of 10^3 in the rates of rearrangement of **2a** and **2b** in benzonitrile at 60° is indeed surprising. We have confirmed this finding using acetonitrile-d_3 as the solvent at 60° and observing first-order rates of 2.30 × 10^{-3} and 3.62 × 10^{-6} sec^{-1} for **2a** (16.0 wt %) and **2b** (12.5 wt % initial concentration), respectively.

The amount of rate difference possibly caused by a "*gem* effect"[8] is estimated to be relatively small in the case under consideration. The curious circumstance of one ring system being converted into a second eliminates the general "*gem*-dimethyl effect" discussed by Allinger and Zalkow[8b] since that effect depends on ring–chain transformations and free rotation in the chain form. In this regard also, examination of Dreiding models indicates maximum eclipsing of the substituents in the five-membered ring and hence a tendency to raise the ground-state energy of **2b** relative to **2a**. The "Thorpe–Ingold effect," which is a special case of the *gem* effect involving bond angle deformation, is now thought to contribute a relatively small amount[8c] compared with the differences under consideration. Finally, steric hindrance to solvation is thought to contribute to the *gem* effect.[8d] However, steric hindrance to solvation of the migrating anion, which would be the critical consideration here, is in reality an integral part of, and inseparable from, the ionization process. We therefore conclude that steric hindrance to ionization is the major factor contributing to the rearrangement rate differences of **2a** and **2b**.

While the processes occurring after reaching the transition state (**3**) do not affect the kinetics in the present instances, they are worthy of brief mention. The previous workers[6] have found that **2a** rearranges to **4**[9] thermally and that **4** is converted to **7a** both thermally[6c] and by heating with base.[6a] Under the conditions used here, the rate of conversion of **4** to **7a** is negligible and the first-order rate constants are measured by following the conversion of **2a** to **4**[9] and **5**.[9] On the other hand, the much slower rate for rearrangement of **2b** and the slightly higher temperatures required allow successful competition of the elimination and ring-opening steps, and intermediates corresponding to **4** and **5** are never present in sufficient quantities for detection. The first-order rate constants are therefore measured by following the directly observed conversion of **2b** to 2-chloro-5-methylhexa-2,4-dienal (**7b**).[10]

(8) (a) T. C. Bruice and W. C. Bradbury, *J. Am. Chem. Soc.*, **90**, 3808 (1968), and previous articles in this series; (b) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960); (c) P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961); (d) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *ibid.*, **81**, 2698 (1959).

(9) The kinetics studies were done by standard methods using nmr spectroscopy to measure concentrations.[7a] While in ref 6 only formation of **4** by rearrangement of **2a** is reported, we have found not less than 100 times that **2a** neat and in CD$_3$CN or C$_6$H$_5$CN always leads to approximately 1:1 mixtures of both isomers **4** and **5**. Characterization of **4** and **5** will be published elsewhere.

(10) Nmr (CDCl$_3$-TMS, 60 MHz): 2Me-5, δ 2.01 and 2.03 (small couplings each); H-3, δ 6.53 ($J_{3,4}$ = 11.2 Hz; small couplings to both methyls); H-4, δ 7.51 ($J_{4,3}$ = 11.2 Hz; possible small coupling to a methyl); CHO, δ 9.60 (singlet); mp 70–71°; λ (MeOH) 299 nm (log ε 4.58). *Anal.* Calcd for C$_7$H$_9$ClO: C, 58.1; H, 6.3; Cl, 24.5. Found: C, 58.2; H, 6.2; Cl, 24.7.

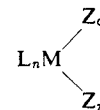**Roy C. De Selms, Ursula T. Kreibich**
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

Model Compounds for Transitional Metal Intermediates in Homogeneous Catalysis[1]

Sir:

In many reactions of unsaturated organic compounds catalyzed by metal complexes, species of the type

$$L_nM \begin{matrix} \nearrow Z_\sigma \\ \searrow Z_\pi \end{matrix}$$

where Z_σ is H$^-$ or a σ-bonded organic moiety and Z_π is a π-bonded organic moiety, have often been postulated to be intermediates.[2] In almost all homogeneous catalytic reactions, however, these intermediates are not isolable. Since previous work in this laboratory has shown that cyanocarbons[3] form more stable complexes with noble metal substrates than do the analogous hydrocarbons, it seemed that it might be possible to isolate and characterize compounds analogous to some of these intermediates of catalytic importance by employing cyanocarbons as the organic reactants instead of hydrocarbons. In order to test this hypothesis, reactions of various cyanoolefins and other activated olefins and acetylenes with the five-coordinate complexes MH(CO)(Ph$_3$P)$_3$ (M = Ir, Rh) have been investigated. These complexes are known to be good catalysts[4,5] for homogeneous hydrogenation of simple olefins and/or acetylenes.

