lower yields, and the corresponding boranes and borates have failed to provide the desired products in any significant amounts.[9] (5) Proper selection of solvents appears to be of crucial importance. Ethyl ether is satisfactory for the Ni-catalyzed reactions and some of the Pd-catalyzed reactions. In more polar solvents such as THF these reactions proceed appreciably faster. However, the relative amounts of undesired isomers and homocoupled products also increase, especially in the Ni-catalyzed reactions. (6) Although our study with functionalized alkenes is limited, the ester group can be tolerated as indicated in eq 4. (7) Finally, the product yield is low, when the alkyl substituent of alkenylalanes is sterically demanding (entry 7). However, the same product can be obtained in considerably higher yields by using the corresponding iodide (entry 5 or 6).

The following procedure for the preparation of methyl (*E*,*E*)-2-methyl-2,4-nonadienoate is representative. To 0.74 g (1 mmol) of dichlorobis(triphenylphosphine)palladium[10] suspended in 20 ml of THF were added sequentially 0.37 ml (2 mmol) of neat diisobutylaluminum hydride (25 °C, 10 min), (*E*)-1-hexenyldiisobutylalane, prepared in a separate flask from 1.64 g (2.28 ml, 20 mmol) of 1-hexyne dissolved in 20 ml of hexane and 2.84 g (3.68 ml, 20 mmol) of diisobutylaluminum hydride, and 3.58 g (20 mmol) of methyl (*E*)-3-bromo-2-methylpropenoate[11] (25 °C). The reaction mixture was refluxed for 15 min, treated with 3 N hydrochloric acid, and extracted with ethyl ether. After the organic layer was dried over $MgSO_4$, filtered, and concentrated at reduced pressure, distillation provided 2.2 g (61%) of methyl (*E*,*E*)-2-methyl-2,4-nonadienoate: bp 78–79 °C (1 mm); ^1H NMR (CCl_4, Me_4Si) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.90 (s, 3 H), 2.0–2.5 (m, 2 H), 3.67 (s, 3 H), 5.7–6.6 (m, 2 H), and 7.10 (d, J = 10 Hz, 1 H) ppm; ir (neat) 1715 (s), 1645 (s), 1620 (w), 1245 (s), 1105 (s), 975 (s), 750 (s) cm^{-1}.

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(6) All isolated products were adequately characterized by spectroscopic analyses. The *E*,*E*, *E*,*Z*, and *Z*,*E* isomers of 2,2-dimethyl-3,5-decadiene are distinguishable by GLC (SE-30) and NMR. In particular, the ^{13}C NMR spectra of these isomers show the following distinct olefinic carbon peaks: ^{13}C NMR ($CDCl_3$, Me_4Si) δ *E*,*E* isomer, 125.7, 131.4, 132.7, and 143.3 ppm; *E*,*Z* isomer, 120.8, 129.6, 130.2, and 145.4 ppm; *Z*,*E* isomer, 126.9, 127.4, 135.5, and 139.4 ppm. Their ^1H NMR spectra exhibit singlets for the *tert*-butyl protons at δ 1.02, 1.04, and 1.16 ppm, respectively. The *Z*,*E* isomer (**3**) was prepared by the procedure recently reported by us[1b] from *tert*-butylethyne and 1-hexyne. Our attempts to prepare **3** by the procedure reported here have not been fruitful due to the tendency of (*Z*)-iodo-3,3-dimethyl-1-butene to isomerize into the *E* isomer during its preparation.

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(10) Neither preformed tetrakis(triphenylphosphine)palladium nor the catalyst prepared in situ from palladium chloride, 2 equiv of triphenylphosphine, and 2 equiv of diisobutylaluminum hydride induces the desired alkenyl–alkenyl coupling.

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The Role of Distance in Electron Transfer in Solution. Experimental Verification of the Hush–Marcus Theory Using Mixed-Valence Complexes

Sir:

Hush and Marcus have shown that for an outer-sphere electron transfer reaction in solution (e.g., $Fe(H_2O)_6^{3+} + Ru(NH_3)_6^{2+} \rightarrow Fe(H_2O)_6^{2+} + Ru(NH_3)_6^{3+}$) the activation free energy $\Delta G_{12}{}^*$ is given by eq 1.[1-5]

$$\Delta G_{12}{}^* = w_r + \frac{\lambda}{4}\left(1 + \frac{\Delta G_R{}^{\circ\prime}}{\lambda}\right)^2 \tag{1}$$

In eq 1, w_r is the work needed to bring together the reactants, $\Delta G_R{}^{\circ\prime}$ is the free energy change on electron transfer within the ion-pair or association complex of the reactants,[6] and $\lambda/4$ is the reorganizational energy arising from rearrangements of the inner- and outer-coordination spheres (eq 2).

$$\lambda = \lambda_i + \lambda_o \tag{2}$$

If it is further assumed that λ is related to the reorganizational λ values for the individual self-exchange reactions ($Fe(H_2O)_6^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$) as in eq 3,[7]

$$\lambda = (\lambda_{11} + \lambda_{22})/2 \tag{3}$$

the relationship in eq 4 can be derived which has been tested extensively, generally with good success.[1-9]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{4}$$

However, correlations using eq 4 are limited in that they fail to give direct insight either into the partitionings of λ suggested in eq 2 and 3, or into other factors such as the effect of distance between reactants on the activation barrier for electron transfer.

