

# The Introduction of Methylene into an Iridium Complex<sup>1</sup>

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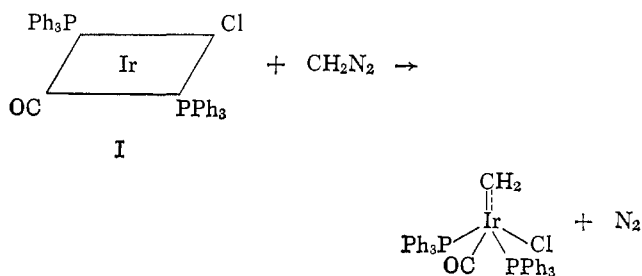
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**Abstract:** Diazomethane reacts with the iridium complex  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  in ether suspension, yielding a crystalline, methylene-containing complex which decomposes excess diazomethane to ethylene and nitrogen. Although the new complex is air stable, it readily decomposes in solution. In chloroform, the product is principally polymethylene; in styrene, the methylene fragment is transferred to the olefin, yielding phenylcyclopropane and  $\alpha$ -methylstyrene. Spectral and chemical evidence indicate that the methylene moiety in the new complex is  $\sigma$  bonded between the iridium and chlorine atoms. The over-all chemistry of the system is interpreted in terms of the intermediacy of an electrophilic methylene,  $\pi$  bonded to the iridium.

The bonding of carbenes to transition metals is of current interest. Intermediate occurrence of carbene-transition metal complexes has been postulated,<sup>2,3</sup> and a tungsten complex was recently reported<sup>4</sup> in which methoxymethylcarbene is bonded to the metal as a ligand. The bonding of methylene itself to a transition metal invites examination. Although methylene-transfer agents containing a methylene moiety bonded to various metals are known, and have achieved synthetic importance for the cyclopropanation of olefins<sup>5-8</sup> and for the ring expansion of benzenes to cycloheptatrienes,<sup>9,10</sup> no such system containing a transition metal has been reported. The particular feature of interest in regard to methylene-transition metal chemistry is the greater capability of transition metals to  $\pi$ -bond the carbene moiety as a ligand *via* back donation of d electrons, by analogy with the known capacity of such metals to bond the electronically similar carbon monoxide.

The present study was stimulated by the possibility of introducing methylene into an iridium complex, through reaction of iridium chlorocarbonylbis(triphenylphosphine)<sup>11</sup> (I) with diazomethane. The open coordination site of the d<sup>8</sup> Ir (I) in the square-planar complex could be expected to decompose diazomethane



*via* electrophilic attack on carbon, and, at least transiently, to accept the resulting  $:\text{CH}_2$  moiety as a fifth ligand.

## Results and Discussion

In solution (benzene or chloroform), I vigorously decomposes diazomethane, yielding mainly polymethylene and decomposition products of I. Treatment of an ether suspension of I with diazomethane at  $-30^\circ$  yields an insoluble, crystalline,<sup>12</sup> orange product which catalytically decomposes excess diazomethane to ethylene and nitrogen. The product contained essentially no starting complex I or polymethylene (infrared and thin layer chromatography). Its infrared spectrum was almost superimposable on that of I. Two new bands (weak) appeared in the C-H stretching region at 2985 and 2933  $\text{cm}^{-1}$ . The single CO band of I at 1961  $\text{cm}^{-1}$  was replaced by a new band at 1942  $\text{cm}^{-1}$ , suggesting a new CO-containing complex. Elemental analysis indicated only a trace of nitrogen, precluding a significant amount of an iridium-diazomethane complex, and was consistent with the incorporation of 1 equiv of methylene. Pyrolysis ( $300^\circ$ ) yielded a gas mixture containing principally methane, with lesser amounts of ethylene and propylene (the gas was essentially free of nitrogen or nitrogen-containing compounds). That the methane formed originated primarily from an introduced methylene moiety was demonstrated by pyrolysis of the product prepared from perdeuteriodiazomethane; the methane produced contained 48% deuterium, the principal species being  $\text{CD}_2\text{H}_2$ .<sup>13</sup>

Although the methylene-containing complex is stable in air, it readily decomposes in solution. It reacts in warm chloroform yielding I and a gray precipitate which appeared to be mainly polymethylene. The latter exhibited strong methylene bands at 2924 and 2850  $\text{cm}^{-1}$  and polymethylene bands at 730 and 719  $\text{cm}^{-1}$ ; its spectrum was free of CO and other bands

(12) The X-ray diffraction pattern of the starting material (a powder) was "spotted," indicating particle sizes  $> 10^3$  Å, while that of the product was free of spots. The particles thus appear to undergo breakdown during the course of the reaction.

