TABLE I

SUMMARY OF KINETIC DATA

Reaction	$k_{YZ}K_X$,[a] sec^{-1}	k_{YZ}, M^{-1} sec^{-1}	K_X, M
$Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl$	5.0×10^{-2}	17 ± 8[b]	$(3.0 \pm 1.5) \times 10^{-3}$[c]
$Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC_6H_5$	1.2×10^{-1}	40 ± 20[b]	$(3.0 \pm 1.5) \times 10^{-3}$[c]
$Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl$	3.0×10^{-3}	...	$(1.8 \pm 0.9) \times 10^{-4}$[d]
$Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5$	5.6×10^{-3}	...	$(1.4 \pm 0.7) \times 10^{-4}$[d]

[a] In benzene at 25°; computed from slopes of plots in Figure 1. [b] Computed from experimental value of $k_{YZ}K_X$ using previously determined[1] value of $(3.0 \pm 1.5) \times 10^{-3}$ for K_X (*i.e.*, $K_{C_2H_4}$). [c] From ref 1. [d] Computed from experimental value of $k_{YZ}K_X$ using value of k_{YZ} determined above from corresponding reaction of $Pt(P(C_6H_5)_3)_2(C_2H_4)$ with YZ.

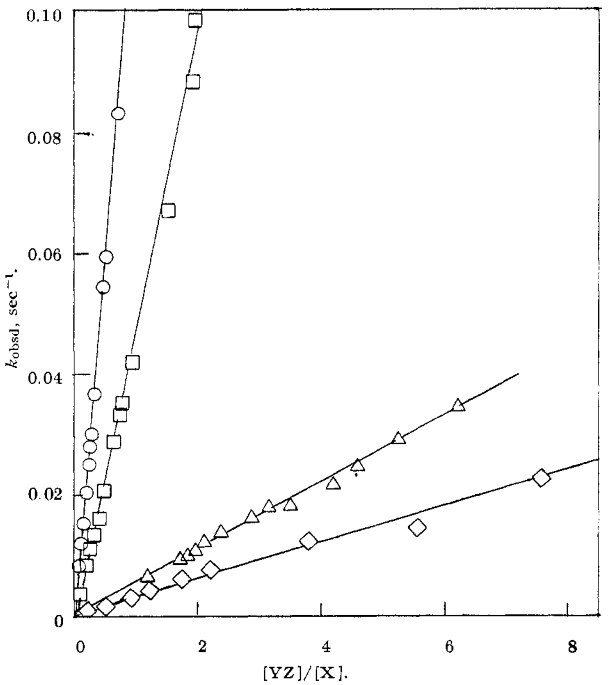

Figure 1.—Plots of k_{obsd} *vs.* [YZ]/[X] according to eq 9 for the reactions: ◇, $Pt(P(C_6H_5)_3)_3 + (C_6H_5)_3SnCl$; △, $Pt(P(C_6H_5)_3)_3 + C_6H_5C{\equiv}CC_6H_5$; □, $Pt(P(C_6H_5)_3)_2(C_2H_4) + (C_6H_5)_3SnCl$; ○, $Pt(P(C_6H_5)_3)_2(C_2H_4) + C_6H_5C{\equiv}CC_6H_5$.

ligible (*i.e.*, $[Pt(P(C_6H_5)_3)_2X] \approx [Pt(P(C_6H_5)_3)_2X]_{tot}$),[4] the observed kinetic behavior was pseudo first order, *i.e.*

$$-d \ln [Pt(P(C_6H_5)_3)_2X]_{tot}/dt = k_{obsd} = k_{YZ}K_X[YZ][X]^{-1} \quad (9)$$

Excellent linear plots, depicted in Figure 1, of k_{obsd} *vs.* $[YZ][X]^{-1}$ were obtained for each reaction, from the slopes of which the values of $k_{YZ}K_X$ listed in Table I were derived.