Cyanoolefins and other activated olefins react with IrH(CO)(Ph$_3$P)$_3$ (I) by displacing one molecule of triphenylphosphine to give hydrido-olefinic complexes of the type IrH(CO)(Ph$_3$P)$_2$(olefin). For example, addition of a tenfold excess of fumaronitrile, NCCH=CHCN, to a bright yellow benzene solution of I at 50° causes the solution to lighten in color, and in a few minutes a white precipitate forms. Recrystallization of the solid from CH$_2$Cl$_2$-CH$_3$OH gives colorless needles of a compound whose elemental analysis indicates a fumaronitrile/triphenylphosphine/iridium ratio of 1:2:1. *Anal.* Calcd for C$_{41}$H$_{33}$N$_2$OP$_2$Ir: C, 59.77; H, 4.04; N, 3.40; P, 7.52; mol wt, 824. Found: C, 59.39; H, 4.23; N, 3.31; P, 7.53; mol wt, 708 (osmometric in CHCl$_3$). The compound is formulated as a hydrido-olefinic complex (compound IIa of Figure 1) rather than the "insertion" product, Ir[-CH(CN)CH$_2$CN]-(CO)(Ph$_3$P)$_2$, which would have the same elemental analysis, on the basis of its infrared spectrum[6] ($\nu_{C\equiv N}$,

(1) Part VI in the series Metal Complexes of Cyanocarbons: (a) part V, C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 798 (1968); (b) part IV, P. Uguagliati and W. H. Baddley, *ibid.*, **90**, 5446 (1968); (c) part III, W. H. Baddley, *ibid.*, **90**, 3705 (1968); (d) part II, W. H. Baddley, *ibid.*, **88**, 4545 (1966); (e) part I, W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(2) For example, see J. Halpern, Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., 1968, p 1; B. R. James, *Coord. Chem. Rev.*, **1**, 505 (1966).

(3) W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2**, 7 (1968).

(4) L. Vaska, *Inorg. Nucl. Chem. Letters*, **1**, 89 (1965).

(5) C. O'Connor, G. Yagupsky, D. Evans, and G. Wilkinson, *Chem. Commun.*, 420 (1968); C. O'Connor and G. Wilkinson, *J. Chem. Soc., A*, 2665 (1968).

(6) Values quoted are for a hexachlorobutadiene mull spectrum. The same type spectrum of the analogous deuterio complex exhibits bands at 2215 s ($\nu_{C\equiv N}$) and 2021 vs ($\nu_{C\equiv O}$) cm^{-1} with no absorption being observed in the 800–900 cm^{-1} range. The fact that $\nu_{C\equiv O}$ in the hydrido and deuterio complexes is different arises from a resonance interaction between Ir—H and C≡O stretching modes, and a *trans* arrangement of hydride and carbon monoxide is indicated as shown in Figure 1. For discussions of the use of resonance interaction to establish stereochemistry, see L. Vaska, *J. Am. Chem. Soc.*, **88**, 4100
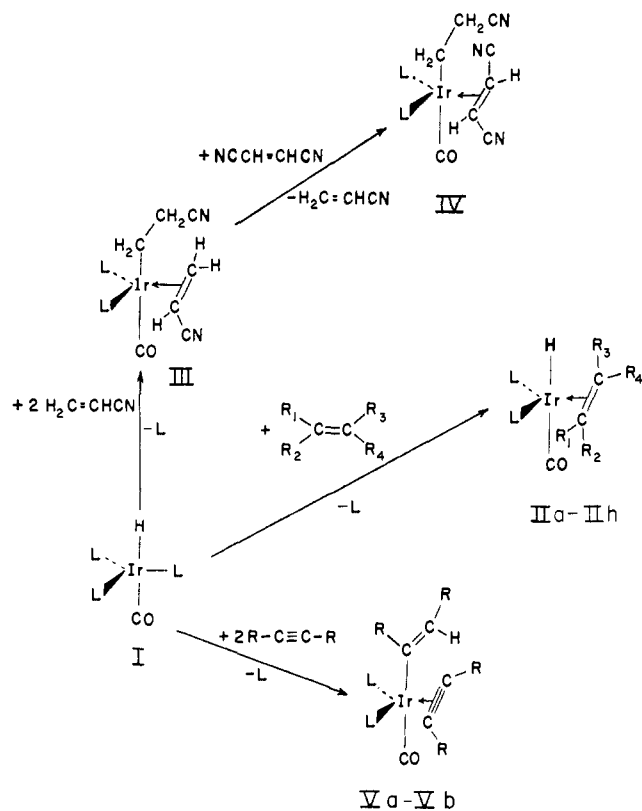
Figure 1. Reactions of IrH(CO)L₃ (L = Ph₃P) with activated olefins and acetylenes. The trigonal-bipyramidal structure has been confirmed for compound IIa. Compound III is depicted arbitrarily as containing a β-cyanoethyl group. For compounds IIa–IIh: IIa, $R_1 = R_4 = CN$, $R_2 = R_3 = H$; IIb, $R_1 = R_2 = R_3 = R_4 = CN$; IIc, $R_1 = Ph$, $R_4 = CN$, $R_2 = R_3 = H$; IId, $R_1 = R_4 = COOH$, $R_2 = R_3 = H$; IIe, $R_1 = R_4 = COOCH_3$, $R_2 = R_3 = H$; IIf, $R_2 = R_4 = COOH$, $R_1 = R_3 = H$; IIg, $R_2 = R_4 = COOCH_3$, $R_1 = R_3 = H$; IIh, $R_1 = Ph$, $R_4 = COOH$, $R_2 = R_3 = H$. For Compound Va–Vb: Va, $R = CF_3$; Vb, $R = COOCH_3$.