(13) The presence of methane in the pyrolysis product suggests the intermediacy of triplet methylene, a predictably active hydrogen atom scavenger under these conditions. It would be reasonable to expect an expelled singlet methylene to undergo spin inversion in the presence of a transition metal in an intermediate paramagnetic oxidation state.<sup>14</sup>

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(4) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964).

(5) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 28-31, and reference cited therein.

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(7) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(8) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(9) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(10) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Ann.*, **675**, 63 (1964).

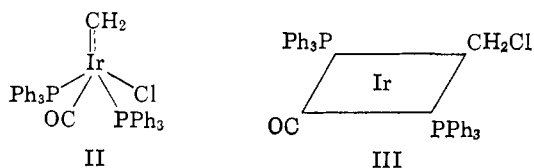
(11) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

characteristic of I. Elemental analysis indicated a H:C ratio of 2.16.

It was of interest to examine the methylene-transfer capabilities of the new complex. Attempts to transfer methylene to the double bond of cyclohexene were without success. Even under severe conditions (20 min at 200°) only a trace (0.3%) of the double-bond addition product, norcarane, was obtained. In view of the relative insolubility of the complex in cyclohexene, methylene transfer to this olefin was also attempted in chloroform solution, again without success. The inactivity of the methylene-containing complex toward cyclohexene, however, is consistent with the earlier finding that catalytic decomposition of diazomethane to ethylene by this complex proceeds cleanly without yielding methylene addition products (*i.e.*, cyclopropane or propylene).

Methylene from the new complex does undergo transfer to the more polarizable double bond of styrene. Upon warming a styrene solution of the new complex on a steam bath, phenylcyclopropane and  $\alpha$ -methylstyrene were obtained in 22 and 9% yields, respectively. Acid-catalyzed isomerization of phenylcyclopropane would be expected to yield  $\beta$ -methylstyrene rather than  $\alpha$ -methylstyrene.<sup>15</sup> In the absence of phenylcyclopropane isomerization by some other route, the observed  $\alpha$ -methylstyrene thus appears to result from methylene insertion into the  $\alpha$  C-H bond of styrene. Consistent with this conclusion is the finding that the ratio of phenylcyclopropane to  $\alpha$ -methylstyrene was essentially constant, even at prolonged reaction times. In addition to phenylcyclopropane and  $\alpha$ -methylstyrene, the reaction product was found to contain I; the amount of I detected varied, apparently depending upon reaction conditions and reagent quality.

Reasonable structural assignments for the new methylene-containing complex include II and III. In II,

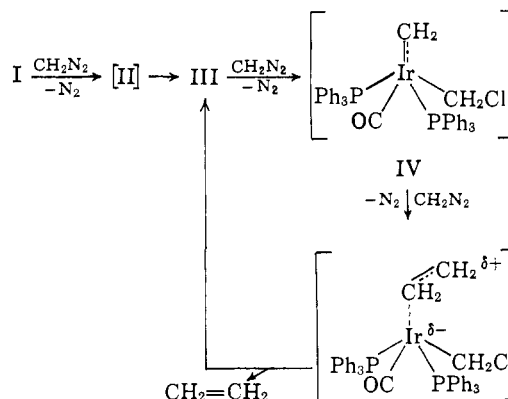


the methylene,  $sp^2$  hybridized, is bound to the iridium as a fifth ligand.<sup>16</sup> Structure III could result from intermediate II undergoing a 1,2-halide shift with rehybridization of the methylene carbon to  $sp^3$ ; there are numerous examples of diazomethane "inserting" its methylene group into metal-halogen bonds.<sup>17</sup> Evidence supporting structure III is the position of the CO band (1942  $cm^{-1}$ ) relative to that of I (1961  $cm^{-1}$ ). A shift to longer wavelengths suggests an increase in metal electron density,<sup>18</sup> consistent with the replacement of a Cl ligand by the less electronegative  $-CH_2Cl$  group.