In the mixed-valence ion $[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$ (bpy is 2,2′-bipyridine) there are discrete Ru(II) and Ru(III) sites and delocalization is slight.[9,10] For such ions, Hush has shown that the energy of the intervalence transfer (IT) band, E_{op} (eq 5; pyz is pyrazine),

$$[(bpy)_2ClRu^{II}(pyz)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow[E_{op}]{h\nu} [(bpy)_2ClRu^{III}(pyz)Ru^{II}Cl(bpy)_2]^{3+*} \tag{5}$$

is related to the activation energy for the related thermal process, E_{th} (eq 6),

$$[(bpy)_2ClRu^{II}(pyz)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow[E_{th}]{} [(bpy)_2ClRu^{III}(pyz)Ru^{II}Cl(bpy)_2]^{3+} \tag{6}$$

as in eq 7,[12]

$$E_{op} \sim 4E_{th} = \lambda = \lambda_i + \lambda_o \tag{7}$$

Using a dielectric continuum model, λ_o as given by eq 8 is predicted to hold both for outer-sphere reactions and for in-

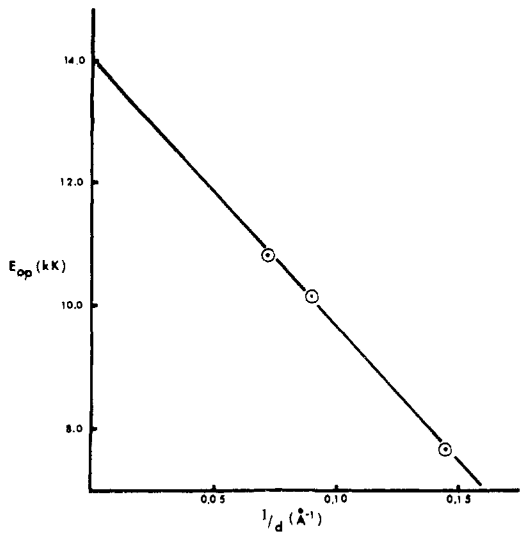

Figure 1. Plot of E_{op} (kK) vs. $1/d$ (Å^{-1}) in acetonitrile at 22 ± 2 °C.

Table I. Effect of Internuclear Separation (d) on λ_i, λ_o, E_{op}, and E_{th}

Bridging ligand (L)	d, Å	λ_i, kcal/mol	λ_o, kcal/mol[a]	E_{op}, kK[a]	E_{th}[a], kcal/mol
Pyrazine	6.9	16.1	5.9	7.69	5.5
4,4′-Bipyridine	11.1	17.2	11.8	10.15	7.2
trans-1,2-Bis(4-pyridyl)ethylene	13.2	15.5	15.4	10.81	7.7
($1/d$ = 0)	∞	16.3[b]	24.0[c]	14.1[c]	10.0

[a] In acetonitrile at 22 ± 2 °C. [b] Average value for the three bridging ligands. [c] Extrapolated values from the figure at $1/d$ = 0.

tramolecular electron transfer between weakly coupled redox sites.

$$\lambda_o = e^2\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d}\right)\left(\frac{1}{n^2} - \frac{1}{D_S}\right) \qquad (8)$$

In eq 8, e is the unit electron charge, $2r_1$ and $2r_2$ are the molecular diameters of the reactants, d is the internuclear separation, and n^2 and D_S are the optical and static dielectric constants of the solvent, respectively. For the mixed-valence ion $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ in several solvents, a plot of E_{op} vs. $(1/n^2 - 1/D_S)$ is linear as predicted.[13] λ_i can be obtained from the intercept of the plot and λ_o calculated for a given solvent using eq 7.[12,13]

We have prepared in solution the series of mixed-valence ions, $[(bpy)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+}$ where L is pyrazine, 4,4′-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene, and have obtained values of E_{op} for the ions in several solvents (acetonitrile, acetone, DMF, Me_2SO, propylene carbonate, nitrobenzene, and water). Solutions containing the mixed-valence ions were prepared by one-electron oxidation of the +2(Ru(II)-Ru(II)) ions or by mixing equal molar amounts of salts of the +2 and +4 (Ru(III)-Ru(III)) ions.[10,11,14]

For each of the three bpy ions, the predicted linear relationship between E_{op} and $1/n^2 - 1/D_S$ (eq 7 and 8) has been found. From the data, both E_{op} and λ_o increase as the internuclear separation increases. λ_i is essentially independent of d which is expected for a weakly coupled system where the electron donor and acceptor sites act as independent oscillators. As in earlier work with symmetrical[10,11,13] and unsymmetrical[15] mixed-valence ions, λ can be partitioned experimentally into λ_i and λ_o from the plots and eq 7. Values for the three ions are given in Table I.