2215 s; ν_{Ir-H}, 2105 s; $\nu_{C\equiv O}$, 1987 vs; δ_{Ir-H}, 830 w cm⁻¹), high-field nmr spectrum (multiplet at τ 21.13 in CH_2Cl_2), and crystal structure.[7] Compounds IIb–IIh have been obtained with other cyanoolefins (cinnamonitrile, tetracyanoethylene) and activated olefins (fumaric acid, dimethyl fumarate, maleic acid, dimethyl maleate, cinnamic acid). While an acrylonitrile complex analogous to complexes IIa–IIh, IrH(CO)(Ph₃P)₂(acrylonitrile), has been obtained from IrH(CO)(Ph₃P)₂, the reaction of I with neat acrylonitrile at 60° for 0.5 hr gives a white compound (III) whose elemental analysis best fits a formulation in which the acrylonitrile/triphenylphosphine/iridium ratio is 2:2:1. *Anal.* Calcd for $C_{43}H_{33}N_2OP_2Ir$: C, 61.00; H, 3.90; N, 3.30; P, 7.31. Found: C, 60.22; H, 4.66; N, 3.62; P, 7.14. An infrared mull spectrum of III includes bands at 2205 m ($\nu_{C\equiv N}$) and 1965 vs ($\nu_{C\equiv O}$) cm⁻¹, but bands ascribable to ν_{Ir-H} and δ_{Ir-H} are not observed. Also, the nmr spectrum of III in CH_2Cl_2 shows no signal in the τ 10–30 region. It is suggested that III is Ir(-CH₂CH₂CN)(CO)(Ph₃P)₂(NCCH=CH₂), which probably results from initial formation of a hydrido-olefinic complex analogous to II. The π-bonded olefin in such a compound could then "insert" into the Ir–H bond, and the four-coordinate σ-cyanoethyl complex so formed

could add a second molecule of acrylonitrile to give the σ-cyanoethyl-π-acrylonitrile complex III. Chemical evidence for this formulation of III comes from the fact that the π-bonded acrylonitrile in III is quite labile and is easily displaced by other olefins. Thus, reaction of III with fumaronitrile gives white crystals of IV. *Anal.* Calcd for $C_{43}H_{36}N_3OP_2Ir$: C, 59.69; H, 4.20; N, 4.86; P, 7.17. Found: C, 59.94; H, 4.26; N, 4.73; P, 7.28. Infrared: 2220 m ($\nu_{C\equiv N}$), 2210 sh ($\nu_{C\equiv N}$), 2035 vs ($\nu_{C\equiv O}$) cm⁻¹.

