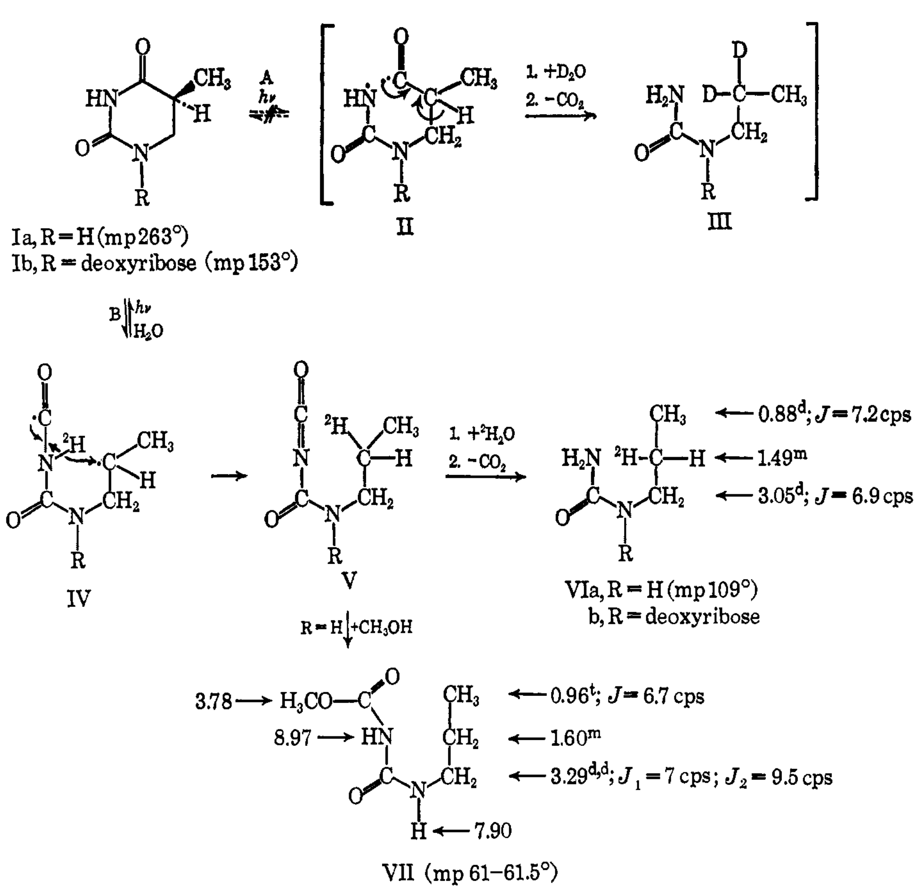

(position 3) to yield, *via* the diradical II, an intermediate ketene, which could add (heavy) water and decarboxylate to III, containing *two atoms of deuterium.* The alternative (pathway B) would start with fission between C-4 and C-5 to give, *via* the diradical IV and intramolecular transfer of $^2H\cdot$, the isocyanate V which would add water with spontaneous decarboxylation to the *monodeuterated n*-propylurea VIa.

When the photolysis of dihydrothymine was carried out in D_2O, the nmr spectrum of *n*-propylurea in D_2O clearly showed the *presence of one deuterium* in support of structure VIa. Undeuterated VIa shows a characteristic triplet at 3.04 ppm for the methylene group adjacent to nitrogen. Additional evidence came from *photolysis of dihydrothymine in methanol* which trapped the isocyanate intermediate V (R = H) by the formation of the crystalline carbamate VII. *n*-Propylurea (VIa) and its deoxyriboside VIb on prolonged irradiation undergo slow dealkylation to deoxyribosylurea and urea (50% yield after 100 hr).