An earlier determination[1] of $K_{C_2H_4}$, although of relatively low accuracy ($(3.0 \pm 1.5) \times 10^{-3}$ M), in combination with the present values of $k_{YZ}K_{C_2H_4}$, yields the values of k_{YZ} listed in Table I, *i.e.*, $k_{(C_6H_5)_3SnCl} = 17 \pm 8$ and $k_{C_6H_5C{\equiv}CC_6H_5} = 40 \pm 20$ M^{-1} sec^{-1}. These data, in combination with the values of $k_{YZ}K_{P(C_6H_5)_3}$ in Table I, lead to the determination of $(1.6 \pm 1) \times 10^{-4}$ M for $K_{P(C_6H_5)_3}$, the equilibrium quotient for the dissociation of $Pt(P(C_6H_5)_3)_3$ according to eq 5.

The available data, including those obtained in the present investigation, reveal that the reactivity of $Pt(P(C_6H_5)_3)_2$ toward various acetylenes increases in the order: $C_6H_5C{\equiv}CC_6H_5$ ($k_{YZ} = 40$ M^{-1} sec^{-1}) < $C_6H_5C{\equiv}CH$ ($k_{YZ} = 2.8 \times 10^2$ M^{-1} sec^{-1})[1] < $HC{\equiv}CH$ ($k_{YZ} = 4.6 \times 10^2$ M^{-1} sec^{-1}).[5] It is of interest that this order is opposite to that of the thermodynamic stabilities of the resulting $Pt(P(C_6H_5)_3)_2$(acetylene) complexes.[6]

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[4] The kinetic measurements on reaction 1 were also extended to lower C_2H_4 concentrations, in the range 2.5×10^{-3} to 1.2×10^{-2} M where this condition is no longer fulfilled, and a correction for the dissociation of $Pt(P(C_6H_5)_3)_2C_2H_4$ is necessary. The results of these experiments yielded a value of $K_{C_2H_4}$ of $\sim 2 \times 10^{-3}$ M, consistent with that determined earlier.[1]

[5] J. P. Birk and J. Halpern, unpublished measurements.

[6] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957)

Correspondence

The Mechanism of Carbonyl Exchange in $Mn(CO)_5X$ Compounds[1]

Sir:

The exchange of CO groups in $Mn(CO)_5X$ compounds was first extensively investigated by Wojcicki and Basolo[2] and somewhat later by Hieber and Wollmann.[3] The results of these studies, which indicated a considerable difference in the rates of axial *vs.* radial CO group exchange, have recently been called into question.[4,5] Infrared techniques have been employed to follow the rate of ^{13}CO or $C^{18}O$ incorporation into $Mn(CO)_5X$ compounds. There appears to be little or no difference in the specific rate constants for substitution at the two positions.

The mechanistic implications of these more recent

[1] This research was supported by a grant from the National Science Foundation, GP 6396X.

[2] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

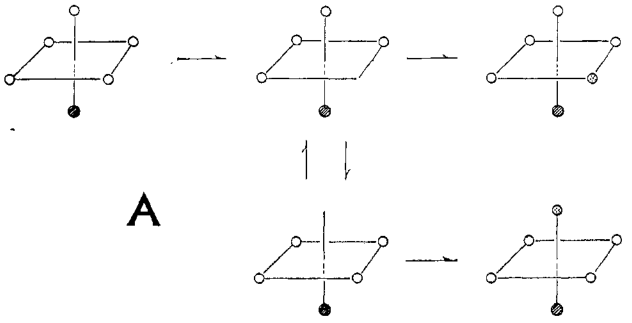
[3] W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).

[4] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

[5] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc., A*, 522 (1968).

results have been discussed.[5] The purpose of this correspondence is to point out an error in the previous discussion and to elaborate on the possible mechanism for CO exchange.

