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Measurement and Manipulation of the Unpaired Electron Density in 18+δ Complexes. Correlation of the Charge Density with Reactivity

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Abstract: An infrared spectroscopic method was devised for measuring δ in 18+δ organometallic complexes containing the chelating diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (L_2) or 2,3-bis(diphenylphosphino)-2-cyclopentene-1,4-dione (L_2'). (18+δ complexes are 19-electron complexes in which the unpaired 19th valence electron is primarily localized on a ligand; δ represents the amount of the unpaired electron's charge on the metal.) δ values for the $Co(CO)_3L_2$, $Co(CO)_3L_2'$, $Fe(CO)_3L_2^-$, and $Fe(CO)_3L_2'^-$ complexes fall in the range 0.01−0.25. The effects of the metal, the ligands, and the solvent on δ were quantitatively evaluated. In addition, the effect of δ on the reactivity was examined by studying the dissociative substitution reactions of $Co(CO)_3L_2$. The following principles emerged: (1) δ is larger for complexes with a more electronegative metal center (e.g., Co(I) vs Fe(0)). (2) δ is smaller for complexes containing the more electronegative L_2 ligand than for those with the less electronegative L_2'. (3) δ increases with decreasing solvent polarity, but increases with increasing solvent donicity. (4) For those cases in which δ is manipulated by changing the solvent, there is no simple correlation between δ and the rate of a dissociative substitution reaction in an 18+δ complex. The latter two results are interpreted in terms of a model in which donor solvents increase the electronic population of the π* SOMO on the L_2 ligand and acceptor solvents decrease the electron density in this orbital. Additional electron density in the π* orbital increases delocalization of the unpaired electron onto the Co fragment, causing δ to increase and weakening the Co−CO bond. (The acceptor orbital on the Co fragment is Co−CO σ antibonding.) There is no correlation between the rate constants and δ because $\Delta S^{\ddagger}$ effects are significant, especially in polar solvents.

Nineteen-electron organometallic adducts, formed via the reactions of 17-electron radicals with 2-electron donors (eq 1), are important intermediates in many reactions.[1,2]

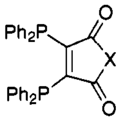
$$\underset{17\text{-}e^-}{L_nM{-}ML_n \xrightarrow{h\nu} 2L_nM} \xrightarrow{2L'} \underset{\text{“}19\text{-}e^-\text{”}}{2L_nML'} \qquad (1)$$

$$L_nM = CpFe(CO)_2,\ CpMo(CO)_3,\ Mn(CO)_5,\ Co(CO)_4,\ MeCpW(CO)_3$$

$$L' = NR_3,\ PR_3,\ \text{etc.}$$

Despite their importance, the short lifetimes of 19-electron complexes have precluded a thorough study of their reactivity and electronic structures.[2] One strategy for stabilizing the 19-electron complexes, so as to make them more amenable for study, is to introduce a ligand with a low-energy π* orbital into the complex.[3,4] With an appropriate ligand, the unpaired electron preferentially occupies the ligand π* orbital rather than a higher energy metal-centered orbital, and the complex is stabilized accordingly. Nineteen-electron complexes of this type have been dubbed "18+δ" complexes because they can be described as 18-electron complexes with partial electron density contributed to the metal by delocalization of the unpaired electron from the reduced ligand.[4−8] (In this nomenclature, δ represents the amount of the unpaired electron's charge on the metal.)

In order to learn more about the 18+δ complexes and their relationship to "genuine" 19-electron complexes, we are studying the chemistry of 18+δ complexes containing the L_2 and L_2' ligands.[7]



L_2, X = O
L_2', X = CH_2

Our investigation is focused on three questions: (1) Is it possible to manipulate the amount of 19-electron character in an 18+δ complex, i.e., is it possible to manipulate the value of δ? (2)

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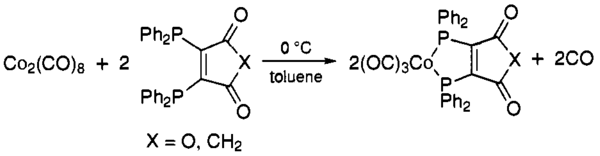
Is it possible to determine experimentally the value of δ? (3) Is there a correlation between the reactivity and the value of δ in an 18+δ complex? In a previous paper,[5] the first of these questions was answered. We showed that the amount of 19-electron character (δ) could be manipulated by changing the solvent. In another paper,[6] we addressed the second question: we determined δ for a particular case, $Co(CO)_3L_2$ in frozen toluene, from the anisotropic cobalt hyperfine coupling. This method, however, is restricted to low temperatures, glass-forming solvents, and the luck of good resolution of ^{59}Co hyperfine structure in the ESR spectrum.

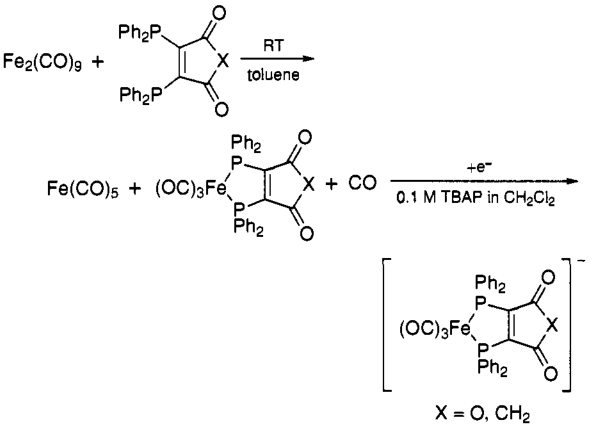
In this paper, we again address the second question and also take a look at the last question: a new method for measuring δ is reported, and δ is correlated with the rates of ligand substitution reactions. Finally, methods for manipulating δ, other than changing the solvent, are also reported and discussed.

Results and Discussion

Synthesis and Generation of the 18+δ Complexes. The 18+δ complexes used in this study were $Co(CO)_3L_2$,[7] $Co(CO)_3L_2'$,[7] $[Fe(CO)_3L_2^-]$, and $[Fe(CO)_3L_2'^-]$. The Co complexes were synthesized by the general route in eq 2,[7] and the Fe complexes were generated in situ in an infrared spectroelectrochemical cell (−1.0 V) from the $Fe(CO)_3L_2$[7] and $Fe(CO)_3L_2'$ complexes (eq 3).



(2)



(3)

Measurement of δ. When the chelating phosphine L_2 or L_2' is used to form an 18+δ complex, there is a decrease in the ligand C=O stretching frequencies compared to the free ligand. As shown in a prior paper,[5] the shift to lower frequencies is caused by electronic population (by the 19th valence electron) of an orbital on the chelating ligands that is C−O π antibonding. It was also established[5] that the unpaired electron is delocalized onto the metal fragment and that ν(C=O) increases with increasing delocalization. The relationship between the extent of delocalization and ν(C=O) can be rationalized as follows: If, in comparing 18- with 19-electron complexes, the additional charge of the 19-electron complex is completely centered on L_2, the C=O stretching frequencies should be those of L_2^-. Conversely, if none of the extra charge is found on L_2, the C=O stretching frequencies should be equal to those of L_2. In practice, the C=O stretching frequencies of 18+δ complexes containing L_2-type ligands occur between the L_2 and L_2^- limits, reflecting a charge on L_2 between 0 and −1.

