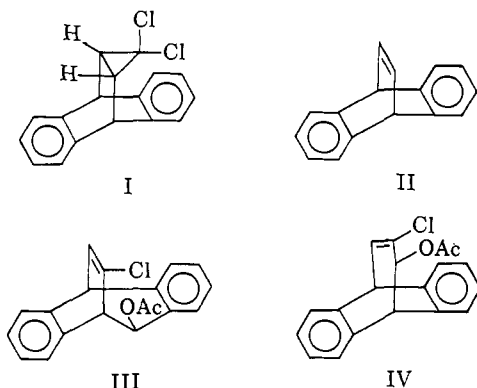


Bridged Polycyclic Compounds.
XXXI. Stereochemical Aspects of the Solvolysis of Cyclopropyl Chlorides¹

Sir:

Our interest in bridged bicyclic systems led us to the preparation of 3,3-dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (I), m.p. 151–153°, as a route to dibenzobicyclo[3.2.2]nonatrienes, by treatment of dibenzobicyclo[2.2.2]octatriene (II)² with phenyl(trichloromethyl)mercury.³ Treatment of I with silver acetate in glacial acetic acid at reflux for 1 hr. produced III, m.p. 143–145°, in quantitative yield.⁴ When I was treated with triphenyltin hydride by the procedure



reported recently⁵ for the stepwise removal of halogen atoms from *gem*-dihalocyclopropanes, a monochloro derivative was produced in 61% yield which was assigned the structure *anti*-3-chlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (V), m.p. 173–175°, on the basis of its n.m.r. spectrum, which had a triplet centered at τ 8.01 with $J = 2$ c.p.s. This assignment is consistent with the values of *trans* coupling constants found for a variety of other cyclopropane derivatives,⁶ although we were surprised that the hydrogen transfer had taken place on the apparently more hindered side. No silver chloride was produced when V was treated with silver acetate in refluxing acetic acid for 23 hr., and V was recovered unchanged.

Although the solvolysis rearrangement of cyclopropyl derivatives to allyl derivatives has been known for some time⁷ and the use of the dihalocarbene addition followed by rearrangement or solvolysis rearrangement has become a general procedure for ring expansion,⁸ the stereochemistry of the rearrangement does

(1) Previous paper in series: S. J. Cristol, F. P. Parungo, D. E. Florde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, **87**, 2879 (1965).

(2) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2196 (1952).

(3) (a) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962); (b) T. J. Logan, *ibid.*, **28**, 1129 (1963).

(4) Details of the formation of III and its interconversion with its epimer and with IV will be reported later.

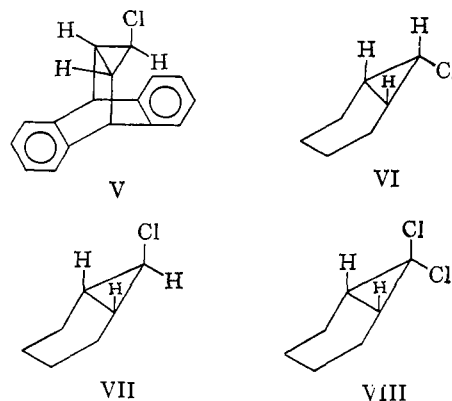
(5) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(6) (a) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (b) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964); (c) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964).

(7) See, for example, J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(8) See, among others: (a) W. E. Parham and H. E. Reiff, *ibid.*, **77**, 1177 (1955); (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); (d) W. R. Moore and H. R. Ward, *Chem. Ind. (London)*, 594 (1961); (e) S. Weinstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962); (f) W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963); (g) R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963); (h) E. Bergman, *ibid.*, **28**, 2210 (1963).

not appear to be known.⁹ Our results with I and V suggested that the solvolysis preferred (by a large factor) the loss of halide ion *trans* to the hydrogen atoms at C-2 and C-4. As we have not succeeded in preparing the epimer of V, we decided to examine the



reactivities of the epimeric 7-chloronorcaranes¹⁰ and of 7,7-dichloronorcarane¹¹ for confirmatory evidence.

