The electrostatic cation–anion interactions will depend on the properties of the anion: its charge, size, shape, and polarizability. The solubility properties of the anion, i.e., its lipophilicity, are extremely important for the dissolution of the complex in solvents of low polarity.

Our data (see Figure 2) indicate the crucial importance of the counterion. This study, along with a more comprehensive experiment currently underway,[21] shows that bulky, spherical, polarizable, monovalent anions enable the cation to interact more effectively with the ligand-binding sites, generating a more selective and specific system.[22] In some cases (Figure 2, column 4) divalent cations are strongly rejected,[23] an important factor in the design of lithium-selective membranes for industrial and medical purposes.[24,25]

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Registry No. Li^+, 17341-24-1; dibenzo-14-crown-4, 14174-06-2.

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Direct Observation of Substitution Reactions of Tricarbonylbis(phosphine)manganese(0) Radicals[1]

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It has become evident during the past few years that reaction pathways involving metal-centered radicals, with 17 electrons in the valence orbitals of the metal, are important in many organometallic systems.[2] The radicals most widely studied to date are those involving only CO groups as ligands or CO and other groups such as η^5-C_5H_5. Since the initial observation of a radical chain pathway for substitution,[3] the substitution lability of metal carbonyl radicals has been recognized as an important aspect of their chemical behavior.[4,5] In addition to the evidence based on radical chain substitution reactions, other indications of lability in the radicals exist: (a) The quantum yields for photochemical substitution, e.g., in $Mn_2(CO)_{10}$, are nearly 1.[6,7] Because the rate of recombination of $Mn(CO)_5\cdot$ radicals approaches the diffusion-controlled limit,[8,9] substitution of the radical must be very rapid. (b) Formation of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ (M = Cr, Mo, W) on irradiation or heating of $(\eta^5\text{-}C_5H_5)M_2(CO)_6$ suggests CO loss from the radicals formed via metal–metal homolysis.[10] (c) Various photochemical reactions of metal carbonyl compounds, e.g., of $Re_2(CO)_{10}$ with H_2[4] or of various dinuclear carbonyl compounds with hydrides,[11] are most readily accounted for in terms of a high lability of the radical formed via metal–metal bond homolysis.

The results of these studies suggest simple mononuclear carbonyl radicals such as $Mn(CO)_5\cdot$, $Re(CO)_5\cdot$, or $Co(CO)_4\cdot$ may react via a rate-determining dissociative loss of CO, followed by rapid uptake of L or by an oxidative addition step. On the other hand, Poë has recently provided convincing evidence that substitutions of $Re(CO)_5\cdot$ by phosphines can also occur via an associative pathway.[12] In substituted metal carbonyl radicals, replacement of one ligand L by another, or possibly substitution of CO to yield a more highly substituted radical, is relatively slower and may occur via an associative pathway.[13,14]

We have earlier reported the formation of persistent zerovalent manganese radicals, $Mn(CO)_3L_2\cdot$ (L = phosphorus donor ligand).[13] The steric requirements of L preclude recombination of the radicals to form a stable dinuclear species. We have recently carried out additional physical and chemical studies of such radicals.[15] We report here the first direct observations of the kinetics of substitution at the metal center in a substituted metal carbonyl radical.[16]

A reaction of particular interest is that with CO as delineated in eq 1 and 2. The reaction is readily followed by mixing hexane

$$Mn(CO)_3L_2\cdot + CO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Mn(CO)_4L\cdot + L \qquad (1)$$

$$2Mn(CO)_4L\cdot \xrightarrow{k_3} Mn_2(CO)_8L_2 \qquad (2)$$

solutions of $Mn(CO)_3L_2\cdot$ and CO and observing the time dependence of the IR bands due to $Mn(CO)_3L_2\cdot$ in the region of CO stretching modes. Neither $Mn_2(CO)_9L$ nor $Mn_2(CO)_{10}$ are observed as products. All of the reactions studied exhibit good first-order kinetics through at least 3 half-lives. Observed pseudo-first-order rate constants, pertaining mainly to the case L = $P(i\text{-}Bu)_3$, for reaction at 20 °C are given in Table I. (This particular phosphine was chosen for detailed study because in preparation of the radical it is possible to achieve low ambient concentrations of the phosphine.)