Plots of E_{op} vs. $(1/n^2 - 1/D_S)$ have been made, and the data fitted using a linear least-squares calculation. For the calculations the correlation coefficients were between 0.92 and 0.99. The variations in E_{op} and λ_o with d are predicted by combining eq 7 and 8 to give eq 9. According to eq 9,

$$E_{op} = \left[\lambda_i + e^2\left(\frac{1}{2r_1} + \frac{1}{2r_2}\right)\left(\frac{1}{n^2} - \frac{1}{D_S}\right)\right] - \frac{e^2}{d}\left(\frac{1}{n^2} - \frac{1}{D_S}\right) \qquad (9)$$

E_{op} and λ_o should vary as $-1/d$. The distance dependence arises because at close proximity solvent molecules are shared between the two redox sites, which decreases the outer-sphere rearrangement energy.[1,4,12] The linear relationship predicted by eq 9 is found as shown by the plot in Figure 1. From the plot the values of the slope and intercept (at $1/d$ = 0) are −46.7 kK/Å and 14.0 kK while the theoretical values are −61.0 kK/Å and 16.4 kK.[16a] The limiting values for E_{op} and E_{th} at an infinite internuclear separation are 14.1 kK (709 nm) and 10.0 kcal/mol, respectively.

The IT data can be used to obtain information about the related outer-sphere self-exchange reaction (eq 10; py is pyridine).

$$[Ru(bpy)_2(py)Cl]^{2+} + [Ru(bpy)_2(py)Cl]^{+} \rightarrow [Ru(bpy)_2(py)Cl]^{+} + [Ru(bpy)_2(py)Cl]^{2+} \qquad (10)$$

Treating reaction 10 as involving initial ion-pair formation (with an associated ion-pairing constant Q), followed by electron transfer within the ion-pair (by analogy to reaction 6), gives eq 11

$$k = \nu_{et}Q\exp(-E_{th}/RT) \qquad (11)$$

where ν_{et} is the frequency factor for electron transfer.[16b] E_{th} can be obtained from the Figure at d = 11.4 Å,[16a] Q can be estimated to be ~0.4,[17] and assuming that $\nu_{et} = 10^{13}$ s^{-1} gives $k = 2 \times 10^7$ M^{-1} s^{-1} which is in good agreement with the experimental value of 4.9×10^7 M^{-1} s^{-1} at 25 °C in acetonitrile.[11]

For an outer-sphere self-exchange reaction, the variation of ΔG^* with the distance of separation between the reacting ions is given by eq 12

$$\Delta G^*(d) = \left[\frac{Z_1Z_2e^2}{D_S} - \frac{e^2}{4}\left(\frac{1}{n^2} - \frac{1}{D_S}\right)\right]\frac{1}{d} + \left[\frac{\lambda_i}{4} + \frac{e^2}{4}\left(\frac{1}{2r_1} + \frac{1}{2r_2}\right)\left(\frac{1}{n^2} - \frac{1}{D_S}\right)\right] - RT\ln\left(\frac{(2.52 \times 10^{-3})d^3\nu_{et}}{Z}\right) \qquad (12)^{16,17}$$

where in eq 1 $w_r = Z_1Z_2e^2/dD_S$ (Z_1 and Z_2 are the ionic charges) and $\Delta G_R{}^{\circ\prime} = 0$. Equation 12 can be evaluated numerically for reaction 10 using the slope and intercept in Figure 1 which gives eq 13.

$$\Delta G^*(d) = \frac{-16.2}{d} + 6.6\ \text{kcal/mol}\ (d \geq 11.4\ \text{Å}) \qquad (13)$$

Equation 13 is remarkable in that contrary to what has often been assumed,[20] $\Delta G^*(d)$ is predicted to *decrease* with d as the ions approach to the limiting position of close contact. This result supports the prediction of close contact between ions of like charge in outer-sphere electron transfer,[1,2,4] and is probably a general result for most reactions involving like-charged ions. Experimental studies are usually carried out under conditions of high ionic strength. Only the $Z_1Z_2e^2/D_S$ term in eq 12 is expected to be highly dependent on ionic strength[1,4] and this term decreases numerically with increasing ionic strength for like-charged ions.