The sequence I → VI assumes intramolecular transfer of hydrogen (deuterium) from NH (position 2).[8] In accordance with this view 1,3-dimethyl-5,6-dihydrothymine (mp 39.5°), which lacks such transferable hydrogen, is stable to photolysis under identical conditions. The stability of dihydrouridine to photolysis supports the assumption of the diradical IV. The corresponding ethyl radical, expected from the photolysis of uridine, would be considerably less stable than the isopropyl radical IV. Recombination to uridine would be faster than hydrogen transfer. That this intramolecular transfer of hydrogen involves the favorable six-membered transition state IV is in agreement with similar cyclic mechanisms postulated for the Hofmann–Löffler–Freytag[9] or Barton[10] reactions. The photolysis of hydantoin derivatives proceeds in an analogous fashion. The isolation of dimers in certain cases lends further support to radical intermediates.[11]

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[8] *Cf.* E. Cavalieri and D. Cravel, *Tetrahedron Letters*, 3973 (1967).

[9] E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

[10] *Cf.* K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964).

[11] Y. Kondo and B. Witkop, unpublished results.

[12] Associate in the Visiting Program of the U. S. Public Health Service, on leave of absence from Tohoku University, Sendai, Japan, 1965–1968.

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The Conversion of Dewar Hexamethylbenzene to Pentamethylcyclopentadienylrhodium(III) Chloride

Sir:

We wish to communicate some details of a very novel ring-contraction reaction whereby Dewar hexamethylbenzene (hexamethylbicyclo[2.2.0]hexadiene) (**1**) is converted to a pentamethylcyclopentadienylrhodium(III) complex. This work was undertaken as part of our investigation of the reactions of Dewar benzenes with transition metals. We have already reported the preparation of Dewar hexamethylbenzenepalladium chloride (dichloro(hexamethylbicyclo[2.2.0]hexadiene)palladium);[1] a number of other workers have also prepared other Dewar benzene–metal complexes. These were all obtained from the Dewar benzene and a suitable metal complex.[2–5]

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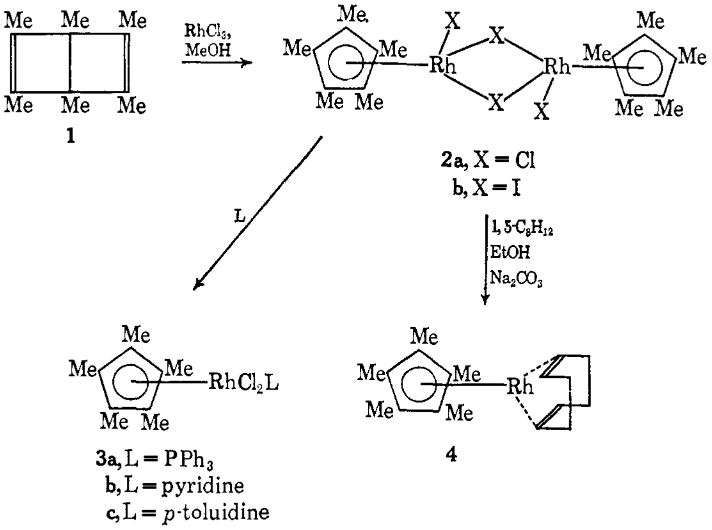
[1] H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).

Table I. Analyses of Pentamethylcyclopentadienylrhodium Complexes

		Calcd, %				Found, %			
		C	H	Cl	Other	C	H	Cl	Other
$[Me_5C_5RhCl_2]_2$	**2a**	38.62	4.89	22.94	Rh, 33.30; M, 618	38.75	5.15	22.87	Rh, 32.91; M, 740[a]
$[Me_5C_5RhI_2]_2$	**2b**	24.42	3.07		I, 51.59; Rh, 20.92; M, 984	24.36	3.55		I, 51.48; Rh, 21.43; M, 943[a]
$Me_5C_5RhCl_2PPh_3$	**3a**	58.86	5.29	12.41	P, 5.42; M, 571	58.49	5.27	12.21	P, 5.96; M, 530
$Me_5C_5RhCl_2C_5H_5N$	**3b**	46.41	5.19	18.27	N, 3.61	46.41	5.17	18.37	N, 3.50
$Me_5C_5RhCl_2C_7H_9N$	**3c**	49.06	5.81	17.04	N, 3.36	49.02	5.87	17.24	N, 3.44
Me_5C_5Rh (1,5-C_8H_{12})	**4**	62.42	7.86		M, 346	61.97	7.79		M, 320,[a] 346[b]

[a] Molecular weight determined osmometrically in chloroform. [b] Mass spectroscopic molecular weight.

