Table III. Comparison of the Kinetic Parameters for Substitution on MFe$_2$(CO)$_{12}$[a]

complex	k(30 °C), 10^{-5} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Fe$_3$(CO)$_{12}$[b]	4.0	29.5 ± 0.8	19 ± 3
Fe$_2$Ru(CO)$_{12}$	17.8[b]	28 ± 4[c]	16 ± 13[c]
Fe$_2$Os(CO)$_{12}$[b]	0.42	27 ± 4	7 ± 7

[a] Error limits are 95% confidence limits. [b] Hexane. [c] 1,2-Dichloroethane.

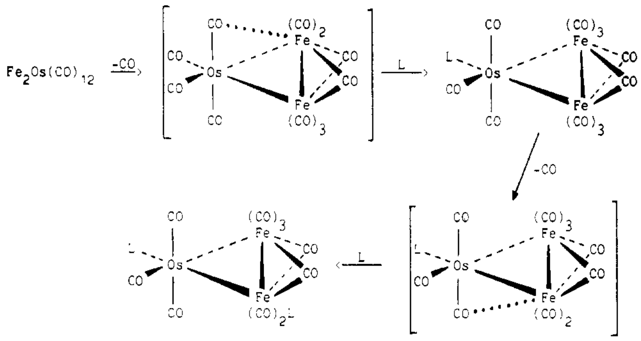

Figure 3. Suggested mechanism for substitution on Fe$_2$Os(CO)$_{12}$.

activation parameters, the kinetic data suggest CO dissociation. A comparison of the rate constants and activation parameters for the structurally analogous complexes MFe$_2$(CO)$_{12}$ (M = Fe, Ru, Os) is shown in Table III. Obviously, the metal M has an effect on the reactivity of the trinuclear cluster with the order of reactivity M = Ru > Fe > Os.

For Fe$_2$Ru(CO)$_{12}$ we were unable to rationalize the reactivity in terms of dissociation of CO from iron or ruthenium.[5] For Fe$_2$Os(CO)$_{12}$ however we believe that CO dissociation occurs from iron for the following reasons: (1) The reactivity of Fe$_2$Os(CO)$_{12}$ is more similar to that of Fe$_3$(CO)$_{12}$ than to that of Os$_3$(CO)$_{12}$. The magnitude of the heterometal effect for the mixed trinuclear clusters of iron and ruthenium is less than a factor of 10.[5] Fe$_2$Os(CO)$_{12}$ undergoes substitution a factor of 10 more slowly than Fe$_3$(CO)$_{12}$, but a factor of 10^4 more rapidly than Os$_3$(CO)$_{12}$. (2) There exists no evidence to suggest that Os–CO bonds would be significantly weaker in Fe$_2$Os(CO)$_{12}$ than in Os$_3$(CO)$_{12}$, yet the activation enthalpies differ by 7 kcal/mol.[4,10] The activation enthalpies for substitution on Fe$_2$Os(CO)$_{12}$ and Fe$_3$(CO)$_{12}$ are nearly identical.[4] (3) The rate of the second substitution of L for CO is similar to the rate of the first substitution. This is typically observed when the site of dissociation is different from the site of substitution.[1,11]

The mechanism shown in Figure 3 is indicated for substitution on Fe$_2$Os(CO)$_{12}$: initial dissociation on an iron center, rearrangement, substitution of L on the osmium, another dissociation on iron, and substitution on iron. On the basis of the similarity of the kinetics and activation parameters, we now believe that substitution on Fe$_2$Ru(CO)$_{12}$ also involves CO dissociation from iron.

Acknowledgment. We acknowledge helpful discussions with M. R. Churchill and J. B. Keister. J.D.A. acknowledges the Alfred P. Sloan Foundation for support during the course of this research.

Supplementary Material Available: Table S1, listing rate constants for reactions of Fe$_2$Os(CO)$_{12}$ in hexane (1 page). Ordering information is given on any current masthead page.

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Additions and Corrections

1988, Volume 27

Andrzej Ozarowski, Bruce R. McGarvey,* Anil B. Sarkar, and John E. Drake: EPR Study of Manganese(II) in Two Crystalline Forms of Fe(C$_6$H$_8$N$_2$S$_2$)$_2$(NCS)$_2$ and the High-Spin–Low-Spin Transition That Occurs in Only One Form. X-ray Structure Determination of Both Forms.

Page 628. The correct crystal system for polymorph B of Fe(C$_6$H$_8$N$_2$S$_2$)$_2$(NCS)$_2$ is monoclinic in space group $C2/c$ and not triclinic $P\bar{1}$ as reported. The redetermined structure gives bond lengths and bond angles within experimental error of those reported. The reported bond length of 2.078 (7) for S(3)–C(7) was a typographical error that should have been 1.740 (8) Å. The crystal structure determination was secondary to the EPR study, and these changes do not in any way alter the interpretation of the EPR data. The corrected crystallographic data, tables, and all deposited material have been supplied to the Cambridge Crystallographic Data Centre and can be obtained directly from J.E.D.—John E. Drake