tion condition prevents the subsequent thermal isomerization of the products.

References and Notes

(1) (a) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N.Y., 1971, p 254, 462; (b) R. Barlet and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3729 (1969); (c) K. J. Drachenberg and H. Hopf, *Tetrahedron Lett.*, 3267 (1974); (d) D. P. G. Hamon and V. C. Trenerry, *ibid.*, 1371 (1974); (e) R. B. Reinarz and G. J. Fonken, *ibid.*, 441 (1974); (f) D. W. Brown, M. E. Hendrick, and M. Jones, Jr., *ibid.*, 3951 (1973); (g) R. B. Reinarz and G. J. Fonken, *ibid.*, 4591, 4595 (1973); (h) L. A. Paquette, G. Zon, and R. T. Taylor, *J. Org. Chem.*, **39**, 2677 (1974).

(2) T. Hiyama, S. Takehara, K. Kitatani, and H. Nozaki, *Tetrahedron Lett.*, 3295 (1974).

(3) (a) M. Braun and D. Seebach, *Angew. Chem.*, **86**, 279 (1974); (b) A. Schmidt and G. Köbrich, *Tetrahedron Lett.*, 2561 (1974); (c) D. Seyferth and R. L. Lambert, Jr., *J. Organomet. Chem.*, **55**, C53 (1973); (d) R. L. Lambert, Jr., and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).

(4) For example, lithiation of II (R^1 = Ph, R^2 = H) with *n*-butyllithium in the presence of PhC≡CCu and in the absence of alkyl halides, followed by the addition of HMPA, afforded *n*-butylbromocyclopropane (III) (R^1 = Ph, R^2 = H, R = n-C_4H_7) in a 35% yield (>97% cis). This fact suggests that the *n*-butyl bromide generated by the lithium-bromine exchange reacts with the resulting carbenoid by virtue of HMPA.

(5) The lithium carbenoid generated from 1,1-dichlorocyclopropane is recorded to be relatively configurationally stable. See G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).

(6) The reactive species seem to be neither a copper carbenoid nor a copper ate complex. The reagent thus prepared actually reacts with cyclohexanone and with crotonaldehyde at carbonyl carbon. Probably, the complexation of the lithium carbenoid with Cu(I) is responsible to decrease the basicity of the carbanion.

(7) The product may be due to hydrogen halide eliminated from the alkyl halide.

(8) (a) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3283 (1964); (b) H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *ibid.*, **90**, 5222 (1968).

(9) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967); *ibid.*, **90**, 5615 (1968); *Tetrahedron Lett.*, 315 (1970).

(10) L. V. Chau and M. Schlosser, *Synthesis*, 115 (1974).

(11) J. Reucroft and P. G. Sammes, *Q. Rev., Chem. Soc.*, **25**, 135 (1972).

(12) Alkylidenecyclopropane synthesis: (a) W. E. Billups, W. Y. Chow, K. H. Leavel, and E. S. Lewis, *J. Org. Chem.*, **39**, 274 (1974); (b) M. S. Newman and G. M. Fraunfelder, *ibid.*, **39**, 251 (1974); (c) T. Sasaki, S. Eguchi, and T. Ogawa, *ibid.*, **39**, 1927 (1974); (d) P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562 (1974); (e) A. S. Kende and E. E. Riecke, *J. Chem. Soc., Chem. Commun.*, 383 (1974); (f) R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969).

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Halide Catalysis of the Oxidative Addition of Alkyl Halides to Rhodium(I) Complexes

Sir:

