

by contrast, there is apparently no change in hybridization.

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P. G. Harrison, J. J. Zuckerman

Department of Chemistry, State University of New York at Albany
Albany, New York 12203

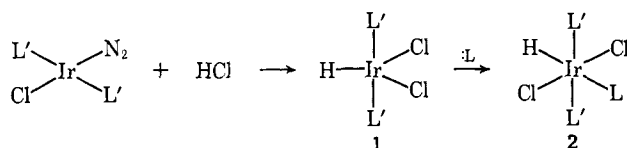
Received December 10, 1969

Stereodirection of Nucleophilic Addition to Five-Coordinated Complexes of Iridium

Sir:

The stereochemistry of substitution reactions on octahedral complexes which proceed by the S_N1 dissociative path is determined by the stereochemical course of nucleophilic addition to five-coordinated intermediates.¹ Is the addition of the nucleophile stereospecific and, if so, what factors can be used to predict the stereochemical course of addition? If one of the ligands on the five-coordinated complex is strongly *trans*-directing, the results reported herein provide a useful solution to the problem.

Addition of anhydrous hydrogen chloride to *trans*-[(C₆H₅)₃P]₂ClIrN₂ in benzene solution gives orange-brown solutions of the five-coordinated iridium(III) complex **1** (d⁶ configuration) which was previously isolated by Chatt and coworkers²⁻⁵ (L' = (C₆H₅)₃P). Addition of nucleophiles, :L, to solutions of **1** gives



high yields of the complexes (**2**) shown in Table I. The configuration shown for **2** is established by four pieces of evidence. (1) When L is dimethylphenylphosphine, the methyl proton resonance appears as a doublet (τ 8.53, $J_{\text{P-H}} = 8.2$ cps) clearly establishing L as *cis* to the two triphenylphosphine ligands.⁷ (2) The observation of a single absorption band at 317 ± 8 cm⁻¹ in the 250–340-cm⁻¹ region for all the complexes is diagnostic of mutually *trans* chloro ligands. Complexes with chlorine *trans* to a hydride absorb in the

(1) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 4; (b) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).

(2) J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Ferguson, *Nature*, **221**, 551 (1969).

(3) Reactions of nucleophiles with a mixture of [(C₆H₅)₃P]₂IrHCl₂ and [(C₆H₅)₃P]₂IrHCl₂ have been previously reported.⁴ The reaction of HCl with [(C₆H₅)₃P]₂IrH₂ was reported⁴ to give [(C₆H₅)₃P]₂IrHCl₂, but the reaction of this compound with CO gave a product unlike that reported herein.

(4) A. Araneo and S. Martinengo, *Gazz. Chim. Ital.*, **95**, 61 (1965).

(5) While the structure of **1** is shown as trigonal bipyramidal, slight increase of the L'-Ir-H angles and decrease of the H-Ir-Cl angles will generate a square-pyramidal structure, such as demonstrated in an analogous five-coordinated d⁶ complex.⁸

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

(7) P. R. Brookes and B. L. Shaw, *J. Chem. Soc.*, **A**, 1079 (1967).

Table I. Infrared Data (cm⁻¹, Nujol) for IrHCl₂[(C₆H₅)₃P]₂L^a

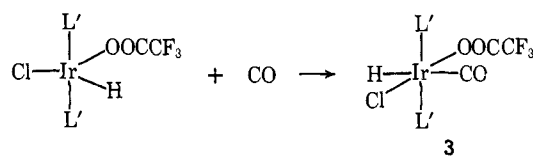
| L | $\nu_{\text{Ir-H}}$ | $\nu_{\text{Ir-Cl}}$ |
|--|---------------------|----------------------|
| CH ₃ OH ^a | 2271 | 318 |
| As(C ₆ H ₅) ₃ | 2232 | 314 |
| As(<i>p</i> -tolyl) ₃ | 2218 | 313 |
| <i>m</i> -NH ₂ -C ₆ H ₄ NO ₂ | 2223 | 312 |
| NC-C ₆ H ₅ ^b | 2213 | 317 |
| P(C ₆ H ₅) ₃ | 2203 | 315 |
| <i>p</i> -NC-C ₆ H ₄ -Cl ^c | 2194 | 320 |
| <i>p</i> -NC-C ₆ H ₄ -NO ₂ ^d | 2193 | 322 |
| <i>p</i> -NC-C ₆ H ₄ -CH ₃ ^e | 2191 | 315 |
| P(<i>p</i> -tolyl) ₃ | 2190 | 312 |
| C ₆ H ₅ N | 2183 | 314 |
| Sb(C ₆ H ₅) ₃ | 2180 | 319 |
| S(C ₂ H ₅) ₂ | 2178 | 313 |
| NH ₂ CH ₂ -C ₆ H ₅ | 2156 | 309 |
| CO ^f | 2154 | 320 |
| NC-C ₆ H ₅ N ^g | 2150 | 320 |
| P(CH ₃)(C ₆ H ₅) ₂ | 2125 | 323 |
| P(OC ₆ H ₅) ₃ | 2120 | 325 |
| P(CH ₃) ₂ C ₆ H ₅ | 2102 | 312 |