The important observations are these: The observed pseudo-first-order rate constant is approximately proportional to [CO], and added $P(i\text{-}Bu)_3$ at a concentration level on the order of that of CO or greater has no effect on the observed reaction rate.

The dependence of the pseudo-first-order rate constant on [CO] suggests strongly that the reaction is associative in character. This conclusion is reinforced by the comparative rate constants for reaction of CO with $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ and $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$. Reaction is faster when the phosphine is less bulky, consistent with an associative transition state. The second-order rate constants for reactions of $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ and $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$ with CO at 20 °C are 0.32 and 42 M^{-1} s^{-1}, respectively.

The fact that the pseudo-first-order rate constant is unaffected by addition of $P(i\text{-}Bu)_3$ suggests that the reverse reaction in 1 is relatively slow in relation to reaction 2.

The present observations for the first time directly establish the lability of the 17-electron metal carbonyl radicals toward thermal substitution.[16] Results for these highly substituted radicals

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Table I. Pseudo-First-Order Rate Constants for Reaction of $Mm(CO)_3L_2\cdot$ Radicals with CO at 20 °C

10^3[CO], M	[L], M	k_{obsd} s^{-1}
	$Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$	
5.0	$<10^{-4}$	1.6×10^{-3}
2.5	$<10^{-4}$	7.9×10^{-4}
1.7	$<10^{-4}$	5.2×10^{-4}
5.0	5×10^{-3}	1.4×10^{-3}
5.0	5×10^{-2}	1.5×10^{-3}
	$Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$	
5.0	$\sim 10^{-3}$	2.1×10^{-1}

are strongly indicative of an associative pathway. The substituted radicals are thus much less labile than $Mn(CO)_5\cdot$, for which the rate constant for thermal loss of CO is estimated to be in the range 10–100 s^{-1}.[7,9] We had earlier inferred that $Mn(CO)_4L\cdot$ radicals are less labile than $Mn(CO)_5\cdot$.[13] Since observation of an associative process places an upper limit on the possible value for the dissociative loss of CO or L, we can infer an order of labilities $Mn(CO)_5\cdot > Mn(CO)_4L\cdot > Mn(CO)_3L_2\cdot$.

$Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ enriched with ^{13}CO was reacted with normal isotopic abundance CO. From the relative rates of disappearance of the IR bands associated with the normal-abundance and ^{13}CO-enriched species it can be inferred that replacement of ^{13}CO by normal-abundance CO occurs at a rate comparable to that for substitution of the phosphine by CO. At this point it is not possible to say whether the replacement of CO by CO occurs via a dissociative or associative process; however, the latter seems more likely. The details of these kinetics studies will be reported later.

The present results, taken together with the results of previous studies, point toward the manner in which replacement of CO by more strongly σ-donating and weaker π-acid phosphines leads to a decreased lability of the metal center. The new observations are consistent with the hypothesis that there may be a transition in the prevalent pathway for substitution, from dissociative for $Mn(CO)_5\cdot$ to associative for $Mn(CO)_3L_2\cdot$ radicals. Clearly, however, much remains to be learned about how the choice of metal and attendant ligands affects lability in the radicals.

Registry No. $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$, 81971-50-8; $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$, 67551-64-8; CO, 630-08-0.