To differentiate between II and III, the methylene-containing complex was prepared from perdeuterio-

diazomethane. The product (exhibiting C-D bands at 2237, 2198, and 2079  $cm^{-1}$ ) was then treated with a known excess of undeuterated diazomethane and the ethylene evolved examined for deuterium content by mass spectrometry. The ethylene was essentially free of deuterium. Further evidence that the methylene moiety remained intact throughout the catalytic decomposition of undeuterated diazomethane was obtained upon pyrolyzing the product of  $CH_2N_2$  treatment. The methane component of the pyrolysis product was rich in deuterium (11%  $CD_4$ , 19%  $CHD_3$ , 41%  $CH_2D_2$ , 10%  $CH_3D$ , and 19%  $CH_4$ ). Since II would be expected to surrender its carbene ligand yielding deuterated ethylene, III is the more reasonable structure; the latter better fulfills the requirement that it continue to decompose diazomethane without surrendering the methylene fragment initially introduced. Other structures for the methylene-containing complex, including octahedral structures with iridium formally trivalent,<sup>19,20</sup> do not as adequately accommodate the observed reactions and spectral data.<sup>21</sup>

The following mechanism is offered for the formation of III and for the catalytic decomposition of diazomethane.



The unique tendency of certain tetracoordinate  $d^8$  complexes to expand their coordination number from four to five without a formal change in valence<sup>23</sup> introduces the possibility of an interconversion between III and pentacoordinate II. The possible intermediacy of II is strengthened by the reported preparation of a stable pentacoordinate Ir(I) complex  $[IrH(CO)(Ph_3P)_3]$ .<sup>24</sup> The higher reactivity of the methylene-containing complex in solution might therefore be attributed to the generation of II, containing the more reactive  $\pi$ -bonded methylene. Solvation of the com-

(19) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(20) R. F. Heck, *ibid.*, **86**, 2796 (1964).

(21) An observation supporting the tetracoordinate structure III is the appearance of new bands in the infrared spectrum of the new complex in a potassium bromide pressed plate. In KBr, the new complex exhibits two bands in the CO stretching region, the usual band at 1942  $cm^{-1}$  and a new band at 1992  $cm^{-1}$ . The spectrum also exhibits a new band at 850  $cm^{-1}$ . The starting complex I behaves in a similar manner. In KBr, the new CO band of I appears at 2004  $cm^{-1}$  and the other at 863  $cm^{-1}$ . The new CO band can be intensified at the expense of the original (1965  $cm^{-1}$ ) by prolonged grinding of the KBr mixture. Since the mixing is carried out in air, it is likely that the new bands are due to the formation of the oxygen adduct of I, a known compound which is reported to exhibit the observed bands.<sup>22</sup> The new CO band in the KBr plate of the methylene-containing complex and the band at 850  $cm^{-1}$  (metal oxide region)<sup>22</sup> thus suggest the formation of its oxygen adduct.

(22) L. Vaska, *Science*, **140**, 809 (1963).

(23) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

(24) S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).

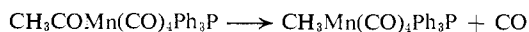
(15) R. Breslow in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers Inc., New York, N. Y., 1963, pp 254-255.

(16) The double bond can be visualized as a  $\sigma$  bond containing the two electrons of the carbene fragment, and a  $\pi$  bond resulting from back-donation of d electrons from the metal to the vacant  $p_z$  orbital of the carbene fragment; the carbene is thus proposed to play the same role in transition metal bonding as does carbon monoxide.

(17) D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955).

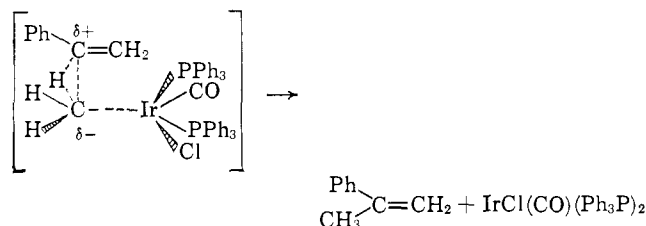
(18) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

plex could conceivably labilize the chloromethyl ligand, the methylene moiety undergoing rehybridization from  $sp^3$  to  $sp^2$  as III is rearranged to II. This rearrangement is analogous to the reverse of the so-called CO insertion reaction, in which a single transition metal-bound acetyl ligand rearranges (with loss of an adjacent CO ligand) to two ligands, one (methyl)  $\sigma$ -bonded to the metal and the other (carbon monoxide)  $\pi$ -bonded to the metal.



This rearrangement is reported<sup>25</sup> to proceed *via* a 1,2-methyl shift, the methyl thus playing the role of the chlorine atom postulated above and the CO moiety assuming that of the methylene.