^a ν_{OH} at 3410. ^b ν_{CN} at 2083. ^c ν_{CN} at 2082. ^d ν_{CN} at 2087. ^e ν_{CN} at 2083. ^f ν_{CO} at 2003. ^g ν_{CN} at 2230. ^h Nine of these complexes were analyzed and gave satisfactory results.

265-cm⁻¹ region, and those with chlorine *trans* to triphenylphosphine absorb in the 275-cm⁻¹ region.⁸ (3) The observed dependence of $\nu_{\text{Ir-H}}$ on L is indicative of a *trans* H-Ir-L relationship. (4) When L is carbon monoxide, deuteration reveals vibrational interaction.⁹

The addition of L is thus directed *trans* to the hydrido ligand. Nucleophilic attack is at the most electropositive site on **1**, which is opposite the ligand which is most strongly σ bonded to iridium. This result is also in consonance with the principle of microscopic reversibility, that nucleophilic attack should occur *trans* to the ligand having the strongest labilizing influence.

Addition of CO to the five-coordinated compound obtained from the reaction of trifluoroacetic acid and the Ir-N₂ complex gave compound **3** with *trans* H-Ir-L geometry ($\nu_{\text{Ir-H}}$ 2145, ν_{CO} 2036, $\nu_{\text{Ir-Cl}}$ 324 cm⁻¹).



Since the Ir-H bond is entirely σ in character, and because the same metal orbitals are used for Ir-L and Ir-H σ bonding, the Ir-H ir frequencies reflect the σ -*trans* effect¹⁰ of L. A plot of $\nu_{\text{Ir-H}}$ vs. pK_a for complexes derived from donor molecules L such as methanol, *m*-nitroaniline, benzylamine, and pyridine indicates a linear correlation. The strong σ -*trans* effect, for the strong π acceptor triphenylphosphite, indicated by the relatively low Ir-H frequency, is apparently the result of synergic effects.

Particularly significant are the complexes formed by nitriles in which the CN stretching frequencies are considerably decreased (to 2080 cm⁻¹) compared to the CN frequencies in the free nitriles (2230 cm⁻¹). Since the hydride does not use the metal π orbitals

(8) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).

(9) L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966).

(10) See ref 1a, Chapter 5.

in the *trans* H-Ir-NCR complexes, the iridium atom can serve as a π donor into antibonding orbitals of the nitrile molecule, leading to the observed decreases in CN frequencies.¹¹ The assignment of the 2080-cm⁻¹ absorption to the Ir-NC mode was confirmed by using deuterium hydrochloride instead of HCl to generate the five-coordinated intermediate **1**. Addition of the nitriles to the deuterated complex **1** gives products with the $\nu_{\text{Ir-N}=\text{C}}$ band (2083 cm⁻¹) unaltered, but with marked diminution of the 2190-cm⁻¹ (Ir-H) band.

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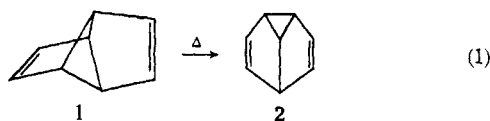
(11) P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968).