Carbon-13 NMR Subspectra of a Protein Based on the Number of Attached Protons. Ferredoxin from *Anabaena variabilis*

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The usefulness of *J*-modulated spin-echo pulse sequences in the determination of spin multiplicities of ^1H NMR peaks in proteins was reported several years ago.[1] Recently, an analogous procedure was described for the determination of spin multiplicities in ^{13}C NMR spectra of small organic molecules.[2,3] We now apply this procedure, which has been given the acronym APT for "attached proton test",[3] to determine the spin multiplicity of peaks in the aromatic region of the ^{13}C NMR spectrum of a 2Fe·2S* ferredoxin, a small protein (M_r = 11 000) involved in photosynthetic electron transport.[4] The APT approach is superior to other methods that have been used to determine ^{13}C NMR multiplicities in proteins; and it is preferable in some cases to a two-dimensional heteronuclear *J*-resolved ^{13}C NMR spectrum in that it provides about the same level of information in much less time. Since the aromatic region contains resonances of carbons with either zero or one attached proton, subspectra containing resonances only of unprotonated or singly protonated carbons can be generated from the sum and difference of the APT spectrum and a normal, noise-decoupled, single-pulse spectrum.

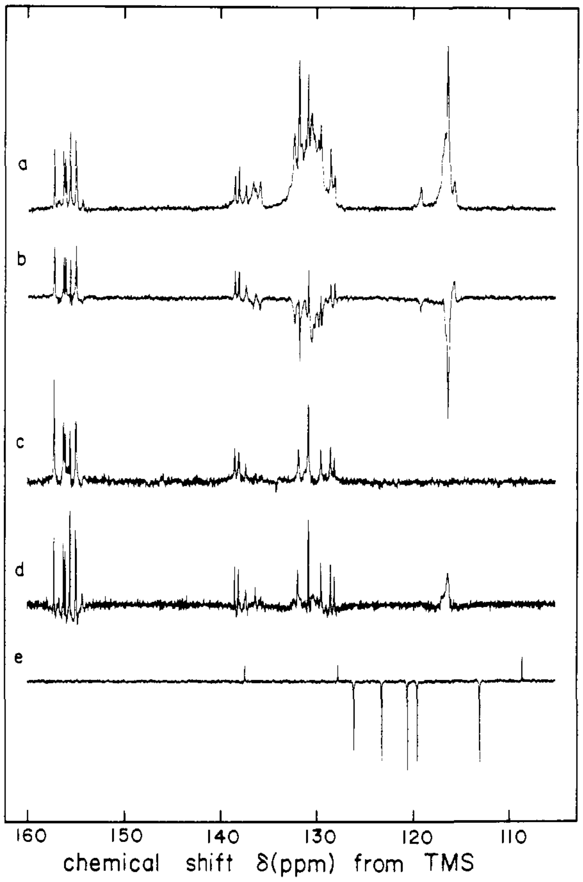

Figure 1. Comparison of different strategies used to obtain 50.31-MHz ^{13}C NMR spectra of the aromatic region of a protein, oxidized ferredoxin from *Anabaena variabilis*:[17] (a) normal, single-pulse experiment with on-resonance broad-band square-wave-modulated ^1H decoupling; (b) *J*-modulated spin-echo pulse sequence with on-resonance, square-wave-modulated ^1H decoupling[2] (APT experiment);[3] (c) spin-echo spectrum with off-resonance, square-wave-modulated ^1H decoupling;[12] (d) convolution difference spectrum obtained from a noise-modulated, off-resonance ^1H decoupled spectrum by subtracting a digitally broadened spectrum from the original;[11] (e) the *J*-modulated spin-echo (APT) spectrum of tryptophan, an aromatic amino acid not present in *A. variabilis* ferredoxin, presented for reference purposes.

Ferredoxin was isolated from *Anabaena variabilis* grown on CO_2 [20% ^{13}C] as the sole carbon source by a modification of the procedure of Ho et al.[5] The ^{13}C enrichment level is well above the ^{13}C natural abundance of 1.1% but below the level at which ^{13}C–^{13}C coupling of labeled neighboring carbons complicates the spectra.[6]

The ^{13}C resonances expected between 110 and 160 ppm arise from the ring carbons of five tyrosines, three phenylalanines, and two histidines, and from the guanidinyl carbon of one arginine present in the sequence of *A. variabilis* ferredoxin.[7] With neglect of long-range couplings which are characterized by small coupling

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