The oxidative addition reaction has become widely recognized as one of the most characteristic reactions of d^8 and d^{10} complexes. Despite the importance of the oxidative addition reaction of methyl iodide to rhodium complexes, detailed studies of such reactions with rhodium(I) phosphine complexes have encountered several difficulties of interpretation.[1] The generally accepted first step in these reactions is nucleophilic attack of the metal complex on the carbon of the methyl iodide.[2] Since halide ions might act to displace neutral ligands to produce highly nucleophilic rhodium(I) anions and halide ions might well be present in systems involving complexes with labile phosphine and arsine ligands in methyl iodide, we felt it worthwhile to explore the effect of halide ions on methyl iodide addition reactions. Accordingly we studied the effect of Bu_4NI on the rate of methyl iodide addition to $[Rh(Ph_3As)_2(CO)I]$, $[Rh(Ph_3Sb)_2(CO)I]$,[3] and $[Rh(Ph_3P)_2(CO)I]$. The reaction involving the triarylstibine complex is a particularly interesting test because triarylstibines are not quaternized by alkyl iodides, and hence this system should be free of halide ions.

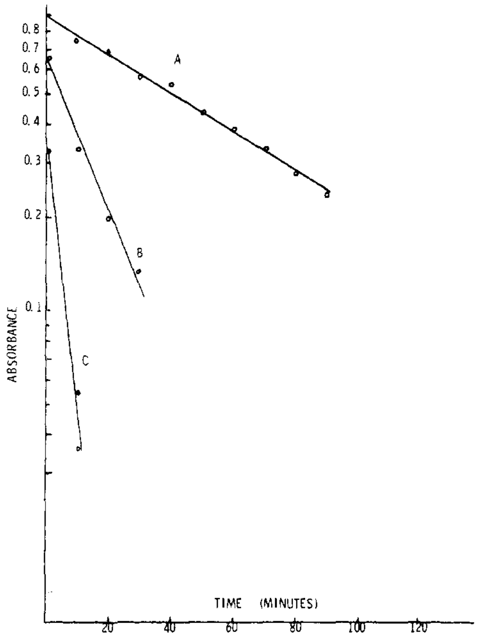


Figure 1. The effect of halide ion on the rate of reaction of $[Rh(Ph_3As)_2(CO)I]$ (0.03 M) with CH_3I (3.25 M) in CH_2Cl_2: A, with no added halide ion; B, Bu_4NI (0.0003 *M*) added; C, Bu_4NI (0.003 *M*) added.

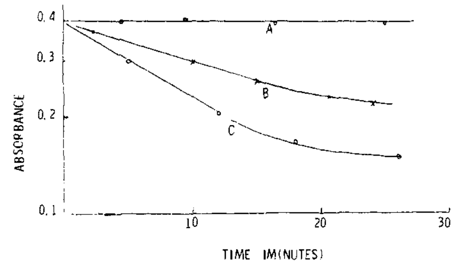


Figure 2. The effect of halide ion on the rate of reaction of $[Rh(Ph_3Sb)_2(CO)I]$ (0.03 *M*) with CH_3I (3.25 *M*) in CH_2Cl_2: A, with no added halide ion; B, with Bu_4NI (0.003 *M*) added; C, with Bu_4NI (0.006 *M*) added.

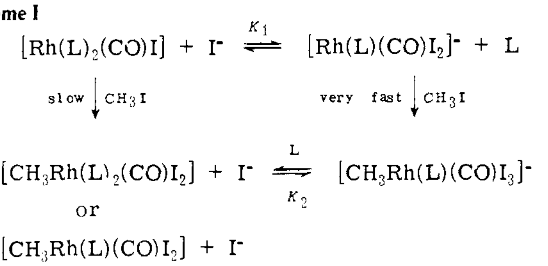
The results of these studies are presented in Figures 1 and 2.[4] It can be seen that added halide ions exert a powerful catalytic effect on the rate of oxidative addition of methyl iodide to the arsine and stibine complexes. However, by contrast there is a negligible effect on the rate of reaction with the phosphine complex.