To calculate the charge on L_2, we made use of the results of previous studies which showed a linear relationship between C=O force constants and the charge on a ligand or molecule.[9-11] That is, the force constant k is given by

$$k = k_0 + k'q \tag{4}$$

where k_0 is the force constant when the charge $q = 0$, and $k_0 + k'$ is the force constant when $q = 1$. The frequency is proportional to the square root of the force constant; thus,

$$\bar{\nu} = \sqrt{a + bq} \tag{5}$$

where a and b are constants related to k_0 and k'. Squaring each side of eq 5 and subtracting the results for two different molecules yields

$$\bar{\nu}_2^{\,2} - \bar{\nu}_1^{\,2} = b\Delta q \tag{6}$$

In this equation, $\bar{\nu}_2$ and $\bar{\nu}_1$ are the C=O stretching frequencies of the 18+δ and 18-electron complexes, respectively, and Δq is the difference in charge on the L_2 ligand between the 18-electron and the 18+δ complexes.[12] The constant b was determined by substituting the C=O frequencies for the L_2 and $[L_2^-]$ species into eq 6 and setting $\Delta q = -1$. (Likewise, the L_2' and $[L_2'^-]$ frequencies were used to determine b for the L_2'-containing complexes.) The b values for the $L_2/[L_2^-]$ and the $L_2'/[L_2'^-]$ couples are given in Table 1. With b determined, values for Δq, and thus δ,[12] were determined by substituting the appropriate frequencies into eq 6.[13,14]

Table 2 shows the ligand C=O stretching frequencies for the

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(11) The linear relationship denoted in eq 4 was first developed empirically by chemists interested in the spectra of metal carbonyl complexes.[9a,10] Later, physical chemists gave theoretical justification for the linear relationship; see: Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442−2443.

(12) The value of δ is equal to $1 + \Delta q$. If $\Delta q = -1$, the electron is completely centered on the ligand ($\delta = 0$). Likewise, if $\Delta q = 0$, the electron is completely metal centered ($\delta = 1$).

Table 1. Calculated b Values Using C═O Stretching Frequencies Obtained from IR Data (Table 2) and Eq 6

couple	b, cm^2	solvent (0.1 M TBAP)
$L_2/[L_2^-]^a$	$(4.32 \pm 0.10) \times 10^5$	THF
	$(4.40 \pm 0.10) \times 10^5$	MeCN
	$(4.42 \pm 0.10) \times 10^5$	acetone
	$(4.53 \pm 0.10) \times 10^5$	CH_2Cl_2
	$(4.66 \pm 0.10) \times 10^5$	2-MeTHF^b
$L_2'/[L_2'^-]^a$	$(5.10 \pm 0.10) \times 10^5$	CH_2Cl_2

[a] Counterion is $[NBu_4^+]$. [b] Saturated in TBAP (<0.1 M).

Table 2. C═O Stretching Frequencies Used for Calculating δ

complex	ν(C═O), cm^{-1}	ν(C═O)$_{rms}$, cm^{-1}	solvent^a
L_2	1835, 1765	1800	THF
$[L_2^-]^b$	1716, 1635	1676	THF
$Co(CO)_3L_2$	1746, 1679	1713	THF
$[Co(CO)_3L_2^+]^c$	1846, 1778	1812	THF
L_2	1838, 1764	1801	CH_2Cl_2
$[L_2^-]^b$	1713, 1628	1671	CH_2Cl_2
$Fe(CO)_3L_2$	1844, 1778	1811	CH_2Cl_2
$[Fe(CO)_3L_2^-]^b$	1723, 1643	1683	CH_2Cl_2
$Co(CO)_3L_2$	1730, 1655	1693	CH_2Cl_2
$[Co(CO)_3L_2^+]^c$	1847, 1783	1815	CH_2Cl_2
L_2	1839, 1764	1802	CH_3CN
$[L_2^-]^b$	1715, 1635	1675	CH_3CN
$Co(CO)_3L_2$	1740, 1671	1706	CH_3CN
$[Co(CO)_3L_2^+]^c$	1847, 1781	1814	CH_3CN
$L_2'^{\,b}$	1742, 1702	1722	CH_2Cl_2
$[L_2'^-]^b$	1572, 1562	1567	CH_2Cl_2
$Co(CO)_3L_2'$	d 1585	1585	CH_2Cl_2
$Fe(CO)_3L_2'$	1747, 1716	1732	CH_2Cl_2
$[Fe(CO)_3L_2'^-]^b$	1620, 1562	1591	CH_2Cl_2
L_2	1844, 1767	1806	2-MeTHF^e
$[L_2^-]$	1711, 1632	1672	2-MeTHF^e
$Co(CO)_3L_2$	1746, 1680	1713	2-MeTHF^e
$[Co(CO)_3L_2^+]$	1845, 1779	1812	2-MeTHF^e
L_2		1802^f	acetone
$[L_2^-]$	1715, 1634	1675	acetone
$Co(CO)_3L_2$	1711, 1691	1701	acetone
$[Co(CO)_3L_2^+]$		1814^f	acetone

[a] All solutions except 2-MeTHF contained 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). [b] Counterion is $[NBu_4^+]$. [c] Counterion is $[ClO_4^-]$. [d] The symmetric C═O stretch was not observed. [e] Saturated in TBAP (<0.1 M). [f] Estimated value because of overlapping solvent bands.

Table 3. Calculated Values of Δq $(1 - \Delta q = \delta)$ Using C═O Stretches from IR Data (Table 2) and b Values from $L_2/[L_2^-](L_2'/[L_2'^-])$ Couples (Table 1)

couple	Δq^a	$\delta(\pm 0.03)$	solvent (0.1 M TBAP)
$Co(CO)_3L_2/[Co(CO)_3L_2^+]^b$	0.75	0.25	2-MeTHF^c
	0.81	0.19	THF
	0.87	0.13	CH_3CN
	0.90	0.10	acetone
	0.95	0.05	CH_2Cl_2
$[Fe(CO)_3L_2^-]^d/Fe(CO)_3L_2$	0.99	0.01	CH_2Cl_2
$[Fe(CO)_3L_2'^-]^d/Fe(CO)_3L_2'$	0.91	0.09	CH_2Cl_2

[a] Error is ±0.03, see text. [b] Counterion is $[ClO_4^-]$. [c] Saturated in TBAP (<0.1 M). [d] Counterion is $[NBu_4^+]$.

18+δ complexes in solvents of varying polarity. Values of δ, calculated by substituting these frequencies into eq 6, are listed in Table 3.[12] The frequencies in Table 2 are liberally estimated as accurate to ±3 cm^{-1}. Using these error limits, error propagation suggests uncertainties in Δq and δ of ±0.03. As discussed in the following sections, the δ values in Table 3 are dependent on the solvent, the metal, and the ligands.

Solvent Effect on δ. In a previous paper,[5] the results of IR, EPR, and electronic absorption spectroscopy were interpreted to indicate qualitatively that a decrease in the solvent polarity led to an increase in δ.[15] The quantitative results in Table 3 do not concur with this prior conclusion. Thus, the δ values for $Co(CO)_3L_2$ are 0.05 in CH_2Cl_2, 0.10 in acetone, 0.13 in CH_3CN, 0.19 in THF, and 0.25 in 2-MeTHF (all with 0.1 M TBAP in solution except 2-MeTHF, which is saturated in TBAP at <0.1 M) yet the solvent polarities (as indicated by the Reichardt E_T^N parameter[17]) are in the order 2-MeTHF < THF ≈ CH_2Cl ≈ acetone < CH_3CN (Table 4). Clearly, the value of δ is controlled by factors other than just the solvent polarity. Further insight into these additional factors comes from the reactivity studies, so a discussion is postponed until after the discussion of the solvent effects on reactivity.

