by contrast, there is apparently no change in hybridization.

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Stereodirection of Nucleophilic Addition to Five-Coordinated Complexes of Iridium

Sir:

The stereochemistry of substitution reactions on octahedral complexes which proceed by the SN1 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*-[(C_6H_5)_3P]_2ClIrN₂ in benzene solution gives orangebrown solutions of the five-coordinated iridium(III) complex 1 (d⁶ configuration) which was previously isolated by Chatt and coworkers²⁻⁵ (L' = (C_6H_5)_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 dimethyphenylphosphine, the methyl proton resonance appears as a doublet (τ 8.53, $J_{P-H} = 8.2$ 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 $[(C_6H_6)_2P]_3IrHCl_2$ and

(3) Reactions of nucleophiles with a mixture of $[(C_6H_6)_8P]_3IrHCl_2$ and $[(C_5H_5)_8P]_3IrHCl_2$ have been previously reported.⁴ The reaction of HCl with $[(C_6H_5)_8P]_2IrHCl_2$, 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 d^6 complex.⁶

(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)₂P]₂L^h

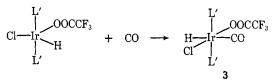
L	$\nu_{\mathrm{Ir-H}}$	ν1rC1
CH₃OHª	2271	318
As(C ₆ H ₅) ₃	2232	314
As(p-tolyl) ₃	2218	313
$m-NH_2-C_6H_4NO_2$	2223	312
NC-C6H56	2213	317
$P(C_6H_5)_3$	2203	315
p-NC-C ₆ H ₄ -Cl ^o	2194	320
p-NC-C ₆ H ₄ -NO ₂ ^d	2193	322
p-NC-C ₆ H ₄ -CH ₃	2191	315
$P(p-tolyl)_3$	2190	312
C ₅ H ₅ N	2183	314
$Sb(C_6H_5)_8$	2180	319
$S(C_2H_5)_2$	2178	313
NH ₂ CH ₂ -C ₅ H ₅	2156	309
CO ⁷	2154	320
NC-C5H5N°	2150	320
$P(CH_3)(C_6H_5)_2$	2125	323
P(OC ₆ H ₅) ₃	2120	325
$P(CH_3)_2C_6H_5$	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. ^{*a*} 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 ν_{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 ($\nu_{\rm Ir-H}$ 2145, $\nu_{\rm CO}$ 2036, $\nu_{\rm Ir-Cl}$ 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 ν_{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

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

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

⁽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 2080cm⁻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 $\nu_{Ir-N=C}$ 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).

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(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.

$$\begin{array}{c} & \stackrel{\scriptscriptstyle \Delta}{\longrightarrow} & \bigoplus_{2} \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

The ultraviolet spectrum⁴ of a solution of 1 in isopentane begins to show absorption at about 320 $m\mu$, and the molar extinction at 300 $m\mu$ 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 meas-
- urement 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) $(55 \sim 60 \text{ mg}/0.3 \sim 0.4 \text{ ml of solvent}; 1:2 = 0.6 \sim 1.2)$ 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,

$$1 \xrightarrow{h\nu} 2 + ()$$

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[3.3.0.02,6]octa-3,7-dienea

Solvent	1, %	2,5 %	3, %
Toluene	62	12	26
Isopentane	52	19	29
Dimethyl ether	91	\sim 4°	\sim 5°

• 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); 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).}