

constraint to rotation in the proper direction developed in the six-membered ring when *trans* to the leaving chlorine as in VII. The lack of reactivity of V may be similarly explained. It may further be assumed that in the *gem*-dihalo compounds the halogen atom *trans* to the hydrogen atoms leaves, and that the small rate depression of VIII compared with VI is a reflection of the inductive effect of the second halogen.¹⁵

Our work has thus provided examples which support the predictions^{14a,b} of the stereochemical outcome of electrocyclic reactions involving cyclopropane rings. Furthermore, it now appears possible to assign correct structures to similar compounds of previously unknown configurations.

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(15) Satisfactory analyses were obtained for all new compounds.

Stanley J. Cristol, R. M. Sequeira, C. H. DePuy
Department of Chemistry, University of Colorado
Boulder, Colorado
Received June 14, 1965

Preparation and Oxidative Addition Reactions of a Monomeric Ruthenium(0) Complex

Sir:

Group VIII complexes of d^8 configuration add a wide variety of covalent molecules to form hexacoordinate complexes of d^6 configuration. Both "unsaturated," four-coordinate and "saturated," five-coordinate d^8 complexes behave in this way, the latter reacting with loss of a neutral ligand such as CO. Although the generality of these oxidative-addition reactions does not seem to be widely recognized, numerous examples have been reported. We are studying the scope, stereochemistry, and mechanisms of such d^8 addition reactions.

The d^8 complex which shows the most tendency to add covalent molecules is $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$, (A), discovered by Vaska.¹ This remarkable compound adds molecular hydrogen at room temperature and atmospheric pressure. The parallel between such additions and chemisorption on metal surfaces is significant.²

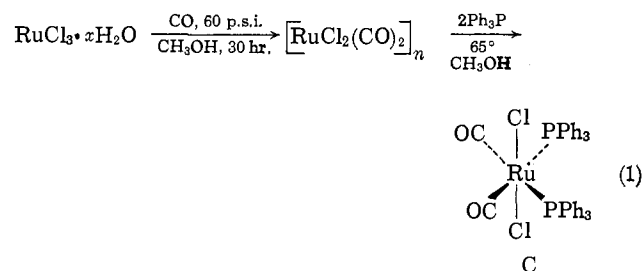
Examples of covalent molecules which add to the more reactive d^8 complexes are halogens,¹⁻⁶ hydrogen halides,^{1,7} trifluoroacetic acid,⁸ sulfonyl chlorides,⁸ sulfenyl chlorides,⁸ mercaptans,⁸ silicon hydrides,⁹ mercuric halides,^{8,10,11} methyl iodide,^{4,8,12} acetyl chloride,⁸ perfluoroalkyl iodides,^{8,13-16} azo compounds,^{17,18}

hydrogen,^{2,19,20} acetylenes,^{8,21} olefins,^{8,21} oxygen,^{2,22} and sulfur dioxide.²² The last four reagents add to the metal without molecular dissociation.

A survey of oxidative additions of d^8 complexes suggests that the tendency to form stable adducts of d^6 configuration increases in passing from first- to third-row elements and in going from right to left in group VIII. Thus complexes of iridium(I), ruthenium(0), and osmium(0) should exhibit the greatest tendency to react in this way.

This anticipated reactivity of ruthenium(0) and osmium(0) complexes led us to attempt the preparation of the substances described herein. At the outset of our work, the pentacarbonyls $\text{Ru}(\text{CO})_5$ ²³ and $\text{Os}(\text{CO})_5$ ²³ were the only known monomeric complexes in this oxidation state. These carbonyls readily trimerize²⁴ to $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$. Recently, Chatt²⁵ described a ruthenium phosphine complex in tautomeric equilibrium between a hexacoordinate ruthenium(II) and a four-coordinate ruthenium(0). The hexacoordinate tautomer is formed by the metal inserting itself into a carbon-hydrogen bond of a methyl group on one of the ligands.

Earlier, we had found that $[\text{IrCl}_3(\text{CO})(\text{Ph}_3\text{P})_2]$ (B) can be reduced to $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$ (A) with zinc in dimethylformamide (DMF). In order to extend this reduction to our present goal, $[\text{RuCl}_2(\text{CO})_2(\text{Ph}_3\text{P})_2]$ (C) was prepared according to eq. 1. *Anal. Calcd.*



for $\text{C}_{38}\text{H}_{30}\text{O}_2\text{Cl}_2\text{P}_2\text{Ru}$: C, 60.64; H, 4.02. Found: C, 60.88; H, 3.96. The infrared carbonyl bands exhibited by C (Table I) indicate that it is of the same

Table I. Carbonyl Stretching Frequencies^a

Compound	$\nu_{\text{C}=\text{O}}$
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ^b	1895
$\text{Ru}(\text{CO})_3(\text{AsPh}_3)_2$	1890
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	2050, 1990
$\text{RuBr}_2(\text{CO})_2(\text{PPh}_3)_2$	2050, 1990
$\text{RuI}_2(\text{CO})_2(\text{PPh}_3)_2$	2045, 1990
$\text{Ru}(\text{CF}_3\text{CO}_2)_2(\text{CO})_2(\text{PPh}_3)_2$	2055, 1995

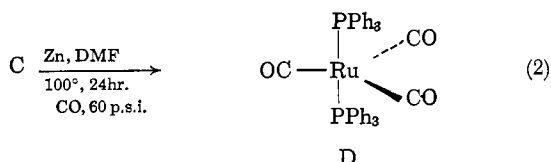
^a All compounds were measured as KBr pellets on a Perkin-Elmer Grating Infracord. ^b Also measured in methylene chloride solution.