From the reaction of an excess of Dewar hexamethylbenzene (**1**) and rhodium trichloride hydrate in methanol, we were able to isolate a nearly quantitative yield (based on $RhCl_3 \cdot 3H_2O$) of very stable dark red crystals (**2a**); in addition high yields of hexamethylbenzene, formed by isomerization of **1**, were also obtained. This reaction has also recently been reported independently by Booth, *et al.*, who claimed the red solid to have the composition and properties consistent with hexamethylbenzenerhodium(III) chloride ($[Me_6C_6RhCl]_2{}^{4+}4Cl^-$).[6] While our compound (**2a**) appears from the published data to be identical with theirs, our results indicate it to be pentamethylcyclopentadienylrhodium(III) chloride. This is shown most eloquently by the analyses for **2a** and a number of derivatives (Table I).



As already reported,[6] the chlorines in **2a** were readily exchanged for iodide on treatment with aqueous sodium iodide. Analysis of the new, purple crystalline complex **2b**, however, agreed with $[Me_5C_5RhI_2]_2$ and not with $[Me_6C_6RhClI_2]_x$ as suggested.[6] From their measured molecular weights, **2a** and **2b** appear to consist largely of dimers in chloroform solution and are probably best represented as shown.[7]

The halogen bridges in **2a** were cleaved by a variety of ligands such as triphenylphosphine, pyridine, and *p*-toluidine to give the monomeric adducts **3**. Both **3c** and in particular **3b** were very labile and reverted readily back to **2a**.

The pmr spectra of **2a** and **2b** showed only unsplit singlets, at τ 8.40 and 8.10, respectively, in $CDCl_3$. The pmr spectrum of **3a** showed a sharp doublet at τ 8.64 (due to coupling of the five equivalent methyls with the phosphorus, J_{P-H} = 4.0 cps both at 60 and 100 Mcps[9]) and multiplets at τ 2.2 and 2.65 due to the phenyl protons. The integration, 1:1, was that expected. The pmr spectrum of **3c** showed two singlets at τ 7.68 and 8.54 (due to the methyl groups of the *p*-toluidine and of the C_5Me_5 ring), a broad singlet at τ 5.13 (NH_2 protons), and a doublet at τ 2.80 (aromatic protons). The integrated intensities of these bands, 2.8:15.4:2:4, agreed with that expected, 3:15:2:4.

One further reaction of interest can be reported at this time. On refluxing **2a** with 1,5-cyclooctadiene in ethanol, no reaction apparently occurred; however, on addition of a small amount of sodium carbonate the red solution rapidly turned yellow and it was possible to isolate an 86% yield of yellow crystals of (π-1,5-cyclooctadiene)(π-pentamethylcyclopentadienyl)-rhodium(I) (**4**). This formulation was confirmed by analyses and molecular weight measurements and by the pmr spectrum in $CDCl_3$, which showed a sharp singlet at τ 8.23 (methyl protons) and two broad resonances at τ 7.05 and 7.94 due to the olefinic and aliphatic protons of the cyclooctadiene. The intensity ratio, 17:4:8, was close to that expected, 15:4:8.

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(2) E. G. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, **89**, 3922 (1967).

(3) E. O. Fischer, C. G. Kreiter, and W. Berngruber, *Angew. Chem. Intern. Ed. Engl.*, **6**, 634 (1967).

(4) H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, **86**, 830 (1967).