Ligand Effects on δ. The calculated charge difference between $Fe(CO)_3L_2'$ and $[Fe(CO)_3L_2'^-]$ ($\Delta q = 0.91$, $\delta = 0.09$) is smaller than that between $Fe(CO)_3L_2$ and $[Fe(CO)_3L_2^-]$ ($\Delta q = 0.99$, $\delta = 0.01$). (Note that the difference in these δ values is outside experimental error.) The larger δ value in $[Fe(CO)_3L_2'^-]$ compared to $[Fe(CO)_3L_2^-]$ reflects the smaller electronegativity of the L_2' ligand and the consequent greater delocalization of the unpaired electron.[18,19] Table 5 shows the $E_{1/2}$ values for L_2 and L_2'. The more positive $E_{1/2}$ value for the L_2 ligand reflects its greater tendency to accept an additional electron compared to the L_2' ligand.

Metal Effects on δ. The results in Table 3 show that δ is larger for the $Co(CO)_3L_2$ complex than for the isoelectronic

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(13) The infrared spectra of L_2, L_2^-, and most of their complexes exhibit bands corresponding to the symmetric and antisymmetric C═O stretches. In order to eliminate the influence of the interaction constant, we used root-mean-square frequencies in our analysis. Note that the solvents used in the δ measurements must have an appropriate electrochemical window and must dissolve the TBAP electrolyte and the 18+δ complexes.

(14) The ν(C═O) ligand frequencies were used rather than the ν(C≡O) metal fragment frequencies because the latter are particularly sensitive to differential solvation effects. For example, the ν(C≡O) frequencies of $Co(CO)_3L_2^+$ in CH_2Cl_2 are actually lower in energy than those of $Co(CO)_3L_2$. Normally, of course, the frequencies of the oxidized molecule would be higher in energy. This anomaly is attributable to differential solvation effects.[4]

(15) In brief, it was established that in polar solvents it is energetically favorable for the electron to remain localized on the L_2 ligand because localization gives the largest molecular dipole and hence the largest dipolar interactions with the solvent. In less polar solvents, however, dipolar interactions with the solvent are energetically less important,[16] and a lower energy state is obtained by delocalizing the electron onto the $Co(CO)_3$ moiety from the $L_2(\pi^*)$ orbital. The ligand ν(C═O) bands increase in frequency with increasing delocalization because the lowest energy π^* orbital on L_2 is C═O antibonding and it is being depopulated. The CO bands decrease in frequency with increasing delocalization onto the $Co(CO)_3$ moiety due to increased π-back-bonding. EPR spectra were also consistent with increased delocalization of the unpaired electron in nonpolar solvents. The a_{Co} and a_P coupling constants, determined in various solvents, increased as the solvent polarity decreased. The larger coupling constants reflect a larger unpaired spin density on the cobalt in nonpolar solvents. Electronic spectra, also measured in solvents of differing polarity, gave a similar result. The λ_{max} of the $\pi^* \rightarrow$ Co LMCT band is solvent dependent, shifting to lower energy in nonpolar solvents. This trend is expected when the ground state dipole is larger than the excited state. Solvent interaction with the larger ground state dipole leads to ground state stabilization. Polar solvents interact favorably with the larger dipole, increasing the stability of the ground state complex and causing the LMCT to occur at higher energy. Nonpolar solvents do not interact favorably with the large dipole. The complex is not as stable; therefore, the LMCT transition occurs at lower energy, demonstrating the inverse solvatochromic effect.

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(17) The value E_T^N is a measurement of solvent polarity. The larger the number, the more polar the solvent. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Publishers: New York, 1988; p 364.

(18) The L_2' ligand is less electronegative than L_2 because the ring O atom in L_2 is replaced by a CH_2 group. A manuscript detailing the effect of ligand reduction potential on the stability of 18+δ complexes is in preparation.

(19) The cobalt adducts of these ligands could not be compared because only one L_2' C═O band was observed in the IR spectrum of the $Co(CO)_3L_2'$ complex.

Table 4. Rate Constants for Substitution of $Co(CO)_3L_2$

solvent/solvent system	E_T^N	D.N.	k_{rate}, s^{-1}	temp, °C	$[PPh_3]$, M	$[Co(CO)_3L_2]$, M
a. toluene	0.117	0.1	$(3.8 \pm 0.3) \times 10^{-2}$	19.2	1.0×10^{-1}	1.74×10^{-3}
b. benzene	0.120	0.1	$(3.14 \pm 0.04) \times 10^{-2}$	19.1	9.8×10^{-2}	1.94×10^{-3}
c. furan	0.164[a]	6	*b*			
d. 1,3-dibromobenzene	0.179		$(3.41 \pm 0.04) \times 10^{-3}$	19.1	*c*	*c*
e. chlorobenzene	0.197	3.3	$(6.3 \pm 0.2) \times 10^{-3}$	19.0	1.1×10^{-1}	2.11×10^{-3}
f. 2-MeTHF	0.202	18	$(5.5 \pm 0.5) \times 10^{-2}$	19.3	9.3×10^{-2}	2.44×10^{-3}
g. anisole	0.209	9	$(7.4 \pm 0.4) \times 10^{-3}$	19.1	9.6×10^{-2}	1.76×10^{-3}
h. 1,3-dichlorobenzene	0.210	2	$(5.47 \pm 0.04) \times 10^{-3}$	19.1	1.3×10^{-1}	1.51×10^{-2}
i. THF	0.210	20.0	$(8.0 \pm 0.4) \times 10^{-2}$	19.2	1.0×10^{-1}	2.53×10^{-3}
j. EtOAc	0.228	17.1	*b*			
k. 3-pentanone	0.265[a]	15	$(3.8 \pm 0.4) \times 10^{-2}$	19.1	*c*	*c*
l. $C_6H_6/[NBu_4^+][BPh_4^-]$[d]	0.289		$(2.3 \pm 0.2) \times 10^{-2}$	19.3	9.7×10^{-2}	2.44×10^{-3}
m. 2-MeTHF/TBAP[e]	0.302		$(3.57 \pm 0.03) \times 10^{-2}$	18.7	9.0×10^{-2}	2.00×10^{-3}
n. 2-pentanone	0.321[a]	~16	$(2.2 \pm 0.2) \times 10^{-2}$	19.3	9.3×10^{-2}	1.58×10^{-3}
o. CH_2Cl_2	0.324	1	$(1.94 \pm 0.03) \times 10^{-3}$	19.1	1.1×10^{-1}	1.86×10^{-3}
p. acetone	0.352	17.0	$(2.57 \pm 0.08) \times 10^{-2}$	19.2	1.0×10^{-1}	1.93×10^{-3}
q. THF/0.1 M TBAP	0.357		$(5.1 \pm 0.4) \times 10^{-2}$	19.0	1.0×10^{-1}	2.02×10^{-3}
r. acetone/0.1 M TBAP	0.358		$(1.9 \pm 0.2) \times 10^{-2}$	19.0	1.0×10^{-1}	2.16×10^{-3}
s. CH_2Cl_2/0.1 M TBAP	0.358		$(1.5 \pm 0.1) \times 10^{-3}$	18.9	1.0×10^{-1}	2.07×10^{-3}
t. CH_3CN	0.473	14.1	$(3.3 \pm 0.2) \times 10^{-3}$	18.9	9.8×10^{-2}	1.42×10^{-3}
u. CH_3CN/0.1 M TBAP	0.483		$(4.0 \pm 0.2) \times 10^{-3}$	20.4	9.2×10^{-2}	2.04×10^{-3}

[a] Value taken from ref 16. [b] Reaction takes place with solvent. [c] Values were not determined, but at least enough for ~50-fold excess of PPh_3 to $Co(CO)_3L_2$. [d] Saturated in $[NBu_4^+][BPh_4^-]$. [e] Saturated in TBAP.