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(17) Q was calculated from the expression, $Q = (2.52 \times 10^{-3})d^3 \exp[-(Z_1Z_2e^2/dD_SkT)]$[5,18] using $Z_1 = 1$, $Z_2 = 2$, and $d = 11.4$ Å.
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(20) Reference 5, chapter 4.
(21) On sabbatical leave at the University of Sydney.

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Stoichiometric Hydrogen Reduction of Carbon Monoxide to Methanol Promoted by Derivatives of Bis(pentamethylcyclopentadienyl)zirconium

Sir:

The lack of a homogeneous analogue of methanol synthesis, methanation, or Fischer-Trospch synthesis of hydrocarbons from CO and H_2 is a conspicuous difference between heterogeneous and homogeneous catalysis. Recently it has been suggested[1] that, since no well-established precedent exists either for the formation of a metal-formyl complex from a metal carbonyl hydride via migratory insertion[2] or for the conversion of a metal-formyl species to CH_3OH, metal clusters may be required to achieve the H_2 reduction of CO. Indeed, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were found to catalyze the dihydrogen reduction of carbon monoxide to methane at 140 °C and ~2 atm, although rates were rather low.

We recently observed reduction of CO in moderate yields when $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ is treated with HCl.[3] Further studies revealed that mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl)zirconium are capable of promoting the stoichiometric H_2 reduction of CO to methoxide under very mild conditions. Herein we report the results of those studies.

Treatment of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (**1**)[3-5] with carbon monoxide in toluene at 25 °C leads to the absorption of CO (3.95 mol/mol of **1**), the evolution of N_2 (2.84 mol/mol of **1**), and the purple-brown crystalline complex $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (**2**).[6] **2** reacts with H_2 (~1.5 atm) in toluene to yield $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (**3**) when photolyzed (366 nm) at room temperature or when heated to 110 °C. H_2 (2.10 mol/mol of **2**) is absorbed and CO (0.984 mol/mol of **2**) is evolved during the reaction.(equation 1).

$$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2 + 2H_2 \xrightarrow[\text{or } 110\ ^\circ\text{C}]{h\nu} (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + CO \quad (1)$$

3 is isolated nearly quantitatively as white crystals upon removal of toluene but may be further purified by sublimation at 130 °C (10^{-3} Torr). Analytical, molecular weight, infrared, and NMR data[7] for **3** are in accord with a monomeric pseudotetrahedral structure analogous to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. Hydrolysis of **3** with aqueous HCl leads to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and to H_2 (0.74 mol/mol of **3**), and CH_3OH[8] (0.78 mol/mol of **3**), slightly lower yields than those expected according to equation 2:

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + 2HCl \rightarrow (\eta^5\text{-}c_5Me_5)_2ZrCl_2 + H_2 + CH_3OH \quad (2)$$

Generation of the reactive, coordinatively unsaturated species $(\eta^5\text{-}C_5Me_5)_2Zr(CO)$ in the thermal or photolytic reaction of **2** with H_2 is supported by experiments with $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (**4**).[3] Treatment of **4** with H_2 (~1 atm) at room temperature leads predominantly[9] to **3** with the absorption of H_2 (3.53 mol/mol of **4**) and evolution of N_2 (1.00 mol/mol of **4**), eq 3.

$$\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2 + 4H_2 \rightarrow 2(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + N_2 \quad (3)$$

It occurred to us that a plausible step in the reaction sequence would involve oxidative addition of H_2 to $(\eta^5\text{-}C_5Me_5)_2Zr(CO)$ generating the intermediate $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$, and furthermore that this complex might be prepared by an alternate route. Treatment of **1** with H_2 in toluene at room temperature affords $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**5**) quantitatively according to eq 4.

$$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2 + 2H_2 \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 3N_2 \quad (4)$$

In contrast to polymeric $\{(\eta^5\text{-}C_5H_5)_2ZrH_2\}_x$,[10,11] **5** is very soluble in hydrocarbons and ethers. Analytical, molecular weight, infrared, and NMR data[12] are indicative of a monomeric structure completely analogous to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$.

5 absorbs CO (0.97 mol/mol of **5**) in toluene at −80 °C to generate the carbonyl hydride $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$ (**6**).[13] Although **6** is not sufficiently stable for its isolation (see below), it has been partially characterized in solution at low temperature. Thus **6** reacts with HCl at −80 °C to yield $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, H_2 (1.78 mol/mol of **6**), and CO (0.85 mol/mol of **6**), equation 5.

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO) + 2HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2H_2 + CO \quad (5)$$