

### Interactions in Metal Clusters. I. Acceleration of Substitution by Prior Substitution at Adjacent Metal Centers

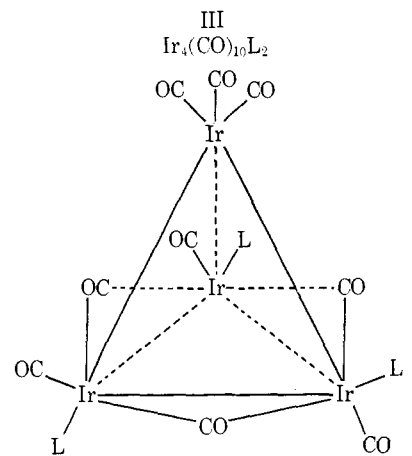
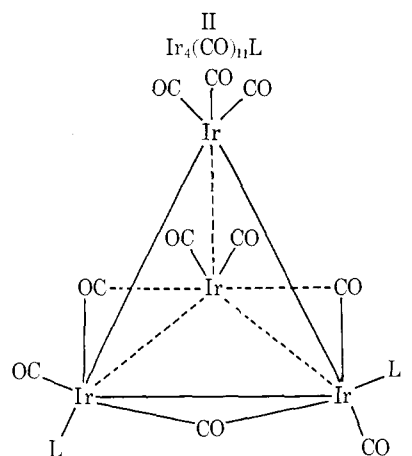
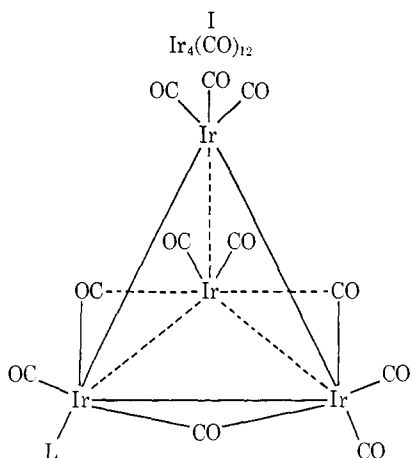
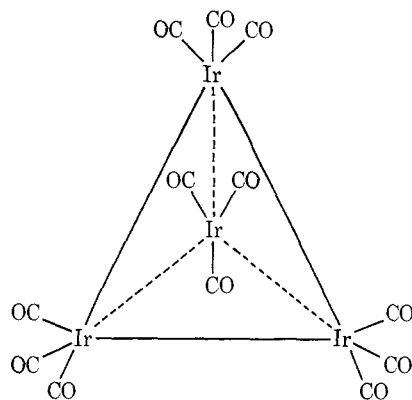
Sir:

We wish to report the first study of a cooperative effect in the reactions of metal carbonyl clusters. Tertiary phosphine substitution on one metal atom in  $\text{Ir}_4(\text{CO})_{12}$  (1) changes the local structure at the other metal atoms, (2) changes their dominant substitution mechanism, and (3) accelerates these subsequent substitutions. These measurements provide quantitative evidence for the importance of interactions among metal atoms in clusters and clearly distinguish their chemistry from that of mononuclear metal complexes.

By analogy to known results for mononuclear metal carbonyls<sup>1</sup> one would expect each phosphine substituent (if it had any significant effect) to decrease the rate of successive substitutions. A classic example is the relative dissociative substitution and/or exchange rates for nickel carbonyls, which decrease from  $\text{Ni}(\text{CO})_4$  through  $\text{Ni}(\text{CO})_3(\text{Ph}_3\text{P})$  to  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in the ratio (at 25°C) 765:71:1.<sup>2</sup>

Unfortunately, while there are some studies of sequential substitution rate relationships for binuclear carbonyls,<sup>3-6</sup> there are almost none on clusters with three or more metal atoms. Substitution on  $\text{Ru}_3(\text{CO})_{10}(\text{NO})_2$  has been shown<sup>7</sup> to involve experimentally equal specific rates for two successive dissociative substitutions. Surprisingly, however, two studies<sup>8,9</sup> of the trisubstitution of  $\text{Ru}_3(\text{CO})_{12}$  have usually noted the absence of observable concentrations of intermediates. Our preliminary experiments showed the same phenomenon during the (much slower) substitution upon  $\text{Ir}_4(\text{CO})_{12}$ ; its direct reaction with triphenylphosphine showed infrared evidence only for starting material and for the trisubstituted product.

We selected the iridium system for detailed examination as crystallographic data were available for I,<sup>10</sup> III,<sup>11,12</sup> and IV.<sup>11,12</sup> The infrared spectrum of II confirms that it has the related structure shown.<sup>13,14</sup> Furthermore, all four compounds are kinetically inert at room temperature: carbonylation of IV at high



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(13) II, not previously reported, has  $\nu_{\text{CO}}$  at 2090, 2058, 2023, 1846, and 1823  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , strongly resembling III and suggesting an analogous structure. The stereochemistry shown at the substituted metal atom is that observed for the similar compound  $\text{CH}_3\text{CCO}_5(\text{CO})_5\text{-}(\text{P}(\text{C}_6\text{H}_{11}))_3$ .<sup>14</sup>

(14) (a) T. W. Matheson, B. H. Robinson, and W. S. Tham, *J. Chem. Soc. A*, 1457 (1971); (b) B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, **6**, 73 (1973).