Table 5. $E_{1/2}$ Values[a]

reaction	$E_{1/2}^{ox}$,[b]	$E_{1/2}^{red}$,[b]
$L_2 \rightarrow [L_2^-]$[c]		−0.69
$L_2' \rightarrow [L_2'^-]$[c]		−0.99
$Co(CO)_3L_2 \rightarrow [Co(CO)_3L_2^+]$[d]	0.07	
$Co(CO)_3L_2' \rightarrow [Co(CO)_3L_2'^+]$[d]	−0.07	
$Fe(CO)_3L_2 \rightarrow Fe(CO)_3L_2^-$		−0.26
$Fe(CO)_3L_2' \rightarrow Fe(CO)_3L_2'^-$		−0.71

[a] 0.1 M TBAP in CH_2Cl_2. [b] vs SCE. [c] Counterion is $[NBu_4^+]$. [d] Counterion is $[ClO_4^-]$.

$[Fe(CO)_3L_2^-]$ species (0.05 vs 0.01). Although these numbers may be equal within experimental error, the larger value for the cobalt adduct is consistent with the larger electronegativity of Co(I) compared with Fe(0).[20]

Comparison to Other Methods for Measuring δ. Three other methods can be (or have been) used to calculate δ in $18+\delta$ complexes. (1) In a previous paper, EPR spectroscopy gave a value of $\delta \approx 0.016$ for the $Co(CO)_3L_2$ complex in frozen toluene.[6] The value obtained by EPR is not directly comparable to that obtained by IR because EPR gives a measurement of the metal 3d spin density, whereas the IR method reported herein yields a charge density. However, the results of the two methods should be reasonably close, as indeed they are. (2) An SCF−Xα−SW calculation on the $Co(CO)_3L_2$ complex found $\delta = 0.02$.[5] The Xα method is good for calculating electronic charges and its results should be comparable to those obtained by IR spectroscopy (0.05 in CH_2Cl_2). (3) A third method of estimating δ has not previously been applied to $18+\delta$ complexes. This method, introduced by Vlcek,[8a,21] uses the reduction potentials of two related metal complexes, ML_1 and ML_2, and the corresponding reduction potentials of the ligands L_1 and L_2 to estimate the average ligand character in the LUMO of the complexes:

$$1 - \bar{\delta} = \frac{E°(ML_1) - E°(ML_2)}{E°(L_1) - E°(L_2)} \tag{7}$$

Using the $E_{1/2}$ values in Table 5, eq 7 leads to $\bar{\delta} = 0.47$ for the average metal character in $Co(CO)_3L_2$ and $Co(CO)_3L_2'$ and to $\bar{\delta} = 1.5$ for the $Fe(CO)_3L_2^-/Fe(CO)_3L_2'^-$ species. The former value is so far out of line with other methods applied in this work (and the latter value is impossible) that we have reexamined the approximations inherent in the derivation of eq 7. It is assumed that reduction potentials of the ligands and complexes are proportional to the LUMO energies so that the ratio of potential differences is equivalent to a ratio of LUMO energy differences,

$$\frac{E°(ML_1) - E°(ML_2)}{E°(L_1) - E°(L_2)} = \frac{\epsilon_{ML_1} - \epsilon_{ML_2}}{\epsilon_{L_1} - \epsilon_{L_2}}$$

For the complexes, the LUMO is written as a linear combination of metal and ligand orbitals,

$$\Psi_{LUMO} = c_M\phi_M + c_L\phi_L$$

Thus, in the Hückel approximation, the LUMO energies are

$$\epsilon_L = H_{LL}$$

$$\epsilon_{ML} = c_M{}^2H_{MM} + c_L{}^2H_{LL} + 2c_Mc_LH_{ML}$$

where $H_{ij} = (\phi_i|H|\phi_j)$. The ratio of energy differences is

$$\frac{\Delta\epsilon_{ML}}{\Delta\epsilon_L} = (c_{M_1}{}^2 - c_{M_2}{}^2)H_{MM} + c_{L_1}{}^2H_{LL}^{(1)} - c_{L_2}{}^2H_{LL}^{(2)} + 2c_{M_1}c_{L_1}H_{ML}^{(1)} - 2c_{M_2}c_{L_2}H_{ML}^{(2)}\Big/H_{LL}^{(1)} - H_{LL}^{(2)}$$

Vlcek assumed that $c_{L_1} = c_{L_2}$, $c_{M_1} = c_{M_2}$, and $H_{ML}^{(1)} = H_{ML}^{(2)}$, in other words that the charge distributions in the two complexes are identical, but that the ligand orbital energies, $H_{LL}^{(i)}$ are significantly different. This seems an unlikely situation since $H_{LL}^{(1)} \neq H_{LL}^{(2)}$ usually implies ligands of different donor or acceptor abilities and thus different ligand character in the LUMO of a complex. Retaining only the assumption that $H_{ML}^{(1)} \cong H_{ML}^{(2)}$, the above expression can be rearranged to

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(20) Because the unpaired electron density resides primarily on the L_2 ligand, the complexes may thus be written as $Co^I(CO)_3(L_2^-)$ and $Fe(CO)_3(L_2^-)$, representing the fact that these complexes are essentially 18-electron complexes with a reduced ligand.

(21) Vlcek, A. A. *Z. Anorg. Allg. Chem.* **1960**, *304*, 109.

$$\frac{\Delta\epsilon_{\mathrm{ML}}}{\Delta\epsilon_{\mathrm{L}}} = \frac{c_{\mathrm{L}_1}{}^2 - c_{\mathrm{L}_2}{}^2}{2} + \left(\frac{c_{\mathrm{L}_1}{}^2 - c_{\mathrm{L}_2}{}^2}{2}\right)\left(\frac{H_{\mathrm{LL}}^{(1)} - H_{\mathrm{LL}}^{(2)} - 2H_{\mathrm{MM}}}{H_{\mathrm{LL}}^{(1)} - H_{\mathrm{LL}}^{(2)}}\right) + \frac{2H_{\mathrm{ML}}(c_{\mathrm{M}_1}c_{\mathrm{L}_1} - c_{\mathrm{M}_2}c_{\mathrm{L}_2})}{H_{\mathrm{LL}}^{(1)} - H_{\mathrm{LL}}^{(2)}}$$

Equation 7 retains only the first term. In order to neglect the second term, either the ligand character must be identical in the two complexes or the average ligand orbital energy must be identical to the metal orbital energy; the energy difference in the denominator might be small for similar ligands, so that even a small numerator could result in a large term. The numerator of the third term will be large unless the ligand:metal ratios are very similar in the two complexes. We conclude that there are very few cases where the Vlcek equation can be used without leading to serious errors.