The observed facile decomposition of diazomethane to ethylene and nitrogen by the new complex points to an electrophilic intermediate. A methylene moiety  $\pi$ -bonded to the iridium as a fifth ligand (II and IV) could reasonably be regarded as an electrophilic site. The intermediacy of an electrophilic methylene moiety is also consistent with the formation of  $\alpha$ -methylstyrene as well as phenylcyclopropane in the reaction of III with styrene. C-H insertion, proceeding *via* the transfer of a hydride ion, would generate a partial charge separation in the transition state with the positive end centered on the  $\alpha$ -carbon atom of styrene.



This charge separation would be stabilized through charge delocalization by the phenyl nucleus of the styrene moiety and by the metal complex of the carbene moiety. A similar insertion at the  $\beta$ -carbon atom would be less favored by this mechanism since positive charge delocalization into the phenyl group is less effective at that carbon. It is significant in this regard that the insertion of chemically generated dichlorocarbene into carbon-hydrogen bonds of alkylbenzenes occurs exclusively in the  $\alpha$  position.<sup>26, 27</sup>

## Experimental Section

Infrared spectra of crystalline compounds except where otherwise specified were measured in Nujol or fluorocarbon mull on a Beckman Model IR4 spectrometer. Thin layer chromatography (tlc) was carried out on silica gel G with chloroform as eluent and ceric sulfate solution (2% in 2 *N* sulfuric acid) as oxidant.

**Iridium Chlorocarbonylbis(triphenylphosphine) (I).** The reaction used to prepare this compound was essentially that reported by Vaska.<sup>11</sup> However, since no experimental details were included in the Vaska communication, the following procedure was adopted. A mixture of  $\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$  (0.53 g, Engelhard Industries Inc., Newark, N. J.), ethylene glycol (60 ml), and triphenylphosphine (5.6 g) was refluxed under nitrogen for 13 hr. The cooled crude product was filtered under nitrogen and the solid residue washed with a mixture of benzene-hexane (1:1). The washed dark solid was then chromatographed under nitrogen on silica gel with chloroform as eluent. The thin layer chromatogram of the principal

chromatography cut showed two spots (both yellow), possibly *cis* and *trans* isomers. Attempts to separate the two-component mixture by repeated recrystallizations (in benzene-hexane and chloroform) were unsuccessful. A single-component product was obtained, however, upon a second purification by adsorption chromatography. One recrystallization from benzene-hexane gave pure I, mp 322–324°; lit<sup>11</sup> mp 323–325°.

*Anal.* Calcd for  $\text{C}_{37}\text{H}_{30}\text{ClIrOP}_2$ : C, 57.0; H, 3.9. Found: C, 58.2; H, 3.9.

**Reaction of Iridium Chlorocarbonylbis(triphenylphosphine) and Diazomethane.** The following procedure is representative. I (*ca.* 1 g), ground to a fine powder, was treated with an excess of diazomethane (prepared from 4.5 g of Du Pont EXR-101 [bis(*N*-methyl-*N*-nitroso)terephthalamide])<sup>28</sup> in anhydrous ether (80 ml) precooled to  $-40^\circ$ . The magnetically stirred mixture, under dry nitrogen, was maintained at  $-30 \pm 2^\circ$ . Stirring under nitrogen was continued for approximately 2 hr, whereupon the orange crystalline product was filtered in air and washed with ether. Tlc of this crude product showed only a trace of I. The main portion of the chromatogram was at the base in the form of a bright orange spot; the intense orange color developed within a few seconds after a chloroform slurry of the product was placed on the adsorbent.

Because of its instability in solution, it was not possible to purify the product by the usual techniques (*e.g.*, recrystallization and chromatography). A sample of the crude material, dried over phosphorus pentoxide at  $80^\circ$  under reduced pressure, was therefore analyzed directly without additional purification.

*Anal.* Calcd for  $\text{C}_{38}\text{H}_{32}\text{ClIrOP}_2$ : C, 57.6; H, 4.1; Cl, 4.5; Ir, 24.3; O, 2.0; P, 7.8. Found: C, 57.8; H, 4.2; Cl, 4.6; Ir, 23.7; O, 2.2; P, 7.0.

In other experiments in which samples of the product gas were desired, the procedure was essentially the same, except that the reaction system, first flushed with dry helium, was connected to a gas-collecting apparatus (brine displacement). In a typical run, 1.26 g of I produced 530 ml of gas in 3 hr at  $-30^\circ$ . Mass spectral analysis of the gas showed 2.4% helium, 3.7% oxygen, 0.2% argon, 11.2% ethylene, and 82.4% nitrogen. No attempt was made to flush the residual ethylene from the ether solution.

