by predominately π bonding and the third-row metal system by largely σ bonding, thus leaving the second-row metal complex to be the most labile. A similar explanation[11] is given in terms of the low electronegativity of the metal of the first transition series as one factor and a good matching of the orbital energies of the third-transition-series metal with those of the CO ligand as the second factor. The latest word[12] on this, to our knowledge, is the detailed molecular orbital calculations based on density functional theory to estimate the first CO ligand dissociation energy ΔH of $M(CO)_m$ for the three binary metal carbonyl triads $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt). For each triad of transition metals, the calculated ordering of the M–CO bond strength (including relativistic effects) is 3d > 5d > 4d. These calculations agree with the experimental observation that second-row (4d) transition metals generally afford the most substitution labile organometallic complexes of a given metal triad.

The anomaly for the $M(CO)_5$ (M = Fe, Ru, Os) triad is the extreme slowness of CO substitution of iron pentacarbonyl relative to the pentacarbonyls of ruthenium and osmium. The reason for this perhaps rests largely in the fact that the transition state/active intermediate for reaction, $Fe(CO)_4$, may be high spin.[13] Thus, a partial explanation for this very slow rate of CO substitution of $Fe(CO)_5$ may be the much less favorable crystal field activation energy (CFAE)[14] in going from low-spin $Fe(CO)_5$ to high-spin $Fe(CO)_4$, compared with the CFAE in going from low-spin $M(CO)_5$ (M = Ru, Os) to low-spin $M(CO)_4$.[15] The electron spin

change for $Fe(CO)_5$ corresponds to a spin-forbidden process, whereas that for $Ru(CO)_5$ and $Os(CO)_5$ should involve a spin-allowed process. This spin change for $Fe(CO)_5$ makes its formation of triplet $Fe(CO)_4$ a slower process than formation of a singlet transition state, so its reaction may involve the less stable singlet $Fe(CO)_4$.

Although the enthalpy of activation (ΔH^*) for CO substitution of $Os(CO)_5$ is about 3 kcal/mol less than for $Os_3(CO)_{12}$,[16] the rate constants at 50 °C for the two reactions are almost the same (Table II). This results from the much smaller value of ΔS^* for the mononuclear metal carbonyl compared to that for the cluster. The rates of CO substitution of the mononuclear and cluster ruthenium carbonyls are also almost the same at 50 °C, but $Fe_3(CO)_{12}$ reacts much faster than does $Fe(CO)_5$ (Table II). As already discussed, the slow reaction of $Fe(CO)_5$ may be associated with its spin change from low spin in the ground state to high spin in the transition state. Also, the greater ease with which the iron cluster $Fe_3(CO)_{12}$ forms bridging COs is believed,[17] in part, to be the reason it reacts faster than do the corresponding ruthenium and osmium clusters.

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Additions and Corrections

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Thomas C. Strekas,* Harry D. Gafney, Steven A. Tysoe, Randolph P. Thummel,* and Francois Lefoulon: Resonance Raman Spectra and Excited-State Lifetimes for a Series of 3,3'-Polymethylene-2,2'-bipyridine Complexes of Ruthenium(II).

Page 2965. The structure near the top of column 1 was incorrectly reproduced, omitting the 2,2'-bond. The correct structure is given below:
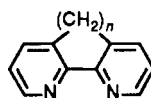
1a, n = 1
b, n = 2
c, n = 3
d, n = 4

—Thomas C. Strekas