Summary of the δ Measurements. In summary of the preceding sections, the second question posed in the Introduction has been answered: the value of δ can be measured in complexes containing L_2-type ligands. Specifically, the results show that ca. 75−100% of the unpaired charge is found in the π^* orbitals of L_2 or L_2' in formal 19-electron complexes containing these ligands. Thus, it is a good approximation to regard a complex such as $Co(CO)_3L_2$ as a radical anion ligand complex of Co(I). (In related work that comes to the same conclusion, we found $\delta = 0.03$ for the $CpFe(CO)L_2'$ complex in CH_2Cl_2/0.1 M TBAP.) The accuracy of the method is such that this conclusion can be stated with confidence. With less confidence, it is possible to look at finer details such as the effect of the solvent, the ligand, and the metal on δ. For the molecules studied here, the effect of the metal and ligands on δ are in accord with what one would intuitively expect, i.e., more electronegative metals yield larger δ values, and likewise, more electronegative ligands (containing the unpaired electron) yield smaller δ values. With regard to the solvent effect, the quantitative evaluation of δ shows that the solvent polarity is not the sole factor controlling the extent of the unpaired electron delocalization. These additional factors play a key role in controlling the reactivity of the 18+δ complexes, and thus they are discussed in the following sections. Finally, it is noteworthy that the infrared method described above for measuring δ is general; with appropriate attention to error limits, the method can be extended to other 18+δ complexes with suitable infrared-absorbing chromophores. The drawback to the method is that the δ values must be obtained in solvent systems containing significant concentrations of an electrolyte. (An electrolyte is necessary for the electrochemical generation of the reduced ligand, which is used as the $\delta = 0$ end point in the calculation.)

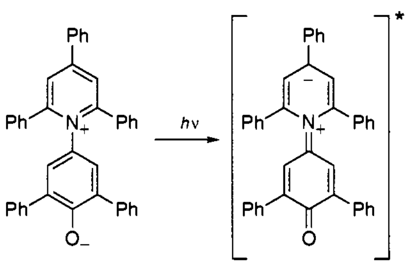
The Effect of δ on Reactivity. At this point, it remains to answer the third question posed in the Introduction. (Is there a correlation between δ and reactivity?) The typical reactivity of 18+δ complexes consists of electron transfer, ligand substitution, and catalysis reactions.[2,3] Of these reactivity types, the focus of this paper is the substitution reactivity.

The rate constants for the substitution of CO by PPh_3 in the $Co(CO)_3L_2$ complex in 2-MeTHF (saturated in TBAP), THF (0.1 M TBAP), CH_3CN (0.1 M TBAP), acetone (0.1 M TBAP), and CH_2Cl_2 (0.1 M TBAP) are given in Table 4. All of the rate constants were independent of the concentration of PPh_3, consistent with our previous studies[4,5] in benzene and CH_2Cl_2 which showed that the complex substitutes by a limiting dissociative mechanism in these two solvents (eq 8).[22] The activation parameters (Table 6) are also consistent with a

$$Co(CO)_3L_2 \xrightarrow{-CO,\ slow} Co(CO)_2L_2 \xrightarrow[fast]{+L'} Co(CO)_2(L')L_2 \quad (8)$$

dissociative mechanism. The results in Tables 3 and 4 show there is not a correlation between the substitution rate constants and δ: $\delta(CH_2Cl_2/TBAP) < \delta(acetone/TBAP) < \delta(CH_3CN/TBAP) < \delta(THF/TBAP) < \delta(2\text{-}MeTHF/TBAP)$; but $k(CH_2Cl_2/TBAP) < k(CH_3CN/TBAP) < k(acetone/TBAP) < k(THF/TBAP) > k(2\text{-}MeTHF/TBAP)$. In order to analyze the relationship between δ and the rate constant in more detail, we examined the substitution rates (eq 8) in 16 other solvents. The results of these kinetics measurements are also reported in Table 4. Before discussing these results, however, it is necessary to digress and examine the Reichardt E_T^N solvent polarity scale in more detail.

The Reichardt E_T^N Scale. As first explained by Reichardt[17] and reiterated by Marcus,[23] the E_T^N polarity scale is also a solvent acceptor scale. The reason is as follows: the E_T^N scale was determined by measuring the energies of the $\pi \rightarrow \pi^*$ transition of Reichardt's dye (eq 9) in various solvents. (The energies are normalized to give the E_T^N scale.[17]) Because of the charge separation in the dye's ground state, polar solvents experience an energetically favorable interaction with the ground state of the dye. All else being equal, this interaction increases the energy of the $\pi \rightarrow \pi^*$ transition. Reichardt and Marcus argue that this energy is a measure of the accepting ability of the solvents because the lone pairs of electrons on oxygen are exposed and the dye acts as a weak Lewis base. They further note that the nitrogen atom in the dye has its charge delocalized over an aromatic system, eliminating the possibility of it acting as a Lewis acid. Thus, the only interaction measured is the stabilization of the phenolate ion with the solvent, which is really just a measure of the electron accepting ability of the solvent. The fact that the E_T^N scale is an acceptor scale provides a critical insight into how the solvent controls the rate of substitution.[24]



(9)

How Solvent Affects the Rate Constant for Substitution. Figure 1 is a plot of the rate constants for the substitution reaction in eq 8 as a function of solvent polarity (as indicated by the E_T^N parameter). As shown in the figure, coordinating and noncoordinating solvents lie on different curves, but within each category, the rate constants decrease with solvent polarity. The existence of two curves clearly shows that solvent polarity is not the only parameter to determine the rate constant. (Recall

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[22] The reaction is irreversible in the presence of a large excess of ligand.

[23] Marcus, Y. *J. Solution Chem.* **1984**, *13*, 599−624.

[24] In the analysis that follows, the Reichardt E_T^N scale was used as a measure of solvent acceptor ability. The Gutmann acceptor number scale[25] gave similar results. We used the E_T^N scale because for several of the solvent/electrolyte solvent systems the values for E_T^N have not been reported in the literature. E_T^N values are easily measured by electronic spectroscopy, whereas the Gutmann numbers are experimentally more complicated to obtain.

[25] Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

Table 6. Activation Parameters for Substitution of $Co(CO)_3L_2$ by PPh_3 in Various Solvents

solvent system	δ	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(K mol)	ref
CH_2Cl_2		23.2 ± 0.8	8 ± 3	this work
CH_2Cl_2		23.8 ± 0.6	11 ± 2	5
CH_2Cl_2/TBAP	0.05	22.6 ± 0.9	6 ± 3	this work
C_6H_6		19.6 ± 0.6	2 ± 2	this work
C_6H_6		19.8 ± 0.5	2 ± 2	5
CH_3CN		27.1 ± 0.6	23 ± 2	this work
CH_3CN/TBAP	0.13	19.0 ± 0.4	−4 ± 2	this work
THF		19.2 ± 0.5	2 ± 3	this work
THF/TBAP	0.19	20.9 ± 0.8	7 ± 3	this work

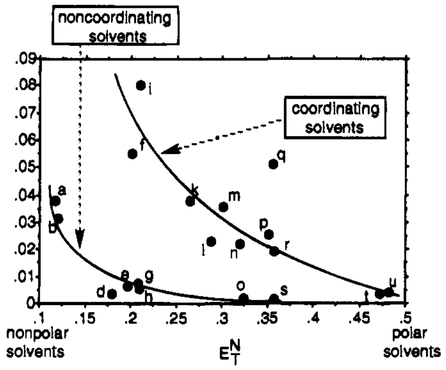

Figure 1. Plot of the substitution rate constant as a function of solvent polarity (acceptor ability); the letters refer to the solvents in Table 4.

that, as discussed in the first half of this paper, polarity is also not the sole factor determining δ.)