Table I

Reaction	Rate law	Rate constants <sup>a</sup>	Obsd specific rates <sup>b</sup> × 10 <sup>6</sup> , sec <sup>-1</sup> , 75°	Relative specific rates <sup>b</sup> (75°)	ΔH <sup>‡,a</sup> kcal/mol	ΔS <sup>‡,a</sup> eu
I → II	k <sub>1</sub> [I][PPh <sub>3</sub> ] <sup>c</sup>	5.6 (2) × 10 <sup>-3</sup> M <sup>-1</sup> sec <sup>-1</sup> (106°)	1.5 <sup>d</sup>	1 <sup>d</sup>	20.6 (6)	-22 (2)
II → III	k <sub>2</sub> [II] <sup>e</sup>	8.8 (3) × 10 <sup>-6</sup> sec <sup>-1</sup> (75°)	44	30	31.8 (7)	+14 (2)
III → IV	k <sub>3</sub> [III] <sup>e</sup>	1.4 (1) × 10 <sup>-3</sup> sec <sup>-1</sup> (75°)	1380	920	31.0 (5)	+17 (2)

<sup>a</sup> Numbers in parentheses are least-squares standard deviations in least significant digit. <sup>b</sup> Corrected for the number of substitutable carbonyl sites assumed: 12 for I, 2 for II, 1 for III (see text). <sup>c</sup> First-order term contributes less than 10% to  $k_{\text{obsd}}$  at  $[\text{PPh}_3] = 3.82 \times 10^{-2} \text{ M}$ . <sup>d</sup> Extrapolated from higher temperatures at  $[\text{PPh}_3] = 3.82 \times 10^{-2} \text{ M}$ . <sup>e</sup> Second-order term contributes less than 10% to  $k_{\text{obsd}}$  at  $[\text{PPh}_3] = 3.82 \times 10^{-2} \text{ M}$ .

temperature gives II and III<sup>11,15</sup> in mixtures from which they can be separated.

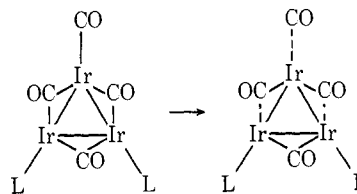
Rates of the substitution reactions in chlorobenzene under nitrogen were determined by following the decrease in sharp infrared carbonyl absorbances of the starting materials I, II, and III. The only product observed was invariably IV. Rate laws, specific rates,<sup>16-18</sup> and activation parameters for substitution on I, II, and III are given in Table I. The activation parameters for initial substitution on I imply an associative process; the observed rate constant is dependent on the nature and concentration of phosphine as expected for a reaction second-order overall. The activation parameters for substitution on II and III, as well as the observed independence of concentration and nature of entering phosphine, correspond well to the observed first-order rate law and to a classic dissociative mechanism. Under 50 psi of CO substitution on III slowed by a factor of 3.

Of course carbonyl dissociation from I must occur at a finite rate, even though its contribution to the phosphine substitution rate is clearly much less than that of the observed second-order term. The maximum possible contribution from a dissociative path can be estimated at  $2 \times 10^{-6} \text{ sec}^{-1}$  at 106°, or less than  $4 \times 10^{-7} \text{ sec}^{-1}$  at 75°. Thus the increase in the rate of carbonyl ligand dissociation from unsubstituted I to disubstituted III is a factor of over 42,000 at 75°.

This remarkable increase offers an example of a phenomenon suggested previously,<sup>7</sup> the increase in substitution lability usually associated with the change from a nonbridged to a bridged system. Substitution on I triggers a change to a bridged structure, just as most substituents do on the  $\text{RCCo}_3(\text{CO})_9$  system;<sup>14,19</sup>

here a change in the dissociation rate, and consequently in the observed mechanism and rate of substitution, results. However, the further increase in the substitution rate of the also-bridged III shows that acceleration by prior substitution can be transmitted by other means than such structural changes.

There is no evidence from the infrared spectra that any Ir-C bond orders are other than as expected:  $\text{I} \leq \text{II} \leq \text{III}$ . A possible explanation of these relative rates involves stabilization of the dissociative transition state by semibridging carbonyl groups,<sup>20</sup> which may well be more readily formed by initially bridged clusters. Perhaps the further substitution (from II to



III) increases the asymmetry in the electron density distribution and hence the ease with which such distortion occurs.

The long-range interaction in  $\text{Ir}_4(\text{CO})_{12}$  is thus chemically significant; each substitution greatly alters the chemical properties of other substitution sites, in a direction contrary to that observed with mononuclear complexes. These results identify the  $\text{Ir}_4$  unit as one likely to possess a unique and interesting chemistry.

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(16) Specific rates are calculated with statistical correction factors equal to the number of substitutable sites related by symmetry to that to be occupied by the entering ligand. The validity of this type of correction depends upon the presumption that during the lifetime of the coordinatively unsaturated intermediate there is no intramolecular rearrangement of carbonyl groups (known to be rapid for related isolable molecules<sup>17,18</sup>). There is no way of assessing the importance of such processes here.

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(19) The apparent<sup>14</sup> lack of rate acceleration upon substitution on  $\text{RCCo}_3(\text{CO})_9$  may reflect the considerably greater steric interference of successive substituents in the cobalt systems or the type and magnitude of interaction among metals observed here in the iridium system may simply not be present.

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