and a previous analogous assignment.[10] X-ray structures of **1-S-**SC_6H_5 and **3-S-**$SCOCH_3$ confirm these assignments.[11] Equilibration of diastereomers of **4-OMe** occurs at 25 °C via PPh_3 dissociation; the equilibrium ratio is 70:1.[8] Isomer **4-A-OMe** is expected to be the more stable,[12,2d] and assignment is made on this basis. Assignments of **5-A-OMe** and **5-S-OMe** were based on NMR comparisons with **4-A-OMe** and

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[3] For examples from the Liebeskind lab, see: (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Liebeskind, L. S.; Fengl, R. W.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3075, 3079. (c) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (d) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

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[5] S. G. Davies has reported diastereoselective hydride additions to complexes of the type $Cp(CO)(PPh_3)Fe{=}C(OR)(R)^+$.

[6] Low-temperature ^1H NMR data of C_α-H: **1** (−114 °C, CD_2Cl_2), 15.92 ppm (synclinal), 17.46 ppm (anticlinal); **2** (−114 °C, CD_2Cl_2), 15.69 ppm (synclinal), 17.65 ppm (anticlinal); **3** (−126 °C, CD_2Cl_2/SO_2ClF), 17.05 ppm (synclinal), 18.24 ppm (anticlinal).

[7] See Supplementary Material for complete spectral and analytical data.

[8] A complete analysis of this diastereomer interconversion has been carried out (Buck, R. C. Ph.D. Dissertation, 1987, University of North Carolina) and will be published elsewhere.

[9] Most of systems studied in ref 1–4 are triphenylphosphine containing systems with the exception of reactions of $[(C_5H_5)Re(NO)(PMe_3)({=}CHC_6H_5)]^+PF_6^-$ reported by Gladysz.[1b] The 20:1 product ratio of **1-S-**$SCOCH_3$:**1-A-**$SCOCH_3$ in entry 2 of Table I shows that PMe_3 can effectively sterically shield one face of carbene moiety.

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