Johnson and co-workers have argued[5] that the approximate equality of axial and radial substitution rates is consistent with reaction scheme A, in which it is presumed that loss of CO occurs preferentially from the radial position. It is further presumed that there is a rapid equilibration of CO groups among the two configurations shown and that addition of labeled CO may occur at either the axial or the equatorial position. This proposal is, however, incorrect. If there is preferential loss of CO from the equatorial position, then, no matter what modes of equilibration may prevail in the five-coordinate intermediate, addition of CO must occur at the equatorial position, with the same degree of preference which characterizes loss of CO. This conclusion follows directly from the principle of microscopic reversibility. If the transition state for loss of axial CO possesses a higher free energy than that for loss of radial CO, the transition state for addition of CO to the intermediate along the axis must lie correspondingly higher. The key to the application of this concept in the present context is that the labeling which is observed resides in the group being added to the intermediate and not in the parent molecule.[6]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The apparent equality of radial and axial substitution rate constants in $Mn(CO)_5X$ compounds and the analogous behavior in $Mn(CO)_5H$[7,8] and $Re(CO)_5H$[8] deserve comment. It is not inconceivable that the result is not related to the kinetics of the substitution process but reflects merely a nondissociative exchange of axial and radial CO which is rapid relative to the dissociative exchange. All of the compounds studied involve substituents which are non-π-bonding toward the metal. The angle θ between the axial and radial MCO vectors in the hydrides is on the order of 98°.[9,10] Despite a notable difference in steric requirement, an angle greater than 90° also obtains in $Mn(CO)_5Br$.[11]

A nondissociative exchange might occur in the hydride merely as a result of the small steric requirement of the hydrogen. On the basis of the united atom model for metal carbonyl hydrides,[12] one would not expect an angular movement of the proton to require a large amount of energy. Thus, a concurrent movement of the proton, with angular motion of the CO's would provide for axial–radial exchange (Figure 1). This could very easily occur at a rate which is rapid with respect to the relatively slow dissociative process. Alternatively, the process might involve a hydride migration step,[13] with formation of an intermediate $CHOMn(CO)_4$.

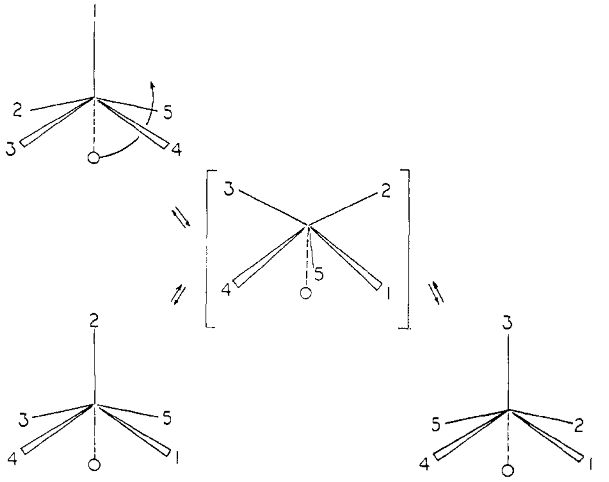

Figure 1.—Diagram of a possible process for nondissociative exchange of axial and radial CO in $M(CO)_5H$ compounds. The bracketed species might also represent a possible intermediate in an $M(CO)_5X$ intramolecular exchange, beginning with the lower equilibrium configuration.[19]

A reasonably facile pathway for axial–radial exchange in the pentacarbonyl halides can also be rationalized. The large angle between axial and radial MCO vectors in the $Mn(CO)_5X$ compounds is indicative of relatively weak covalent bonding between metal and halide.[14] A form of twist motion in $M(CO)_5X$ would provide a pathway for exchange. One possible pathway is illustrated as in the bracketed intermediate in Figure 1. Alternatively, the intramolecular axial–radial exchange might occur through a halide migration, producing an intermediate $Mn(CO)_4COX$. Evidence for formation of an acyl halide from a carbonyl halide in the $Fe(CO)_5$–halogen systems was recently presented by Noack.[15]

It should be kept in mind that a process of this sort need only have a characteristic rate constant on the order of perhaps 0.1 min^{-1} to produce the observed infrared spectroscopic results. The model has the virtue of accommodating the notion of more rapid dissociation of a radial CO as opposed to an axial CO, as

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(6) A related but not identical consideration is involved in the results of CO displacement of olefins in molybdenum olefin carbonyl compounds: R. W. Harrill and H. D. Kaesz, *J. Am. Chem. Soc.*, **90**, 1449 (1968).