There is no indication from the kinetics results that the reactions in coordinating and noncoordinating solvents are following different mechanisms. Thus, the separation of coordinating and noncoordinating solvents in Figure 1 indicates that solvent-donating ability can also influence the rate and the value of δ. The difference between THF and 2-MeTHF demonstrates this point convincingly. If solvent polarity (accepting ability) were the only factor governing the rate constant then the rate constant should be essentially the same in 2-MeTHF as in THF (E_T^N of 0.202 vs 0.210). In fact, k_{rate} is considerably larger in THF (8.0×10^{-2} s^{-1} vs 5.5×10^{-2} s^{-1}). The difference between these two solvents, of course, is their donor ability.[26] The effect of the solvents' donating ability on the rate constant was quantified using Gutmann's donor number (D.N.).[27,28] (It is important to note there is no inverse relationship between the Gutmann D.N. and the Reichardt E_T^N scale, i.e., a good donor is not necessarily a poor acceptor. For example, CH_3CN is both a good donor and a good acceptor, and benzene and toluene are neither good donors nor good acceptors. For future reference, THF is an excellent donor and a poor acceptor, and CH_2Cl_2 is a good acceptor but a poor donor.) A three-dimensional plot of k_{rate} vs E_T^N and D.N. is shown in Figure 2. Note that solvents with good donor and poor acceptor properties have large rate constants. Likewise, solvents with poor donor and good acceptor properties have small rate constants.

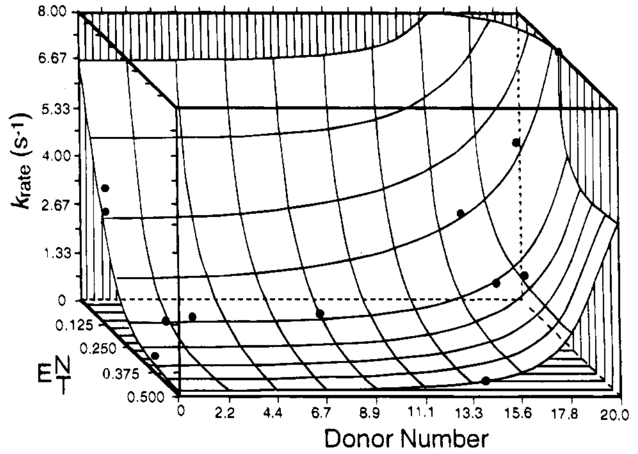

Figure 2. Plot of k_{rate} as a function of the acceptor ability (polarity) and the donor ability of the solvent (E_T^N and D.N.).

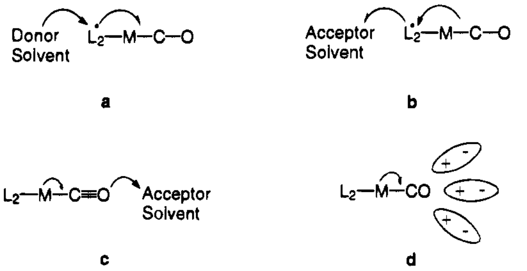

Figure 3. (a) Donor solvent interaction with $Co(CO)_3L_2$. The donor solvent increases the electron density on the L_2 ligand; δ is increased by an inductive effect. (b) Acceptor solvent interaction with $Co(CO)_3L_2$ (σ-effect). Acceptor solvent withdraws electron density from an M−CO σ^* orbital, decreasing labilization of CO for substitution reaction. (c) Acceptor solvent interaction with 18-electron complex (π-effect). The acceptor solvent induces increased π-back-bonding from the metal to the CO. (d) Interaction of polar solvent molecules with the electronegative O atom of a CO ligand in a metal carbonyl complex. π-Back-bonding increases with increasing solvent polarity.

The following model is proposed to account for why these relationships hold: (1) Good donors will add electron density to the L_2 π^* molecular orbital (which has Co−CO$_{equatorial}$ σ antibonding character[5,29]) and thereby weaken the Co−CO$_{equatorial}$ bond (Figure 3a). (2) Good acceptor solvents will depopulate the L_2 π^* molecular orbital (again, which has Co−CO σ antibonding character; Figure 3b) and also increase Co−CO π^*-back-bonding (Figure 3c or 3d);[30] both effects will

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[26] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028−7030.

[27] The D.N. value is defined as the molar enthalpy value for the reaction of the donor solvent with $SbCl_5$ as a reference acceptor in a 10^{-3} M solution of dichloroethane.

$$D + SbCl_5 \rightarrow D{-}SbCl_5 \; (-\Delta H_{D-SbCl_5} = \text{D.N.})$$

See ref 25 for complete details.

[28] The possibility that the reactive species was $Co(CO)_2L_2(S)$ (where S represents a solvent molecule) was ruled out based on rate measurements made without first equilibrating the $Co(CO)_3L_2$ complex in the solvent (see Experimental Section for details). Also, no selective solvation was observed when conducting the substitution reactions in various concentrations of THF in benzene.

[29] The $Co(CO)_3L_2$ molecule has a distorted square pyramidal structure with one of the CO ligands occupying the axial site and the other two CO ligands in cis equatorial sites.

[30] From studies of 18-electron metal carbonyls, it is well-established that the rate of dissociative substitution correlates with solvent polarity;[31] generally, the rate slows with increasing solvent polarity. This fact is attributed to an increase in (ground state) π back-bonding because the solvent dipoles induce an inductive effect as shown in Figure 3d.[32,33]

[31] An example is provided by the rate constants for dissociative substitution of the $Mn(CO)_5X$ complexes (X = Cl, Br, I): $k = 2.6 \times 10^{-3}$, 3.3×10^{-4}, and 1.6×10^{-5} s^{-1} respectively for substitution of the Cl, Br, and I complexes by $AsPh_3$ in $CHCl_3$ solvent. For further examples and further discussion of this point see: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; pp 561−571. Note that the rule of thumb assumes that only electronic factors are variable and that steric factors are held constant.

[32] Solvent effects on C≡O stretching frequencies are reviewed in: Haines, L. M.; Stiddard, M. H. B. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 53−133 (see p 100).

[33] Alternatively, the correlation is explained if the transition state is less solvated than the ground state. The difference in solvation is thus larger for more polar solvents.