Daniel M. Blake, Mitsuru Kubota
Department of Chemistry, Harvey Mudd College
Claremont, California 91711
Received January 26, 1970

(CH)₈ Hydrocarbons. Photochemistry of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene¹

Sir:

The highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**), a valence isomer of cyclooctatetraene, has recently been prepared and characterized.^{2,3} This diene undergoes remarkably facile thermal rearrangement to semibullvalene (**2**),^{2,3} and in further examining its place on the (CH)₈ hydrocarbon energy surface we have explored its photochemistry. We now report the unusual electronic absorption spectrum of **1** as well as its photochemical conversion to cyclooctatetraene and semibullvalene.



The ultraviolet spectrum⁴ of a solution of **1** in isopentane begins to show absorption at about 320 m μ , and the molar extinction at 300 m μ is *ca.* 190. While this absorption seems remarkable for a simple nonconjugated diene, it should be noted that the related monoolefin, tricyclo[3.3.0.0^{2,6}]oct-3-ene,^{5,6} shows a long-wavelength ultraviolet absorption in isooctane with a molar extinction of 150 at 250 m μ . This abnormal electronic spectrum undoubtedly merits further investigation.

(1) The partial support of this research by grants from the National Science Foundation (GP-13085) and the National Institutes of Health (GM-10090) is acknowledged with pleasure.

(2) J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969).

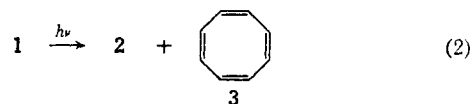
(3) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(4) The sample was a mixture of **1** and **2** (1:2 = 1.4:1) and the measurement was carried out on a Cary Model 14 at 1°. At this temperature the rearrangement of **1** to **2** is quite slow.

(5) J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967).

(6) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).

Solutions of a mixture of **1** and semibullvalene (**2**) (55~60 mg/0.3~0.4 ml of solvent; 1:2 = 0.6~1.2) placed in a Pyrex nmr sample tube were irradiated at -60°, using a 450-W Hanovia medium-pressure lamp through a Vycor immersion well. Under these conditions, the thermal rearrangement of **1** was shown to have a negligible rate. Monitoring the reaction mixtures by means of their nmr spectra showed the appearance of one new component as evidenced by the development of an nmr singlet at τ 4.3; at the same time there was an increase in area of the peaks in the nmr spectrum due to **2**. The new component was identified as cyclooctatetraene (**3**) by infrared and nmr spectral comparisons and by its gas chromatographic retention time. After 80 min of irradiation, the amounts of **2**,



3, and unchanged **1** reached the values shown in Table I. No nmr spectral peaks beyond those accounted for by **1**, **2**, and **3** were observed.

Table I. Results of Low-Temperature Irradiation of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene^a

| Solvent | 1, % | 2, ^b % | 3, % |
|----------------|------|-------------------|-----------------|
| Toluene | 62 | 12 | 26 |
| Isopentane | 52 | 19 | 29 |
| Dimethyl ether | 91 | ~4 ^c | ~5 ^c |

^a Reaction temperature was maintained at -60° and the reaction time was 80 min. ^b Increase in semibullvalene. ^c The small conversion makes these yields inaccurate.

Since the cyclooctatetraene formed in these experiments might have arisen from photochemical reaction of semibullvalene⁷ in addition to, or even instead of, from the diene (**1**), control experiments were performed as follows. Semibullvalene (**2**) was irradiated as previously described in isopentane and in toluene at -60° and at -20 to -30°. No nmr singlet corresponding to **3** was observed in these experiments, confirming the formation of cyclooctatetraene⁸ (**3**) from tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**) itself.

In the pyrolysis of **1** to **2**, a concerted, suprafacial [1,3] sigmatropic process (observed in the thermal conversion of bicyclo[2.1.1]hexene derivatives to the corresponding bicyclo[3.1.0]hexenes)⁹⁻¹¹ seems unlikely, since the tricyclic structure does not permit inversion of the migrating center.¹² A two-step rearrangement by way of the doubly allylic diradical intermediate **4** seems to provide the best rationalization of this process.

(7) Acetone-sensitized conversion of **2** to **3** is reported: H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

(8) The possible formation of **2** from **3** was also excluded, since irradiation of **3** in isopentane under the same conditions described gave no nmr spectral peaks due to **2**. A slow, sensitized conversion of **3** to **2**, however, has been demonstrated by H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

(9) W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

(10) H. M. Frey, R. G. Hopkins, H. E. O'Neil, and F. T. Bond, *Chem. Commun.*, 1069 (1969).

(11) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).