Acetylenes also react readily with I. Products could not be isolated from the dark mixtures obtained from reaction of dicyanoacetylene, methyl propiolate, or ethyl phenylpropiolate with I, but when hexafluorobutyne is bubbled through a benzene solution of I at 70° for 15 min, off-white microcrystals may be obtained after removal of solvent and recrystallization of the residue from CH_2Cl_2-hexane. Analysis indicates that two molecules of C_4F_6 are present per iridium atom. *Anal.* Calcd for $C_{45}H_{31}F_{12}OP_2Ir$: C, 50.50; H, 2.92; F, 21.32; P, 5.78. Found: C, 50.24; H, 3.22; F, 21.06; P, 5.80. The infrared mull spectrum includes bands at 1991 vs ($\nu_{C\equiv O}$), 1742 s ($\nu_{C=C}$), and 1610 m ($\nu_{C=C}$) cm⁻¹, and there is no indication of an Ir–H bond; the compound (Va) is formulated as shown in Figure 1. A compound of analogous formulation (Vb) was obtained with dimethyl acetylenedicarboxylate. The ¹H nmr spectrum of Vb is consistent with this formulation in that four different signals are observed for the CH_3 protons, these being at τ 6.40, 6.58, 6.68, and 6.77, and having relative intensities of 1:1:1:1. A white, crystalline compound obtained from the reaction of phenylacetylene with I has an elemental constitution analogous to Va and Vb, but it is structurally different in that an Ir–H bond is present.

Several points are to be made in connection with these results. First of all, in the homogeneous hydrogenation of olefins, a scheme as given by eq 1 has been invoked. In only a few instances[1b,8] have hydrido-olefinic com-

$$H \qquad\qquad H \qquad\qquad\qquad H$$
$$L_nM + \quad \overset{\textstyle \diagdown}{\underset{\textstyle \diagup}{C}}=\overset{\textstyle \diagup}{\underset{\textstyle \diagdown}{C}} \quad \rightleftharpoons \quad L_nM \leftarrow \overset{|}{\underset{|}{\overset{C}{\underset{C}{\|}}}} \quad \overset{H_2}{\longrightarrow} \text{ alkane} + L_nM \quad (1)$$

plexes been isolated. The syntheses of compounds IIa–IIh are, therefore, of interest in regard to homogeneous hydrogenation. It may not be true for all transitional metal homogeneous hydrogenation catalysts that the H and olefin need be simultaneously coordinated to the metal,[9] but these results support the idea that such simultaneous coordination is operative when IrH(CO)(Ph₃P)₃ functions as a catalyst.

Secondly, in the polymerization of olefins by Ziegler–Natta catalysts and other transition metal catalysts,[10] intermediates containing both σ-bonded and π-bonded organic moieties have been proposed. Such an intermediate, π-CpRhCl(-C₂H₅)(π-C₂H₄), was detected[11] in solution by nmr but was not isolated. The synthesis of compound III apparently is the first instance of the isolation of such a compound, and on the basis of this preparation, it can be anticipated that MH(CO)(Ph₃P)₃
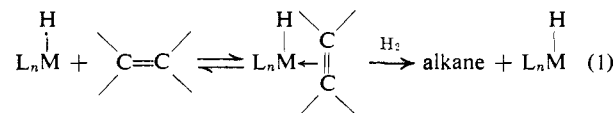
(1966); P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

(7) K. N. Muir and J. A. Ibers, private communication.

(8) S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, 1301 (1964); H. A. Tayim and J. C. Bailar, *J. Am. Chem. Soc.*, **89**, 4330 (1967).

(9) J. Halpern and L.-Y. Wong, *ibid.*, **90**, 6665 (1968).

(10) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(11) R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

(M = Rh, Ir) will catalyze the polymerization of olefinic hydrocarbons.

Finally, in the linear polymerization of acetylenes catalyzed by transition metal substrates, a Ziegler–Natta type of process involving σ-vinyl-π-acetylene complexes may be operative.[12] The compounds Va

R—C(=C(R)(H))...L$_n$M
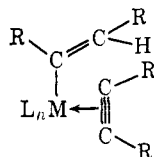
and Vb are the first examples of isolated compounds analogous to these intermediates.

A number of complexes have been prepared from the reactions of activated olefins and acetylenes with RhH(CO)(Ph$_3$P)$_3$, but these compounds, which are generally not analogous structurally to the iridium complexes reported herein, will be described elsewhere.

Acknowledgment. This work was supported by the National Science Foundation, Grant GP-6769.

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The Structure of

(AsMe$_2$)C=CCF$_2$CF$_2${(AsMe$_2$)Fe$_3$(CO)$_9$}

Sir:

The chelating properties of ditertiary arsines have been extensively studied; in particular, their ability to form complexes with metal carbonyls is well known. The recently discovered[1] compound

$$(CH_3)_2AsC=CAs(CH_3)_2CF_2CF_2$$

(ffars) acts as both a bidentate and tridentate[2] ligand (the double bond acting as the third electron donor in the latter case).