Table 7. Donor and Acceptor Abilities: Qualitative Effects of Solvents on the Rate of Substitution

donor ability	acceptor ability	example	substitution rate constant (k_{rate})	δ value
poor	good	CH_2Cl_2	small	small
good	good	CH_3CN	larger than poor/good	larger than poor/good
poor	poor	C_6H_6	smaller than good/poor	smallerthangood/poor
good	poor	THF	large	large

increase the Co−CO bond energy and decrease the rate of Co−CO dissociation. (Note that this model is based on changes in the reactant state energy. Changes in the transition state impact the entropy and are discussed further below.)

In this two-parameter solvent effect model, there are four extremes: good acceptor/poor donor; good acceptor/good donor; poor acceptor/poor donor; and poor acceptor/good donor. Using the two relationships in the preceding paragraph, it is straightforward to determine the effect of these solvent classes on the rate of substitution. The results are summarized in Table 7. As an application of the results in Table 7, the following sequence in the rate constants was observed, as predicted by Table 7: $k(CH_2Cl_2)$ (poor donor/good acceptor) < $k(C_6H_6)$ (poor donor/poor acceptor) < k(THF) (good donor/poor acceptor).

Note in Table 7 that solvents that are good donors/good acceptors cannot be compared to solvents that are poor donors/poor acceptors. Reactions in both types of solvents are expected to be faster than those in poor donors/good acceptors, but slower than in good donors/poor acceptors. For example, CH_3CN (good acceptor/good donor) cannot be compared directly to benzene (poor donor/poor acceptor). But, CH_3CN can be compared to CH_2Cl_2 and THF; the expected trend is observed: $k(CH_2Cl_2)$ (poor donor/good acceptor) < $k(CH_3CN)$ (good donor/good acceptor) < k(THF) (good donor/poor acceptor).

The Effect of Entropy. The analysis in the preceding paragraphs is based on a model in which unpaired electron density controls the rate of substitution by changing the Co−$CO_{equatorial}$ bond energy. If this is the case then trends in the bond energy should be reflected in the $\Delta H^{\ddagger}$ values for a dissociative reaction. In fact, there is not a strict correlation of k with $\Delta H^{\ddagger}$ (Table 6): $k(THF) > k(C_6H_6) > k(CH_3CN) > k(CH_2Cl_2)$ but $\Delta H^{\ddagger}$ (THF) < $\Delta H^{\ddagger}$ (C_6H_6) < $\Delta H^{\ddagger}$ (CH_2Cl_2) < $\Delta H^{\ddagger}$ (CH_3CN). The Co−CO bond energy is evidently not the sole factor in determining the rate. The data in Table 6 show that acetonitrile reacts faster than its place in the $\Delta H^{\ddagger}$ ordering would indicate because of the large positive $\Delta S^{\ddagger}$ value (+23 cal/(K mol)). Thus, in certain solvents, the activation entropy also plays an important role in determining the rate. For a dissociative reaction, $\Delta S^{\ddagger}$ is expected to become more significant as solvation becomes more important because the solvation of $Co(CO)_3L_2$ likely decreases in going to the 17-electron $Co(CO)_2L_2$-like transition state.[34] Consistent with this interpretation, Table 6 shows that $\Delta S^{\ddagger}$ is larger for CH_2Cl_2 and CH_3CN, both polar solvents.

Literature precedents support the interpretation that for dissociative reactions $\Delta S^{\ddagger}$ effects are more significant in more highly solvating solvents. As an example, the data in Table 8 are for the dissociative substitution of $Mn(CO)_5Br$ by phosphines. Note that the activation entropy increases along the series toluene < $CHCl_3$ < nitrobenzene, paralleling the polarity of the solvents.[36]

Table 8. Solvent Dependence of $\Delta S^{\ddagger}$ in the Limiting Dissociative Substitution Reactions of $Mn(CO)_5Br$

solvent	$E_T^{N\,a}$	$\Delta S^{\ddagger}$, cal/K mol	ref
toluene	0.117	<10	35b
$CHCl_3$	0.259	18.9^b	35a
nitrobenzene	0.324	22.1^b	35a

[a] At 25 °C. [b] $\Delta S^{\ddagger}(C_6H_5NO_2) - \Delta S^{\ddagger}(CHCl_3) = 3.2 \pm 2.1$ cal/(K mol).

Another specific solvent effect that in certain reactions could be important is the ability of a coordinating solvent to bond directly to the metal center of a metal radical intermediate. For example, coordination of a solvent to a 17-electron metal radical would stabilize the radical. However, in a limiting dissociative mechanism such as we are dealing with here, stabilization of the 17-electron intermediate in this way would not affect the rate.

Summary of the Relationship between the Value of δ and the Reactivity. Experiments in 21 solvents showed that the rate constant for reaction 8 is controlled by two solvent properties, acceptor ability (equivalent to polarity) and donicity. The rate constant increases with an increase in donicity and with a decrease in acceptor ability. The results are interpreted using a model in which donor solvents add electron density to the L_2 π^* orbital and acceptor solvents remove electron density from this orbital. Additional electron density in the π^* orbital increases delocalization of the unpaired electron onto the Co fragment. The acceptor orbital on the Co fragment is a Co−CO σ antibonding orbital, so the Co−CO bond will weaken and the rate constant will increase. Conversely, an increase in solvent acceptor ability will strengthen the Co−CO bond and the rate constant will decrease. Because an increase in the electronic occupation of the Co−CO σ antibonding orbital corresponds to an increase in δ, the general correlation should be that the rate constant for limiting dissociative substitution in an 18+δ complex will increase with an increase in δ. However, as the data show, there is not a strict correlation of δ with k, and it is necessary to "fine-tune" this conclusion when dealing with polar solvents. In polar solvents (e.g., CH_3CN, acetone), the increase in entropy in going to the transition state ($\Delta S^{\ddagger}$) can be substantial, making these reactions faster than predicted based solely on enthalpy considerations. In conclusion, for those cases in which δ is manipulated by changing the solvent, there is no simple correlation between δ and the rate of a dissociative substitution reaction in an 18+δ complex. However, on the basis of the work reported herein, we understand why the relationship is complex.

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(34) Because the transition state is less polar than the reactants, the solvent should be less ordered in the transition state. Consequently, $\Delta S^{\ddagger}$ will be larger in a polar solvent than in a nonpolar solvent. This effect[35] will increase the rate in a polar solvent relative to a nonpolar solvent.

(35) (a) Angelici, R. J.; Basolo, F. *J. Am. Chem. Soc.* **1962**, *84*, 2495−2499. (b) Schmidt, G.; Paulus, H.; van Eldik, R.; Elias, H. *Inorg. Chem.* **1988**, *27*, 3211−3214.

(36) This ordering of activation entropies may also simply be a demonstration of the fact that "if a bond is made stronger, it is more broken in the transition state".[37] π-Back-bonding increases with solvent polarity with a resultant increase in M−CO bond energy. The entropy ordering in Table 8 may thus be a reflection of an increasingly looser transition state as well as an indicator of solvation changes during the reaction.

(37) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915−2927.

Experimental Section

Materials and Reagents. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere with the use of standard Schlenk or vacuum line techniques or a Vacuum Atmospheres Co. glovebox.

