trate below 220 mμ with the samples used. The data so obtained were identical with those produced by the newer machine at the same wavelengths. Depolarization due to scattering would not, therefore, seem to be a serious problem in this case. Absorption measurements were made on a Cary 15 recording spectrophotometer.

The interpretation of these data requires an analysis of the crystal structures and of relevant solution measurements. This work is in progress and will be reported in the near future.

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## Ligand Exchange and Isomerization in Tris(triphenylphosphine)chlororhodium(I)

*Sir:*

Osborn, Jardine, Young, and Wilkinson[1,2] have reported that Rh{P($C_6H_5$)}$_3$Cl and its Br and I analogs effectively catalyze the homogeneous hydrogenation of olefins. On the basis of molecular weight data they suggested that these complexes are highly dissociated in solution to Rh{P($C_6H_5$)$_3$}$_2$X + P($C_6H_5$)$_3$ and considered the bisphosphine complex to be the catalytically active species. We therefore included these compounds as part of a more extensive study of the mechanisms of ligand exchange of phosphine complexes with the expectation of finding a dissociative (first-order) mechanism for exchange rather than the associative (second-order) mechanism previously demonstrated for both square-planar[3] and tetrahedral[4] $d^8$ complexes. We do indeed find a dissociative mechanism for ligand exchange but have also obtained some evidence suggesting that the dissociation is a two-step process and wish to suggest that the existence of such a mechanism has relevance to the problem of understanding why these complexes are catalytically active.

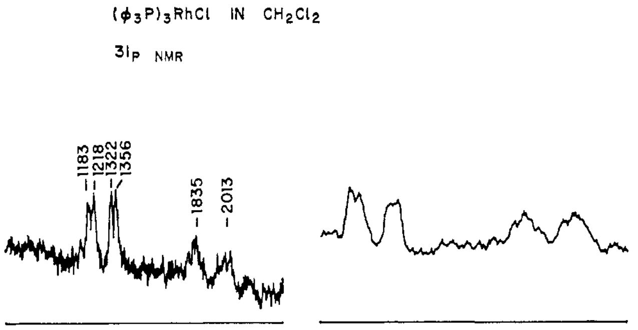

Figure 1. $^{31}$P nmr spectra at 40.5 Mc/sec of tris(triphenylphosphine)rhodium chloride in methylene chloride at +30° (reference, 85% $H_3PO_4$).

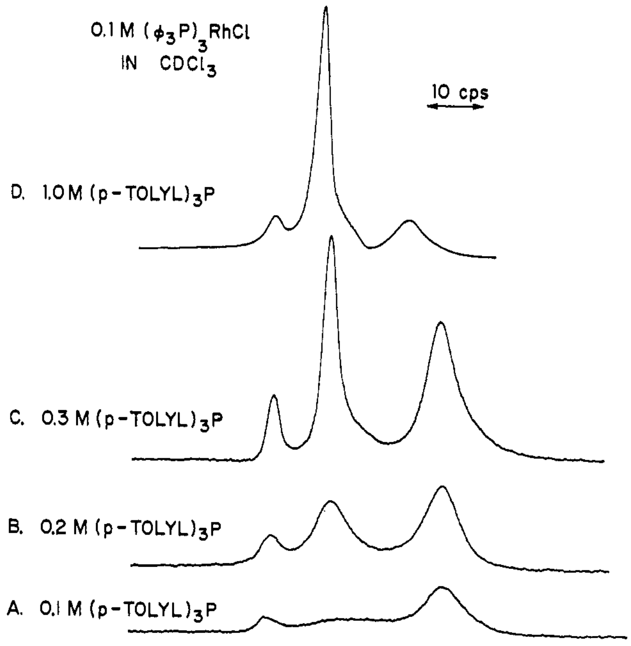

Figure 2. 220-Mc/sec $^1$H nmr spectra of $CH_3$ resonance of 0.1 *M* tris(triphenylphosphine)rhodium chloride and tri-*p*-tolylphosphine in $CDCl_3$ at +23°.