In so far as increased nucleophilicity should increase the rate of reaction with methyl iodide, a logical mode of rate enhancement by halide ion is generation of anionic rhodium species. Accordingly we have studied the following equilibria spectrophotometrically.[5]

$$[\mathrm{Rh(L)_2(CO)I}] + \mathrm{I^-} \rightleftharpoons [\mathrm{Rh(L)(CO)I_2}]^- + \mathrm{L}$$

We find that the equilibrium constants in CH_2Cl_2 at 22° are as follows: for L = Ph_3P, $K < 3 \times 10^{-5}$; for L = Ph_3As, $K \approx 0.05$; and for L = Ph_3Sb, $K \approx 2 \times 10^{-3}$. It is apparent that the neutral species are strongly favored in systems containing small amounts of excess halide, but of course a mechanism involving anionic species as intermediates might still be possible if the rate of reaction of the anionic species with methyl iodide greatly exceeds that of the neutral species. We therefore studied the relative rate of reaction of the anionic and neutral species with methyl iodide. While we find that the anionic rhodium species react so rapidly at room temperature, even at very low concentrations of meth-

Scheme I



$$\begin{tikzcd}
{[Rh(L)_2(CO)I] + I^-} \arrow[r, shift left, "K_1"] \arrow[d, "slow"', "CH_3I"] & {[Rh(L)(CO)I_2]^- + L} \arrow[l, shift left] \arrow[d, "very\ fast"', "CH_3I"] \\
{[CH_3Rh(L)_2(CO)I_2] + I^-} \arrow[r, shift left, "L"] & {[CH_3Rh(L)(CO)I_3]^-} \arrow[l, shift left, "K_2"] \\
\text{or} & \\
{[CH_3Rh(L)(CO)I_2] + I^-} &
\end{tikzcd}$$

yl iodide, that we were unable to obtain accurate kinetic data; it is still possible to place a lower limit for the relative rates of $>10^5$; i.e., the anionic species are far more reactive than the neutral rhodium species in this type of oxidative addition.

We therefore propose that the catalytic effect of halide ions in these systems arises from the type of mechanism shown in Scheme I.

The liberation of free halide ion from a rhodium(III) complex is necessary in the above scheme. Now it is well known that the alkyl group on a transition metal is a powerful trans labilizing ligand, and indeed the reaction of $[Rh(Ph_3P)_3Cl]$ with CH_3I results in formation of a five-coordinated rhodium(III) complex with the coordination position trans to the methyl group being vacant.[6] Thus it is reasonable to assume that the halide ion is liberated from an anionic rhodium(III) species with sufficient speed that the catalytic effect is produced. In agreement with this scheme the addition of excess triphenylstibine to the $[Rh(Ph_3Sb)_2(CO)I]$-CH_3I reaction inhibits the catalytic effect of halide. Also the reaction is first order in added halide ion and methyl iodide, at least during the first part of the reaction in the stibine complex system. The gradual loss of rate which occurs in the stibine complex system at high conversions (see Figure 2) is not accompanied by any marked spectroscopic change and it seems likely that an equilibrium between the rhodium(III) species, as shown in Scheme I, is reducing the amount of free halide in the system and hence the overall reaction rate.

It is apparent from this study that trace levels of halide ion can play an important role in reactions involving nucleophilic behavior by a labile metal complex. The lack of halide catalysis with the phosphine complex presumably results from the position of the equilibrium between neutral and anionic rhodium(I) species in the presence of halide ion (vide supra). This is not to imply that ionic species are not also important in the reaction of methyl iodide with $[Rh(Ph_3P)_2(CO)I]$ since we find that the conductivity of the solutions steadily increases over the course of the reaction. By contrast no evidence of halide catalysis in the reaction of $[Ir(L)_2(CO)X]$ complexes with methyl iodide is observed and neither is there an appreciable increase in conductivity during these reactions.

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References and Notes

(1) I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).

(2) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

(3) $[Rh(PH_3Sb)_2(CO)I]$ was charged as the solid complex $[Rh(Ph_3Sb)_3(CO)I]$ which is apparently completely dissociated into $[Rh(Ph_3Sb)_2(CO)I]$ + Ph_3Sb in methylene chloride and chloroform as judged from molecular weight determinations. This dissociation phenomena has also been documented for the arylstibine chloro-rhodium complexes by P. E. Garrou and G. E. Hartwell, *J. Organomet. Chem.*, **69**, 445 (1974). We also studied methyl iodide addition to the chloro complex and find the same behavior as described here for the iodo complex. Detailed studies of chloro complexes were not performed, however, after it was observed that halide exchange was occurring in the system $[Rh(Ph_3P)_2(CO)Cl]$ + CH_3I. Similarly we observed that chloride and bromide salts would catalyze the reactions as described above for $[Bu_4N]I$.