**Thermal Decomposition of the Methylene-Containing Complex.** The methylene-containing iridium complex (*ca.* 1 g) was placed in a 15-ml test tube connected to a liquid-nitrogen-cooled gas trap. The system was evacuated and the sample portion heated to  $300^\circ$ . The condensed pyrolysis products were analyzed by mass spectrometry: 19.4% methane, 14.2% ethylene, 3% propylene, 11.1% benzene, 22% carbon dioxide, air, and a mixture of oxygen-containing compounds consisting mainly of diethyl ether. The solid pyrolysis product, a dark tarry material, was analyzed by tlc. The chromatogram showed a large spot corresponding to I.

**Reaction of Iridium Chlorocarbonylbis(triphenylphosphine) and Perdeuteriodiazomethane.** Perdeuteriodiazomethane was prepared by the method outlined by Leitch, Gagnon, and Cambron.<sup>29</sup> Their procedure was altered as follows. An ether solution of diazomethane (90 ml, from 4.5 g of Du Pont EXR-101)<sup>28</sup> was stirred magnetically with 25 ml of  $\text{D}_2\text{O}$  containing 17 g of potassium hydroxide at  $0^\circ$  for 2 hr. The ether solution was then stirred for an additional hour at room temperature with 25 ml of pure  $\text{D}_2\text{O}$  containing 1 g of sodium metal. To prevent evaporation of diazomethane during this period, the flask was closed with a rubber stopper. The ether solution of  $\text{CD}_2\text{N}_2$  was then dried over potassium hydroxide pellets for 15 min and used without further purification.

Finely powdered I (0.45 g) was treated with the ether solution of  $\text{CD}_2\text{N}_2$  under dry nitrogen and at room temperature. Stirring was continued (*ca.* 30 min) until the evolution of gas ceased (230 ml). The iridium complex was then filtered, washed with dry ether to remove any remaining diazomethane, and air-dried. No evidence of I in the product mixture was found (tlc and infrared). The infrared spectrum of the product (which appeared a deeper orange than the undeuterated product) showed three new bands (weak) at 2237, 2198, and 2079  $\text{cm}^{-1}$ .

**Reaction of the Deuterated Methylene-Containing Complex with Diazomethane.** The deuterated methylene-containing complex (0.48 g) was placed in a dry 25-ml flask, flushed with dry nitrogen, cooled to  $-35^\circ$ , and then treated with an excess of dry diazomethane in ether (*ca.* 25 ml) precooled to  $-40^\circ$ . The stirred mixture was

(25) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

(26) E. K. Fields, *ibid.*, **84**, 1744 (1962).

(27) D. Seyferth and J. M. Burlitch, *ibid.*, **85**, 2667 (1963).

(28) J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

(29) L. C. Leitch, P. E. Gagnon, and A. Cambron, *Can. J. Res.*, **28B**, 256 (1950).

allowed to warm slowly (2 hr) to room temperature while 200 ml of gas (12.4% ethylene) was collected by water displacement. The ethylene fraction of the gas product was purified by glc and analyzed for deuterium content by high-resolution mass spectrometry. Only a trace of deuterated ethylene was noted (0.16%  $C_2H_3D$ ); the product was essentially free of higher-deuterated ethylenes.

The solid product was then filtered, washed with anhydrous ether, air-dried, and pyrolyzed at 320°. The methane fraction of the gas product was analyzed by mass spectrometry: 11%  $CD_4$ , 19%  $CHD_3$ , 41%  $CH_2D_2$ , 10%  $CH_3D$ , 19%  $CH_4$ .

**Decomposition of the Methylene-Containing Complex in Chloroform.** The methylene-containing complex (0.14 g) was dissolved in 2 ml of chloroform with warming. After approximately 3 min, a gray precipitate formed which was filtered and dried over phosphorus pentoxide. The infrared spectrum of the dried product (15 mg) exhibited only minor bands which could be attributed to I or to the methylene-containing complex and showed strong methylene bands at 2924 and 2850  $cm^{-1}$  and polymethylene bands at 730 and 719  $cm^{-1}$ . *Anal.* Found: C, 46.7; H, 8.4; H:C (atomic), 2.16. The thin layer chromatogram of the chloroform-soluble product showed a yellow spot of high intensity which corresponded in position and hue to that of I.