The n.m.r. spectrum of the mixture of VI and VII, prepared as previously described,¹⁰ indicated a ratio of 1.9 parts of VI to 1.0 part of VII in the fraction boiling at 56° (11 mm.). Structure VI was assigned to the isomer with the n.m.r. coupling constant of 7.5 c.p.s. for the 7-proton (τ 6.80), while VII had $J = 3.3$ c.p.s. at τ 7.35 for the analogous proton.¹² The mixture was separated by v.p.c. at 150° on a 5 m. \times $\frac{3}{8}$ in. 25% Carbowax 20M on 60–80 mesh Chromosorb W support with a flow rate of 90 ml./min. of helium. The retention times of VI and VII were 39 and 30 min., respectively.

Solvolyses of VI, VII, and VIII were carried out in glacial acetic acid containing a slight excess of sodium acetate. The reaction was followed by Volhard titration of liberated chloride ion. The rate constants obtained at 124.6° are: for VI, 1.4×10^{-6} sec.⁻¹; for VIII, 4.5×10^{-7} sec.⁻¹; and for VII, no observable reaction in 692 hr., $k < 8 \times 10^{-9}$ sec.⁻¹. VII was recovered unchanged after treatment with 2 *M* silver acetate in acetic acid at 210° for 2 hr.

While this work was in progress, certain theoretical discussions concerning the stereochemical basis of electrocyclic transformations appeared¹⁴ in which it was adduced that the groups *trans* to the leaving group in the cyclopropane ring opening should move outward while the *cis* groups should move inward. The relative reactivities of VI and VII are consistent with the idea^{14a,b} that a concerted disrotatory process in VI is favored over a similar process in VII by the large

(9) It was clear^{8b,c} that the reaction was stereospecific; for example, in the bicyclo[4.1.0]hexane system, one epimeric 7,7-*gem*-chlorobromide lost chloride ion and the other lost bromide ion when treated with silver nitrate in water.

(10) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(11) W. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

(12) This is in contrast with the previous assignment¹⁰ of structure VI to the isomer with the smaller coupling constant and *vice versa*. Our assignments, however, are consistent with other n.m.r. data⁵ and with later work of Closs.¹³

(13) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).

(14) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (b) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (c) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (d) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

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.

Acknowledgment. This investigation was supported by Public Health Service Grant GM-12139, from the Institute of General Medical Sciences.

(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 sulfonyl 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}

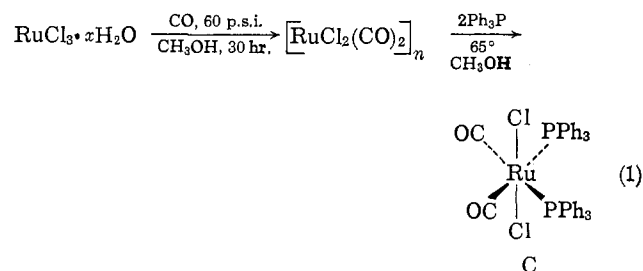
- (1) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).
- (2) L. Vaska and J. W. Diluzio, *ibid.*, **84**, 679 (1962).
- (3) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).
- (4) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959).
- (5) W. Hieber and E. Weiss, *Z. anorg. allgem. Chem.*, **287**, 223 (1956).
- (6) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962).
- (7) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).
- (8) J. P. Collman and W. R. Roper, to be published.
- (9) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).
- (10) R. S. Nyholm and K. Vrieze, *Chem. Ind. (London)*, 318 (1964).
- (11) D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *Nature*, **205**, 589 (1965).
- (12) R. F. Heck, *J. Am. Chem. Soc.*, **86**, 2796 (1964).
- (13) P. M. Maitlis and F. G. A. Stone, *Chem. Ind. (London)*, 1815 (1962).
- (14) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).
- (15) G. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

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.

- (16) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 249, 3604 (1961).
- (17) J. Kleinman and M. Dubeck, *ibid.*, **85**, 1544 (1963).
- (18) A. C. Cope and R. W. Siekman, *ibid.*, **87**, 3272 (1965).
- (19) L. Vaska, Abstracts, VIIIth International Conference on Coordination Chemistry, Vienna, 1964, p. 99.
- (20) L. Malatesta, M. Angoletta, and G. Caglio, ref. 19, p. 210.
- (21) R. Cramer and G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 1392 (1965).
- (22) J. A. Ibers and S. J. LaPlaca, ref. 19, p. 95.
- (23) E. W. Abel, *Quart. Rev. (London)*, **17**, 133 (1963).
- (24) R. S. Nyholm and M. L. Tobe, *Experientia Suppl.*, **9**, 112 (1964).
- (25) J. Chatt and G. M. Davidson, *J. Chem. Soc.*, 843 (1965).