The $^{31}$P nmr spectrum of Rh{P($C_6H_5$)$_3$}Cl (Figure 1) has the expected pattern with different chemical shifts for *cis* and *trans* phosphines, each split by $^{103}$Rh and by $^{31}$P. Free triphenylphosphine cannot be detected. Addition of triphenylphosphine gives a resonance at the expected frequency but causes no other change. Therefore, the complex does not dissociate extensively at these concentrations (>0.1 *M*) and ligand exchange is slow by the nmr criterion. Additional peaks which appear after about 30 min of standing are ascribed to the dimer reported by Wilkinson.[1] These conclusions have been verified by examination of the H spectra at 220 Mc/sec. The lines are broad at room temperature, but the spectrum is analyzable at −35°. Again no resonance can be ascribed to the free ligand (the most intense line of which does not coincide with the complex lines) and addition of free ligand gives an additional line in the expected place. These observations set a lower limit for the lifetimes of free and complexed ligand of ~$10^{-2}$ sec and an upper limit for the degree of dissociation. These nmr experiments have been extended to concentrations as low as $10^{-3}$ *M* by using a computer of average transients (CAT). Below $10^{-2}$ *M* there is some evidence for free ligand, and additional resonance lines appear. However, the principal new lines have been identified as triphenylphosphine oxide which must arise from the presence of adventitious oxygen. It is very difficult to eliminate these lines at low concentrations even though the solvents were carefully degassed and all manipulations carried out in a drybox. At the lowest concentration ($10^{-3}$ *M*) there are additional lines not due to triphenylphosphine oxide. We therefore deduce that there is some dissociation of the complex but that contrary to the molecular weight evidence the degree of dissociation is small (<5%) at concentrations above $10^{-2}$ *M*. Spectra obtained with the addition of halide ions provide no evidence for ionic dissociation.

A lower limit to the rate can be obtained by studying the exchange with tri-*p*-tolylphosphine and examining

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(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(2) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid.*, 1574 (1967).

(3) F. Basalo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

(4) W. D. Horrocks and L. H. Pignolet, *J. Am. Chem. Soc.*, 88, 5929 (1966).

the methyl resonance at 220 Mc/sec. These experiments also proved to be the most informative with respect to mechanism. Figure 2 shows the spectra obtained by adding varying amounts of ligand at room temperature and Figure 3 the effect of lowering the temperature to −35°. At room temperature separate resonances for free and complexed ligands are readily discernible, and at −35° the complex resonance is split into two peaks with intensity ratio 2:1, assigned as *cis* and *trans* phosphines. The lowest field line is due to tri-*p*-tolylphosphine oxide which is present in the added tri-*p*-tolylphosphine and cannot be easily removed by recrystallization or by zone refining. Integration of these spectra shows that the distribution of complexed triphenyl- and tri-*p*-tolylphosphine is, within experimental error, statistical at all concentrations and temperatures. *p*-Tolylphosphine can therefore be treated as labeled phenylphosphine. Equilibrium is reached within the time taken to position the sample in the nmr spectrometer, *i.e.*, in less than $\sim 10^2$ sec. Lines due to the *cis* and *trans* isomers collapse around 0°, and the free and complexed ligand lines are collapsed at +35°. An approximate treatment of the data gives an activation energy of 6 kcal for the *cis–trans* isomerization. For the analogous bromide and iodide, the *cis–trans* collapse occurs at $\sim -15$ and $\sim -30°$, respectively. The temperature changes in the spectrum of the aromatic protons are consistent with these observations but less easily resolved and assigned.

As regards mechanism, two important points emerge from these data. The associative (eq 1) and dissociative (eq 2) mechanisms predict the following values for the lifetimes of complexed ($\tau_C$) and free ($\tau_L$) ligand.

$$\mathrm{Rh\{P(C_6H_5)_3\}_3Cl + P(C_6H_5)\,_3} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Rh\{P(C_6H_5)_3\}_4Cl} \qquad (1)$$

$$\frac{1}{\tau_C} = k_1[\mathrm{P(C_6H_5)_3}] \qquad \frac{1}{\tau_L} = k_1[\mathrm{Rh\{P(C_6H_5)_3\}_3Cl}]$$

$$\mathrm{Rh\{P(C_6H_5)_3\}_3Cl} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Rh\{P(C_6H_5)_3\}_2Cl + P(C_6H_5)_3} \qquad (2)$$

$$\frac{1}{\tau_C} = k_1 \qquad \frac{1}{\tau_L} = 3k_1\frac{[\mathrm{Rh\{P(C_6H_5)_3\}_3Cl}]}{[\mathrm{P(C_6H_5)_3}]}$$

For the first mechanism, $1/\tau_C$ is directly proportional to the free ligand concentration, and $1/\tau_L$ is independent of the free ligand concentration. For the second mechanism, $1/\tau_C$ is independent of $[\mathrm{P(C_6H_5)_3}]$ and $1/\tau_L$ is inversely proportional to $[\mathrm{P(C_6H_5)_3}]$. The data of Figure 2 clearly show the second alternative to becor rect. The other significant point is that the rate of *cis–trans* isomerization is greater than that of ligand exchange. This clearly eliminates a simple dissociative exchange as the mechanism for *cis–trans* isomerization.