(4) The products of methyl iodide addition to $[Rh(Ph_3P)_2(CO)X]$ and $[Rh(Ph_3As)_2(CO)X]$ are mixtures of compounds containing both methyl-rhodium bonds and acetyl-rhodium as indicated by both infrared and NMR data.[1] The reaction product of $[Rh(Ph_3Sb)_2(CO)I]$ + CH_3I can be isolated as an orange solid by evaporation and recrystallization from CH_2Cl_2-CH_3OH. This material analyzes as the simple adduct $[RhI_2$-$CH_3(CO)(Ph_3Sb)_2]$. Anal. Calcd for $C_{38}H_{33}I_2ORhSb_2$: C, 41.28; H, 2.98; I, 22.96. Found: C, 41.23; H, 3.15; I, 23.65. The infrared spectrum shows γCO at 2049 cm^{-1} and the PMR spectrum of this material shows the CH_3-Rh at $\delta - 1.30$ ppm (downfield from TMS) with $J(RhH) = 2$ Hz. The compound shows no tendency to isomerize to an acetyl-containing species. The same product is formed with or without the halide catalyst.

(5) Salts of the anions $[Rh(L)(CO)X_2]^-$ have been prepared by D. E. Morris et al. by reaction of compounds of the type $[Rh(L)(CO)X]_2$ with halide salts (private communication).

(6) P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).

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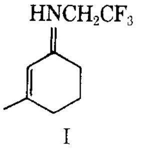
Primary Amine Catalysis of the Isomerization of a β,γ-Unsaturated Ketone to Its α,β-Unsaturated Isomer. A Possible Model for Enzymatic Double Bond Migration in Unsaturated Ketones

Sir:

Enzymes which catalyze the interconversion of β,γ-unsaturated ketones and their α,β-unsaturated isomers have been objects of growing interest lately. The most thoroughly characterized enzymes of this type are the Δ^5-3-ketosteroid isomerases which catalyze the isomerization of β,γ-unsaturated-3-ketosteroids to their α,β-unsaturated isomers.[1] The enzyme from *Pseudomonas testosteroni* has been investigated in some detail, although little is known about the mechanism of the mammalian enzymes. The reverse reaction, α,β to β,γ isomerization, is catalyzed in the prostaglandin series by prostaglandin A isomerase.[2] In addition, Abeles[3] has postulated that the mechanism of action of 2-keto-3-deoxy-L-arabonate dehydratase includes a similar isomerization as one step. We wish to report that primary amines are capable of catalyzing the isomerization of β,γ-unsaturated ketones to their α,β-isomers. This reaction, involving the intermediate formation of a Schiff base, is very efficient and may represent a model for the corresponding enzymatic isomerizations.[4]

When 3-methyl-3-cyclohexenone is added to an aqueous solution of a 2,2,2-trifluoroethylamine buffer, the formation of 3-methyl-2-cyclohexenone can be monitored at 240 nm (the λ_{max} of 3-methyl-2-cyclohexenone) by uv spectroscopy. At moderate concentrations of buffer ($<0.4\ M$) the appearance of the α,β-unsaturated isomer is pseudo first order after an initial induction period. If, however, the reaction is monitored at 268 nm, a rapid initial absorbance increase is observed, followed by a slower decay which corresponds to the rate of formation of 3-methyl-2-cyclohexenone. NMR and uv spectra taken of solutions before significant decay of the absorbance at 268 nm indicated the presence of the protonated Schiff base (I) of 3-methyl-2-cyclohexenone and trifluoroethylamine.[6] We were able to isolate I from the reaction of trifluoroethylamine and 3-methyl-3-cyclohexe-



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