(5) F. G. A. Stone, Abstracts, 3rd International Symposium on Organometallic Chemistry, Munich, 1967, p 9.

(6) B. L. Booth, R. N. Haszeldine, and M. Hill, *Chem. Commun.*, 1118 (1967)

(7) From the measured molecular weight of 2a it would appear that oligomers higher than dimers are also present. One of us has previously commented on the fact that, particularly in Cl-bridged rhodium complexes, aggregates of different sizes appear to have similar energies, and hence the molecular weights observed are probably dependent on the previous history of the complex.[8]

(8) S. McVey and P. M. Maitlis, *Can. J Chem.*, **44**, 2429 (1966).

(9) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

Perhaps the most convincing evidence for the presence of a pentamethylcyclopentadienyl ring in **2a** and its derivatives comes from the mass spectra of **2a** and **4**. The mass spectrum of **4** showed a very strong molecular ion peak (*m/e* 346) and another strong peak at *m/e* 238 ($C_5Me_5Rh^+$). The mass spectrum of **2a** was more difficult to obtain; however, a sample run at 210° gave peaks at *m/e* 237 ($C_5Me_4CH_2Rh^+$, corresponding to loss of HCl from $C_5Me_5RhCl^+$) and 134 ($C_5Me_4CH_2^+$). Peaks at *m/e* 162 ($C_6Me_6^+$) and 147 ($C_6Me_5^+$), both of which are very strong in samples containing hexamethylbenzene, were absent in both spectra.

The parent compounds $[C_5H_5Rh(hal)_2]_x$ have been briefly described by Angelici and Fischer[10] and by Powell and Shaw.[11] The properties of our complexes **2** agree well with those described for $[C_5H_5Rh(hal)_2]_x$.

After completion of this work, our attention was drawn to the recent note by Kasahara, *et al.*,[12] in which they described the conversion of chloro(1,5-cyclooctadiene)rhodium(I) dimer to diiodocyclopentadienylrhodium(III) on treatment with iodine in ether.

While there is an obvious analogy between these reactions we feel that mechanistically they will probably prove quite different since the reaction of Kasahara, *et al.*, was carried out under oxidizing conditions while that described here occurred under reducing conditions.[13] Both reactions, however, testify to the remarkable stability of cyclopentadienylrhodium(III) complexes. Ring-contraction and ring-expansion reactions in organometallic chemistry, while not unknown,[15,16] still remain novel, and none have previously been described which occur so simply and in such high yields as these.

Acknowledgment. We thank the National Research Council of Canada for supporting this work, Johnson, Matthey, and Mallory for the loan of rhodium trichloride, and Dr. W. Schäfer for a gift of Dewar hexamethylbenzene.

[10] R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, **85**, 3733 (1963).

[11] J. Powell and B. L. Shaw, *Chem. Commun.*, 323 (1966).

[12] A. Kasahara, T. Izumi, and K. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 699 (1967).

[13] The formation of an unstable intermediate, "$RhHCl_2$," by reaction of rhodium trichloride hydrate with hot alcohol has been postulated by a number of authors; *e.g.*,[14] the first step in this reaction (which does not proceed under conditions where "$RhHCl_2$" is not formed) is probably addition of Rh–H to a double bond of Dewar hexamethylbenzene (**1**). A complex series of rearrangements (which may involve ring-opening and ring-closing steps) must then occur to form the complex **2a** with elimination of a "CH_3CH" moiety. Further work to elucidate this mechanism is in progress; however, the "CH_3CH" fragment does not appear as free ethylene.

[14] K. C. Dewhirst, *Inorg. Chem.*, **5**, 319 (1966).

[15] E. O. Fischer and S. Breitschaft, *Chem. Ber.*, **99**, 2213 (1966).

[16] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3479 (1961).

[17] Fellow of the Alfred P. Sloan Foundation and author to whom inquiries should be addressed.