One possibility would be that the isomerization is an intramolecular process involving a tetrahedral isomer as an intermediate. Such an isomer would be expected to be paramagnetic, and esr signals have been observed from solutions of these compounds by Wilkinson.[1] We have confirmed this observation. However, the nature of this signal (a doublet at $g = 2.12$) is not that expected from a triplet-state molecule, and the long relaxation time demanded by the observation of the signal at room temperature would be most unexpected for a $d^8$ complex. We prefer Wilkinson's explanation that it arises from a Rh(II) impurity. An alternative would be an

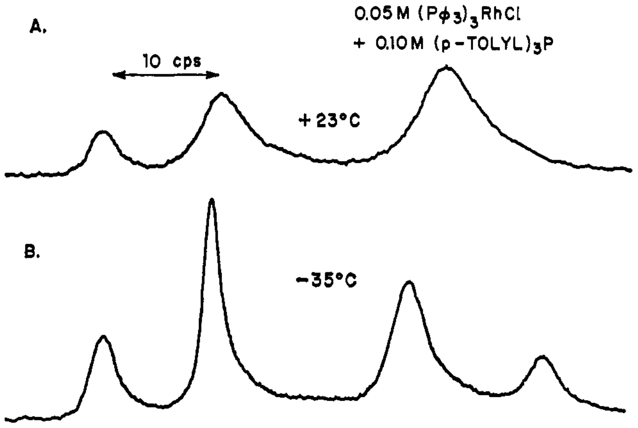

Figure 3. 220-Mc/sec $^1H$ nmr spectra of $CH_3$ resonance of 0.05 *M* tris(triphenylphosphine)rhodium chloride and 0.1 *M* tri-*p*-tolylphosphine in $CDCl_3$: (A) +23°; (B) −35°.

intermolecular mechanism involving a structure in which one of the phosphine ligands is more loosely bound than the other two, *i.e.*, $[\mathrm{Rh\{P(C_6H_5)_3\}_2Cl]P(C_6H_5)_3}$. Such a process would be analogous to the ion-pair intermediate mechanism postulated by Winstein[5] in the SN1 reactions of *p*-chlorobenzhydryl chloride. This mechanism is supported by the observation that the rate of racemization in these systems is greater than that of radiochlorine exchange which is analogous to our observation that the rate of *cis–trans* isomerization is greater than that of ligand exchange. The kinetic data on ligand exchange are entirely consistent with the existence of such an intermediate. We find this possibility attractive since it is perhaps in line with the expected chemistry of a Rh(I) complex. Thus $\mathrm{Pt\{P(C_6H_5)_3\}_4}$ with a formal charge on the metal of zero loses a ligand spontaneously and exchanges ligands by a dissociative mechanism.[6] For $\mathrm{Pt\{P(C_6H_5)_3\}_2Cl_2}$ (formal charge +2) the loss of a ligand is not initiated until the bond with the replacing ligand begins to form; *i.e.*, the mechanism is second order. For $\mathrm{Rh\{P(C_6H_5)_3\}_3Cl}$ (formal charge +1) there is a compromise in which the bond is weakened by a first-order process, but the ligand is not entirely lost. The existence of such an intermediate state is also very attractive in rationalizing the catalytic activity of the compound and may have much wider implications in the field of homogeneous catalysis. Thus, not only does it provide for an available reactive site on the metal, but the existence of loosely held ligands also suggests that catalytically active compounds may be able to accumulate molecules in such a "second coordination sphere" and hold them until they are required in the reaction. However, the present experimental results are insufficient to unambiguously distinguish between an intramolecular and an intermolecular mechanism for isomerization.

Finally it should be noted that the above results in no way contradict the very elegant work of Osborn, *et al.*,[1,2] on the mechanism of catalytic hydrogenation using these complexes. It does appear that $\mathrm{Rh\{P(C_6H_5)_3\}_2Cl}$, which is the starting point of their kinetic scheme, is present in lesser concentration than they have

(5) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960).

(6) Unpublished results based on nmr experiments similar to those described in this communication.

deduced from molecular weight measurements, but this does not affect their conclusions. We have repeated the osmometry experiments of these authors and obtain essentially the same molecular weights. We have no ready explanation of this disagreement with the nmr results but consider the latter to be the more direct and less ambiguous method.

**Acknowledgment**. We wish to thank Dr. J. J. Mrowca for providing the sample of the compound tris(triphenylphosphine)chlororhodium(I).

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## Some Reactions of the $C_4$ Molecule

*Sir:*

The $C_4$ molecule has been recognized as a minor constituent of carbon vapor.[1–9] We are not aware of any previous report on its chemical interaction with other substances.