If the product of the reaction between ffars and Fe$_3$(CO)$_{12}$ is refluxed in benzene, a compound which analyzes as ffars–Fe$_3$(CO)$_9$ may be obtained.[3] The difficulty which is encountered in formulating a reasonable chemical structure for this molecule prompted this structure analysis. Figure 1 illustrates the structure, and it can readily be seen that the empirical formula gives no structural guidance since the ligand suffered cleavage of an AsMe$_2$ group, while the Fe$_3$(CO)$_{12}$ molecule has undergone skeletal changes. The nearest precedent to this type of rearrangement is in the recent[4] report of the compound formerly thought to be [Ni-(diars)$_3$](ClO$_4$)$_2$ (diars = σ-phenylenebis(dimethylarsine)) as [Ni(diars)(triars)](ClO$_4$)$_2$.

The crystals of composition ffars–Fe$_3$(CO)$_9$ are monoclinic; a = 13.70, b = 19.00, c = 9.42 Å; β

(1) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, 6, 2256 (1967).
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(3) W. R. Cullen, private communication.
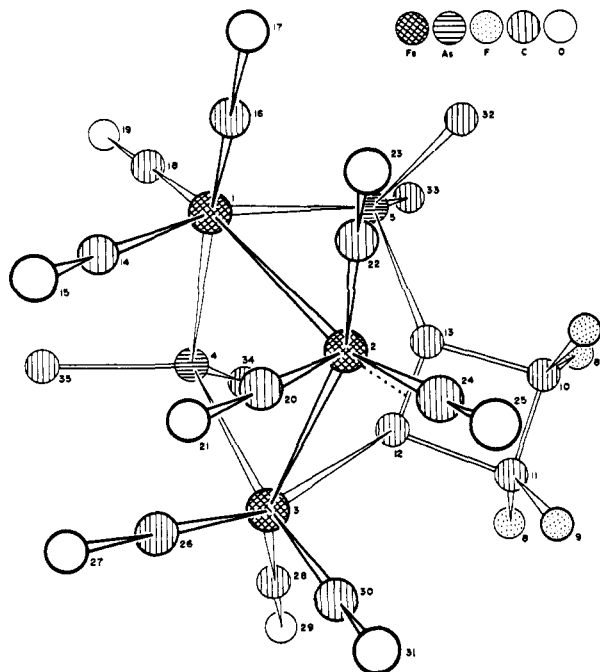(4) B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Am. Chem. Soc.*, 90, 474 (1968).

Figure 1. (AsMe$_2$)C=CHCF$_2$CF$_2${(AsMe$_2$)Fe$_3$(CO)$_9$}.

= 82.8°; space group P2$_1$/n. The observed density of 2.03 g cm^{-3} by flotation is consistent with a unit cell containing four molecules; 2265 intensities were measured using Mo Kα scintillation counter data of which 1364 were regarded as observed. The heavy atom positions were determined from the three-dimensional Patterson function; all the light atoms were located from a subsequent electron density difference map. Isotropic block diagonal least-squares refinement has led to a conventional R of 0.10.

The geometry of the molecule is illustrated in Figure 1 which together with the interatomic distance and angles given in Table I indicates that the structure may best be

Table I. Selected Interatomic Distances (Å) and Angles (deg)[a]

Bond	Distance
Fe(1)–Fe(2)	2.91 (1)
Fe(1)–As(4)	2.36 (1)
Fe(1)–As(5)	2.31 (1)
Fe(2)–Fe(3)	2.66 (1)
Fe(3)–As(4)	2.36 (1)
Fe(3)–C(12)	1.87 (3)
Fe–C(carbonyl)	1.69–1.78
Fe(2)–C(12)	2.05 (3)
Fe(2)–C(13)	2.16 (3)
Fe(2)–midpoint[b]	1.97 (3)
As–C(methyl)	1.92–1.97
C–O(carbonyl)	1.14–1.20
C–F	1.32–1.36
C(10)–C(11)	1.51 (4)
C(10)–C(13)	1.52 (4)
C(11)–C(12)	1.60 (4)
C(12)–C(13)	1.47 (4)

Angle	Value
As(4)–Fe(1)–Fe(2)	76.8 (2)
As(5)–Fe(1)–Fe(2)	70.7 (2)
As(4)–Fe(1)–As(5)	90.1 (2)
Fe(1)–Fe(2)–Fe(3)	88.6 (2)
Fe(2)–Fe(3)–As(4)	82.2 (2)
Fe(1)–As(4)–Fe(3)	111.3 (2)

[a] Values in parentheses are the estimated standard deviations in the last significant figure. [b] Midpoint of the C(12)–C(13) bond.