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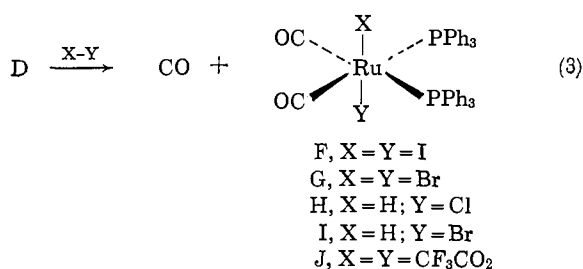
configuration as the related dialkylphenylphosphine complexes described by Chatt, *et al.*²⁶ The stereochemistry of these complexes was elucidated by dipole moment and infrared measurements.

Treatment of C with zinc dust in hot DMF yielded intractable complexes of ruthenium(0) containing tightly bound DMF. This expected tendency of ruthenium(0) to attain the five-coordinate state²⁴ suggested reduction in the presence of CO. Such a process afforded pale yellow crystals of $[\text{Ru}(\text{CO})_3(\text{Ph}_3\text{P})_2]$ (D) in high yield (eq. 2). *Anal.* Calcd. for



$\text{C}_{39}\text{H}_{30}\text{O}_3\text{P}_2\text{Ru}$: C, 66.01; H, 4.26; P, 8.73; Ru, 14.24; mol. wt., 709.7. Found: C, 65.97; H, 4.15; P, 8.75; Ru, 14.45; mol. wt., 644 (Mechrolab osmometer, benzene). It is of interest that the over-all preparation of D requires CO pressures less than 100 p.s.i. obviating the need for high pressure CO equipment. The single carbonyl stretching frequency at 1895 cm.^{-1} suggests the structure depicted with apical phosphines and equatorial CO ligands about a trigonal bipyramid. Cotton²⁷ reports that the iron(0) complex $[\text{Fe}(\text{CO})_3(\text{Ph}_3\text{P})_2]$ exhibits a single CO stretch at 1887 cm.^{-1} . The related triphenylarsine complex $[\text{Ru}(\text{CO})_3(\text{Ph}_3\text{As})_2]$ (E) having the same infrared spectrum as D was prepared in the same way. *Anal.* Calcd. for $\text{C}_{39}\text{H}_{30}\text{O}_3\text{As}_2\text{Ru}$: C, 58.72; H, 3.79. Found: C, 58.24; H, 4.08. The monomeric ruthenium(0) compounds D and E are soluble in common organic solvents and show no apparent tendency to trimerize.

As anticipated, D undergoes a series of oxidative additions with consequent loss of one CO ligand (eq. 3). Iodine reacts with D to form $[\text{RuI}_2(\text{CO})_2(\text{Ph}_3\text{P})_2]$



(F) having the same stereochemistry as C. *Anal.* Calcd. for $\text{C}_{38}\text{H}_{30}\text{O}_2\text{I}_2\text{P}_2\text{Ru}$: C, 48.79; H, 3.23. Found: C, 48.81; H, 3.51. Hydrogen chloride and hydrogen bromide also add to D to form the dihalides C and G, presumably by way of the intermediate hydrides H and I. *Anal.* Calcd. for $\text{C}_{38}\text{H}_{30}\text{O}_2\text{Br}_2\text{P}_2\text{Ru}$ (G): C, 54.24; H, 3.59. Found: C, 54.48; H, 4.08. In a similar manner trifluoroacetic acid combines with D to form the bistrifluoroacetate (J). *Anal.* Calcd. for $\text{C}_{42}\text{H}_{30}\text{O}_6\text{F}_6\text{P}_2\text{Ru}$: C, 55.56; H, 3.33. Found: C, 55.54; H, 3.77.

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Mercury halides and methyl iodide add to D affording mercury-ruthenium and carbon-ruthenium bonds. These and other reactions will be discussed subsequently. Currently we are extending this synthesis to osmium(0) analogs.

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James P. Collman,²⁸ Warren R. Roper

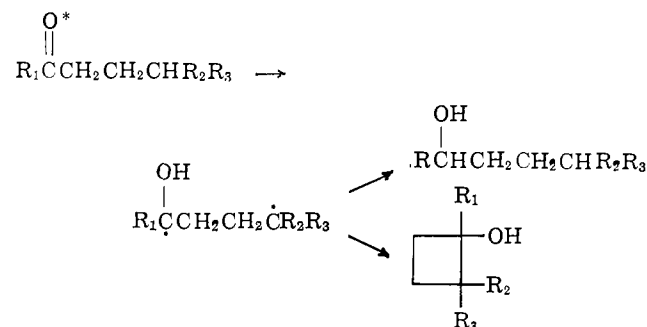
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina

Received June 14, 1965

Mechanism of Type II Photoelimination¹

Sir:

Irradiation of aldehydes and ketones which bear hydrogen atoms attached to a γ -carbon atom often effects molecular cleavage to an alkene and the enol of a smaller carbonyl compound.^{2,3} Frequently formation of cyclobutanols accompanies this photoelimination.^{4,5} Both reactions may be visualized as arising from a common biradical intermediate.



Identification of the excited state(s) responsible for this reaction is of considerable interest, but previous studies in the vapor phase have given seemingly equivocal results. Michael and Noyes⁶ studied the effect of biacetyl on the photochemistry of both 2-pentanone and 2-hexanone. From the slight quenching observed, they concluded that excited singlets were primarily responsible for the photoelimination. Ausloos and Rebbert⁷ also studied 2-pentanone and concluded that excited triplets were involved on the very reasonable grounds that addition of biacetyl quenches the type II reaction without affecting the weak fluorescence of pentanone.

We wish to report the results of study of the effect of piperylene (1,3-pentadiene) on the photoreactions of both ketones in solution. Piperylene was chosen as a quencher since it accepts only triplet energy from excited ketones, and that very efficiently.⁸

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