**Table I.** Reactions of $C_4$ with Selected Substrates

| | Weight % of total carbon vaporized | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Product | Hexane | *cis*-2-Pentene | *t*-Butyl chloride | Methanol | Ethanol | 1-Propanol | 2-Propanol | *t*-Butyl alcohol |
| Ethylacetylene | 0.61 | 0.24 | 0.13 | 0.30 | 0.34 | 1.10 | 0.54 | 1.02 |
| Methylallene | 0.18 | 0.08 | 0.35 | 0.28 | 0.34 | 0.65 | 0.60 | 0.61 |
| 1,3-Butadiene | 0.20 | 0.55 | 0.71 | 0.03 | 0.05 | 0.71 | 0.18 | 0.72 |
| Vinylacetylene | 0.20 | *a* | 0.13 | 0.09 | 0.11 | 0.16 | 0.11 | Nil |
| Total | 1.19 | 0.87 | 1.32 | 0.70 | 0.84 | 2.62 | 1.43 | 2.35 |

[a] Not detectable in large quantities of *cis*-2-pentene by the isolation technique employed.

Simultaneous depositions of carbon vapor, from a high-vacuum arc,[10] and a variety of hydrogen-containing substrates (>1000-fold molar excess) on a liquid nitrogen cooled surface produce the $C_4$ hydrocarbons ethylacetylene, methylallene, 1,3-butadiene, and vinylacetylene (Table I). The total yields are similar and small, 1-2%, but the relative yields vary. Very small amounts of more highly hydrogenated $C_4$ hydrocarbons could be recognized with sensitive glpc detection systems, but the other $C_4H_4$ and $C_4H_6$ acyclics, 1,2,3-butatriene and 2-butyne, were not detected;[11] diacetylene, $C_4H_2$, was found in trace quantities only.

The hydrogenation of $C_4$ is analogous to the hydrogenation of $C_2$[12] and excited state $C_3$.[13] The high-

$$C_4 + \xrightarrow[\text{substrates}]{\text{hydrogen-containing}} \begin{array}{l} CH_3CH_2C{\equiv}CH \\ CH_3CH{=}C{=}CH_2 \\ CH_2{=}CHCH{=}CH_2 \\ CH_2{=}CHC{\equiv}CH \end{array}$$

dilution conditions of these experiments make unlikely the formation of these hydrocarbons by couplings of $C_2$ or $C_3$ radicals.

Preparations of the $C_4$ hydrocarbons employing $^{14}C$-enriched graphite electrodes[12] confirm the electrodes as the sole source of their carbon skeleton; their relative molar activities are four times the activity of a product resulting from reaction of $C_1$, by addition, with two molecules of alcoholic substrate (Table II).

The $C_4$ hydrocarbons from carbon vapor and $C_2D_5$-OH are 60–75% $d_5$ and $d_6$, from $CH_3CD_2OH$, 80–85% $d_0$, $d_1$, and $d_2$. Thus the substrates are the sources of the hydrogen atoms. The $C_4$ hydrocarbons are not formed from substrates which have rather high bond dissociation energies for removal of a hydrogen atom, such as water, benzene, and chlorobenzene.

**Table II.** Relative Molar Activities of $C_4$ Hydrocarbons Produced by the Reactions of $^{14}C$-Enriched Carbon Vapor with Methanol and Ethanol

| | Relative molar activities | |
|---|---|---|
| Product | Methanol | Ethanol |
| $C_1$ product,[12] $CH_2(OR)_2$ | 1.00 | 1.00 |
| Ethylacetylene | 4.12 | 4.02 |
| Methylallene | 4.00 | 3.86 |
| Vinylacetylene | 3.75 | 3.89 |
| 1,3-Butadiene | *a* | *a* |

[a] Produced in insufficient quantity for accurate measurement.

The $C_4$ from a carbon arc produces these hydrocarbons; carbon vapor from thermal vaporization (resistive heating of a carbon filament) deposited on a −196° ethanol surface does not produce them. It is not clear at this time whether thermal vaporization (1) produces much less $C_4$ than arc vaporization or (2)

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(1) R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).
(2) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).
(3) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.*, 31, 1131 (1959).
(4) K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.*, **81**, 4477 (1959).
(5) E. Clementi, *ibid.*, **83**, 4501 (1961).
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(10) P. S. Skell, L. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).
(11) 1,2,3-Butatriene would not be expected to survive the detection conditions: (a) W. M. Schubert, T. H. Liddicoet, and W. A. Lanka, *ibid.*, **76**, 1929 (1954); (b) S. J. Cyvin, *Acta Chem. Scand.*, **17**, 2123 (1963); (c) S. G. Frankiss and I. Matsubara, *J. Phys. Chem.*, **70**, 1543 (1966).
(12) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).
(13) P. S. Skell and R. F. Harris, unpublished results.