(7) F. Basolo, A. T. Brault, and A. J. Poë, *J. Chem. Soc.*, 676 (1964).

(8) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

(9) S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *ibid.*, **86**, 2288 (1966).

(10) P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

(11) R. F. Bryan, private communication. Preliminary X-ray results indicate an angle of about 93° in $Mn(CO)_5Br$.

(12) W. G. McDugle, Jr., A. F. Schreiner, and T. L. Brown, *J. Am. Chem. Soc.*, **89**, 3114, (1967).

(13) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 578.

(14) M. J. Bennett and R. Mason, *Nature*, **205**, 760 (1965).

(15) K. Noack, *J. Organometal. Chem.* (Amsterdam), **13**, 411 (1968).

seems entirely reasonable on the basis of indications of MCO bond orders from vibrational data.[4,16]

One alternative to the above proposal is that the axial and radial CO groups dissociate at essentially equal rates, by pathways in which distinct axial–radial stereochemistry is preserved in the transition states (the alternative scheme proposed by Johnson and coworkers[5]). This seems an unlikely situation; $Mn(CO)_5Cl$, $Mn(CO)_5Br$, and $Mn(CO)_5I$ exhibit a very wide variability in exchange and substitution[17] rates, although the CO groups vary less in the infrared spectral characteristics from compound to compound than the axial and radial CO groups in any one compound. It would seem a remarkable coincidence that the two types of CO should exchange at identical rates in five quite different compounds, over a range of temperature or in different solvent.

The *only* alternative pathways, always assuming dissociation as the rate-determining step, are those in which the axial CO group becomes equivalent to one or more of the previously radial CO groups *in the transition state* (as opposed to a five-coordinate intermediate). It is difficult to imagine a likely transition state in which all five CO groups are simultaneously equivalent.[18] More detailed work may reveal that in fact the axial CO need become equivalent with only one of the radial CO. This would be evidenced by an equality of axial and *total* radial exchange rates. A transition state in which this requirement is met is diagrammed as the bracketed configuration in Figure 1.[19]

On the basis of this discussion, it is clear that the strong inference experiment[20] which will distinguish among the plausible hypotheses has yet to be carried out. It seems clear that one requirement on the experiment will be that the label of interest be incorporated in the parent compound. Intermolecular exchange could then be distinguished from intramolecular rearrangement. There are a number of feasible synthetic routes to the properly labeled compounds.

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[16] F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, **6**, 1357 (1967).

[17] R. J. Angelici and F. Basolo, *ibid.*, **2**, 728 (1963).

[18] The equivalence of the axial CO groups with all of the radial CO's is required to preserve the ratio of exchange rates reported by Kaesz and coworkers.[4] A lower ratio was reported by Johnson and coworkers.[5]

[19] Although the intermediate could be envisaged as forming by a classical twist mechanism involving rotation about the axis centered on the 3–2–5 face, the intermediate proposed is assumed to be different from the product of a simple twist. CO groups 4, 5, and 1 are equivalent and form a trigonal set around the M–X bond axis. CO groups 3 and 2 are equivalent and lie in a plane with the M–X bond. The bracketed species might also represent a transition state in a CO dissociation, beginning from the lower equilibrium configuration. In this case CO groups 2 and 3 are equivalent, and either could dissociate.

[20] J. R. Platt, *Science*, **146**, 347 (1964).