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Received February 24, 1968

Optically Induced Overhauser Effect in Solution. Nuclear Magnetic Resonance Emission

Sir:

We wish to report the observation of nuclear magnetic resonance (nmr) stimulated emission in the proton nmr spectrum of anthraquinone induced by the optical excitation of this molecule to its lowest lying electronic triplet state. In the experiment, a solution (at 25°) containing 0.005 *M* anthraquinone in perfluorobenzene was irradiated with 3000- to 4000-Å wavelength light using a 3500-W mercury lamp. Under these conditions a steady-state concentration of anthraquinone in the triplet state is obtained.[1,2] Because of the low concentration of the triplet state, only the nmr of the ground state of anthraquinone is observed. Thus the experiment consists of creating a steady-state concentration of triplet-state anthraquinone and looking at the effect on the nmr of the ground state of this molecule.

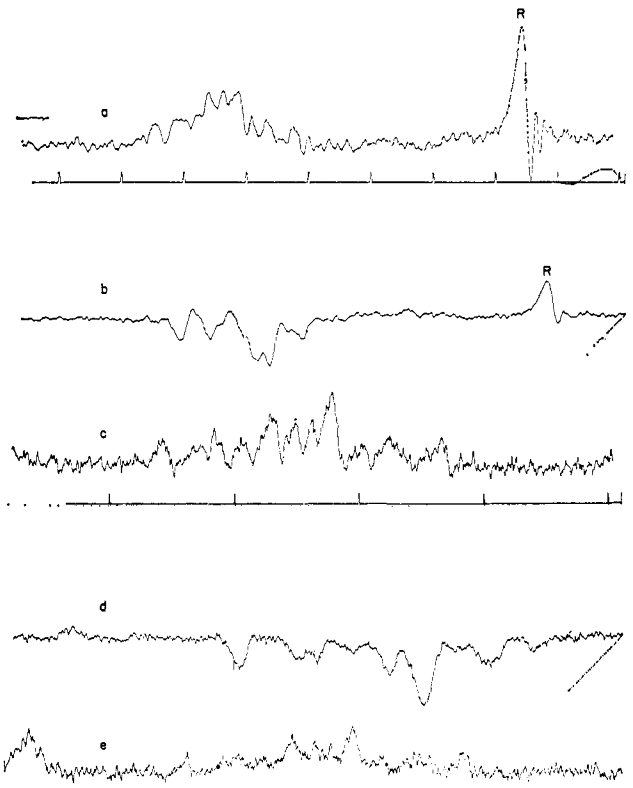

Figure 1. (a) Proton nmr spectrum of 0.005 *M* anthraquinone in perfluorobenzene in the absence of the exciting light. The line labeled "R" is due to benzene which is used as a reference. The other lines which occur at lower field relative to "R" are due to the protons of anthraquinone. This spectrum which is a time-average of 47 passes is not a slow-passage spectrum and the lines are not well resolved. The frequency scale is given below the spectrum. Each marker represents 10.63 Hz. (b) Proton nmr spectrum of the same sample during irradiation. This emission spectrum is a time-average of 12 passes. All other conditions are identical with those used to obtain Figure 1a. The frequency scale for 1b is given in 1a, and the shift of 1b relative to 1a is real. (c) Slow-passage proton nmr spectrum of anthraquinone in the absence of the exciting light. This spectrum is a time-average of 65 passes. The frequency scale is given below the spectrum, and each marker represents 10.63 Hz. This scale also applies to Figures 1d and 1e. (d) Slow-passage proton nmr of anthraquinone during irradiation. This emission spectrum is a time-average of 16 passes. (e) Slow-passage proton nmr of anthraquinone after the sample had been irradiated for 30 min. This spectrum is a time-average of 65 passes.

The nmr emission spectrum which is shown in Figure 1 is the result of an Overhauser effect[3] probably involving

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[1] For anthraquinone, the quantum yield for singlet–triplet crossover is 0.88 in benzene.[2]

[2] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 309.