$Co(CO)_3L_2$, $Co(CO)_3L_2'$, and $Fe(CO)_3L_2$ were synthesized as previously described.[7] $Fe(CO)_3L_2'$ was synthesized using the procedure for the $Fe(CO)_3L_2$ ($\nu(C{\equiv}O)$ = 2002, 1936, and 1914 cm^{-1} in CH_2Cl_2/0.1 M TBAP) complex;[7] characterization was by infrared spectroscopy ($\nu(C{\equiv}O)$ = 1997, 1929, and 1913 cm^{-1} in CH_2Cl_2/0.1 M TBAP). Reduction (−1.0 V) of the $Fe(CO)_3L_2$ and $Fe(CO)_3L_2'$ complexes in the infrared spectroelectrochemical cell (described below) afforded $Fe(CO)_3L_2^-$ ($\nu(C{\equiv}O)$ = 1884 and 1977 cm^{-1} in CH_2Cl_2/0.1 M TBAP) and $Fe(CO)_3L_2'^-$ ($\nu(C{\equiv}O)$ = 1971, 1883 (sh), and 1879 cm^{-1} in CH_2Cl_2/0.1 M TBAP). Tetrahydrofuran (THF) and anisole were distilled under nitrogen from potassium benzophenone ketyl. Acetone was stored over Drierite for 3 weeks, then distilled under nitrogen from fresh Drierite. Benzene and toluene were distilled under nitrogen from sodium. Methylene chloride and acetonitrile were distilled from CaH_2 under nitrogen. Chlorobenzene, 1,3-dichlorobenzene, and 1,3-dibromobenzene were distilled under nitrogen from P_2O_5. 2-Methyltetrahydrofuran (2-MeTHF) was filtered through a bed of basic alumina before distilling under nitrogen from potassium benzophenone ketyl. Ethyl acetate (EtOAc) was purified by washing 200 mL with a 5% solution of Na_2CO_3 (3 × 50 mL) followed by washing with 50 mL of a saturated $CaCl_2$ solution. The EtOAc was then dried by stirring over anhydrous $MgSO_4$, filtering, and then distilling under nitrogen from P_2O_5. 2-Pentanone and 3-pentanone were prepared by distillation under nitrogen from $CaSO_4$. The tetrabutylammonium perchlorate (TBAP) was recrystallized four times from EtOAc−isooctane (1:1) and dried under high vacuum at 40 °C for 48 h. Triphenylphosphine (PPh_3) was purified by hot crystallization from hexanes. 2,6-Diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (Reichardt's dye) was used as received from Aldrich.

Equipment. Infrared spectra were obtained with a Nicolet 5 DXB FT-IR spectrometer. Spectroelectrochemical data were obtained with this IR using a modified cell[38] and a Bioanalytical Systems CV-27 to control the applied potential. Cyclic voltammetry experiments were performed with a PAR Electrochemical Station including a Model 175 universal programmer, a Model 173 potentiostat-galvanostat, and a Model 174 A polarographic analyzer. UV/vis spectra and kinetics data were collected with a Perkin-Elmer Lambda 6 UV/vis spectrophotometer interfaced with a computer running PECSS software.[39] The temperature was kept constant using a Techne C-85A refrigerated circulator.

Polarity (E_T^N) Measurements. Approximately 2 mL of the solution of interest was placed into a cuvette along with ~2 mg of Reichardt's dye (~1.0 × 10^{-3} M). Ten spectra were then taken of the resultant solution, recording the maximum absorbance of each spectrum. The average absorbance values were then used to calculate the polarity of the solution under study using the equation previously described by Reichardt.[17]

Kinetics. The kinetics were carried out by dissolving 10−15 mg of the $Co(CO)_3L_2$ complex in a 10.0 mL volumetric flask in the appropriate solvent (~1.8−2.5 × 10^{-3} M). Excess PPh_3 (0.6−0.7 g, ~0.5 M) was then dissolved in the same solvent in a 5.0 mL volumetric flask. In a two-compartment UV/vis cell, 2.00 mL of the $Co(CO)_3L_2$ solution was added to the first compartment and 0.50 mL of the PPh_3 was added to the second compartment to give a final mixture resulting in ~1.5−2.0 × 10^{-3} M $Co(CO)_3L_2$ and ~0.1 M PPh_3. The cells were then temperature equilibrated for a minimum of 10 min before mixing the two solutions and measuring the disappearance of the $Co(CO)_3L_2$ by monitoring the LMCT band.[40] The reaction was followed for a minimum of 5 half-lives with A_∞ values determined by letting the reaction go to completion. Plots of $-\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time were made to determine the first-order rate constant of the reaction.

An alternative method consisted of dissolving 0.6−0.7 g of PPh_3 in 10.0 mL of the appropriate solvent (0.23−0.27 M) and then adding a 2.00-mL aliquot of this solution to the cuvette. The solution was temperature equilibrated for a minimum of 10 min before adding ~2 mg of $Co(CO)_3L_2$ (~1.6 × 10^{-3} M) and observing the disappearance of the LMCT band associated with the $Co(CO)_3L_2$. Plots were then made to determine the first-order rate constant of the reaction. Results obtained using this method did not differ from those obtained by the first method.

δ Measurements. The modified IR cell for spectroelectrochemistry was made by replacing the standard back plate with one measuring 19 mm in depth.[38] The working electrode is a Pt gauze (52 mesh, Aldrich) centered between the NaCl windows which are separated with a 0.5 mm Teflon spacer. Electrode wires (Pt working, Pt auxiliary, and Ag reference) are introduced through the Luer lock fittings of the needle plates and are passed through the drilled windows. The wires were then sealed with wax and cement and prevented from establishing contact with the cell via insertion into glass sleeves. Electrical contact between the working electrode and the auxiliary electrode was accomplished by threading the Pt wire through the Pt gauze.

Measurements were accomplished by dissolving the appropriate material (~10^{-2} M) in a 0.1 M TBAP solution and applying the appropriate potential (−1.0 V for L_2, L_2', $Fe(CO)_3L_2$, and $Fe(CO)_3L_2'$ complexes, +0.2 V for the $Co(CO)_3L_2$ and $Co(CO)_3L_2'$ complexes). Spectra were recorded while the electrochemistry was taking place.

Cyclic Voltammetry. All experiments were conducted inside the drybox. The electrolyte was tetra-*n*-butylammonium perchlorate (TBAP). The runs were performed with a three-electrode cell. The auxiliary electrode consisted of a 24-gauge wire coiled around the Pt bead working electrode which was made from a 1 cm long 18-gauge Pt wire with one end melted into the form of a spherical bead. This Pt wire was sealed into the end of a 10 cm long Flint glass tube (4 mm in diameter). A copper wire was then inserted into the glass tube and connected to the Pt wire with a small amount of solder. A 24-gauge Ag wire was used as a quasi-reference electrode separated from the test solution by a fine glass frit and a Luggin capillary. Potentials were calibrated against the ferrocene/ferrocenium couple by adding ferrocene as an internal standard directly to the solution under investigation and are referenced to the aqueous saturated calomel electrode (SCE).

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Supporting Information Available: A table of λ_{max} values for Reichardt's dye in various solvents used in this paper, a plot of k_{rate} vs the Guttman donor number, and a sample kinetics plot showing the excellent data used to determine k_{rate} (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[38] Saravanamuthu, S.; Bruce, A. E.; Bruce, M. R. M. *Vib. Spectrosc.* **1991**, *2*, 101−106.

[39] PECSS software was obtained from Perkin-Elmer.

[40] The LMCT band is the low-energy band, typically with λ_{max}'s between 716 nm (for CH_3CN) and 835 nm (for benzene). See ref 5.