**Reaction of the Methylene-Containing Complex with Cyclohexene.** The methylene-containing complex (0.15 g) was added to cyclohexene (4.2 g) and the mixture refluxed with stirring for 6 hr. Glc of the crude product showed only a trace of a compound corresponding to norcarane. The reaction was repeated in a sealed tube at 200° for 20 min. Again, only a trace (ca. 0.3%) of norcarane was noted in the liquid product.

**Reaction of the Methylene-Containing Complex with Styrene.** A mixture of the methylene-containing complex (0.86 g) and styrene (1.29 g) was warmed on a steam bath for 20 min. The resulting dark mixture, upon treatment with pentane, yielded a yellow precipitate and turned amber in color. The infrared spectrum of the yellow solid was essentially that of I with minor bands corresponding to unchanged methylene-containing complex. The

quantity of I (approximated by tlc and infrared) found in the crude solid product seemed to be sensitive to reaction conditions and reagent quality. The products varied between being nearly all I and containing only detectable quantities in addition to decomposition products. In all cases, however, the solid product appeared richer in I than did the starting methylene-containing complex. The filtrate contained two products which were isolated by glc and analyzed by mass spectrometry. Both compounds were  $C_9H_{10}$  hydrocarbons and gave fragmentation patterns consistent with those found for genuine samples of phenylcyclopropane and  $\alpha$ -methylstyrene. In addition, the two products proved identical with phenylcyclopropane and  $\alpha$ -methylstyrene by glc (peak enhancement with genuine samples) on three different columns (SF-96, Bentone, and Ucon Polar). Yields (based on the iridium complex) were as high as 22% for phenylcyclopropane and 9% for  $\alpha$ -methylstyrene.

**Phenylcyclopropane.** The procedure used for the preparation of phenylcyclopropane was essentially that reported by Doering and Roth.<sup>9</sup> Diazomethane (prepared from 4.5 g of Du Pont EXR-101)<sup>28</sup> was distilled from ether solution into a stirred mixture of 25 ml of ether, 0.5 g of cuprous chloride, and 1.5 g of styrene at 0°. After 1 hr of stirring, the product was filtered and the ether solvent distilled from the filtrate. The product contained two components (glc), the larger having the composition  $C_9H_{10}$  (mass spectrometry),  $n^{20}D$  1.5322; lit<sup>30</sup>  $n^{20}D$  1.5325. The infrared spectrum (film) contained all the characteristic bands reported<sup>30</sup> for phenylcyclopropane.

**Acknowledgments.** We are indebted to R. E. Thorpe and P. A. Wadsworth, Jr., for mass spectrometric analyses. We are particularly grateful to Dr. G. N. Schrauzer and Dr. R. G. Hayter for helpful comments and discussion.

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## Kinetics and Mechanism of Substitution Reactions of $\pi$ -Cyclopentadienyldicarbonylrhodium

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*Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. Received December 10, 1965*

**Abstract:** This paper reports the synthesis and properties of some mono- and disubstituted derivatives of  $C_5H_5$ -Rh(CO)<sub>2</sub> containing phosphines, phosphites, and isonitriles. The rate of replacement of carbon monoxide is first order in both the substrate and the reagent concentrations. Phosphine, phosphites, and isonitriles are good reagents, whereas under similar conditions pyridine and triphenylarsine do not react. The results are in agreement with the substrate being a class b or soft metal.

Several kinetic studies have been made of the exchange of carbon monoxide and of substitution reactions with metal carbonyls and their derivatives. Most of the systems investigated react at rates that do not depend on the entering ligand, and the results obtained provide information on the properties that affect the reactivities of different substrates. For example, Meriwether and Fiene<sup>2</sup> observed that the rate of replacement of phosphine from Ni(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> decreases with increasing base strength of the phosphine. Likewise, the rate of replacement of carbon monoxide from

Mn(CO)<sub>5</sub>Cl is greater than it is from Mn(CO)<sub>5</sub>I,<sup>3</sup> and the rate of carbon monoxide exchange<sup>4a</sup> with Mo(CO)<sub>6</sub>, and of its substitution reactions,<sup>4b</sup> is faster than it is for the corresponding chromium and tungsten hexacarbonyls. Heck<sup>5</sup> finds that the reaction of RCOC(CO)<sub>4</sub> with triphenylphosphine is subject to steric acceleration.

Although quantitative kinetic data are available on substrate reactivities in these systems, no systematic

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(4) (a) G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. Chim. Ital.*, **90**, 1486 (1960); G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, **97**, 1 (1963); (b) H. Werner and R. Prinz, private communication.

(5) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963).

(1) Exchange graduate student from the Technischen Hochschule, München, Germany.

(2) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).