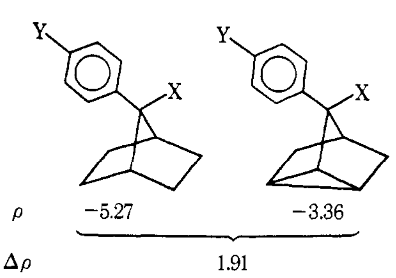
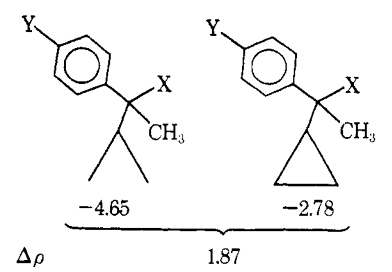
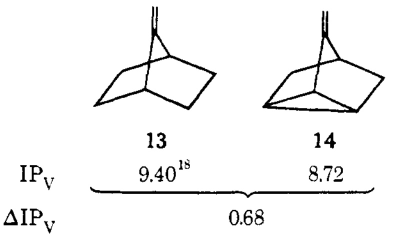
tabulated the ρ values for the solvolyses of the compounds shown below.

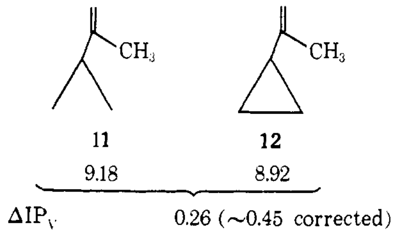




Again, the effect of closing the ring upon the ρ slope is the same in the two systems.

We have also prepared olefins[13,14] related to **3** and **4** and determined the effects of ring closure upon ionization potentials.[15–17]





The changes in ionization potential upon ring closure are 0.68 eV for the rigid systems **13** → **14** and, after correction for two alkyl groups,[19] about 0.45 eV for **11** → **12**. These changes correspond pretty well with the changes in solvolysis rates.

It is clear that these three probes, while not giving accurate quantitative agreement, indicate that the rigid cyclopropyl carbinyl system is afforded at least as much stabilization as is the free-rotating system, in contrast to the conclusions based upon cmr spectra.[20,21]

Finally, the calculations of Hehre and Hiberty[7] indicate that the parent cyclopropyl carbinyl cation is "bisected" and that the slight movement in going from the starting cyclopropane to the cation is in the *opposite direction* to that leading to a bridged ion. This structure, according to our definitions[3] and according to several theoretical and three experimental studies, is stabilized by hyperconjugation (vertical stabilization) in the usual sense and does not require the postulate of bridging in the usual sense.[2]

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(13) Nortricyclan-3-one was prepared according to the method of Meinwald and Crandall,[14] converted to 3-methylenenortricyclane in 76% yield using the Wittig method, and the olefin was purified by gas-liquid chromatography: nmr (CCl_4) δ 4.7, s (1 H), 4.6 s (1 H), 2.2 broad (1 H), 1.5 m (6 H), 0.96 m (1 H); ir 3180, 3030, 2850, 1695 cm^{-1} (CCl_4). Other olefins, synthesized by standard procedures or purchased, were identified with known structures by nmr after purification by gas-liquid chromatography.

(14) J. Meinwald and J. Crandall, *Org. Syn.*, **45**, 74 (1966).

(15) Photoelectron spectra were determined on an instrument constructed according to Turner,[16] as we have previously described.[17]

(16) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966); D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970.

(17) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organometal. Chem.*, in press.

(18) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).

(19) One alkyl group on the cyclopropane ring lowers the IP of phenylcyclopropane or 2-propenylcyclopropane about 0.1 eV.[3b]

(20) Although Olah and Westerman[21] state, "We cannot recollect, in contrast to Brown, any suggestion that ^{13}C nmr shifts could be used to predict solvolytic rates and stabilities of carbocations or any reason why they should," Olah and Liang[8] had previously stated, "Both cmr and pmr parameters showed that the secondary cation 1–H and the tertiary cations 1–CH_3 and 1–C_2H_5 are stabilized by charge delocalization the degree of which, as anticipated, is greater in the former." The discussions in ref 8, typified by the sentence above, are almost entirely directed at stabilization of cations. We agree with Brown and with ref 21 that ^{13}C chemical shifts do not relate in any direct way to cation stabilities.

(21) G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 7530 (1973).

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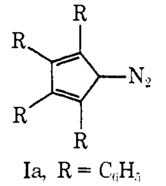
Reactions of Diazocyclopentadienes. Preparation and Structure of Halogen Substituted *Pentahapto*cyclopentadienylrhodium Complexes

Sir:

Reaction of a diazoalkane with a transition metal compound may result in (a) complex formation with retention of the diazo group,[1] (b) insertion into metal halogen, hydride, or alkyl bond,[2] or (c) carbene formation.[3] We report that the diazocyclopentadienes (Ia,b) insert into halogen-bridged dirhodium species to give new halo-substituted cyclopentadienyl complexes IIa–e. Reaction 1 proceeds conveniently in benzene in nitrogen atmosphere at room temperature. The reactions are complete within 24 hr and can be followed by watching the disappearance of the band at 2060 cm^{-1} due to the nitrogen group. The products are air stable and range in color from yellow (IIa,b,e) to red (IIc,d). The ease with which these reactions produce halo-sub-



Ia, R = C_6H_5
b, R = H

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(1) S. Otsuka, A. Nakamura, T. Kayama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972).

(2) (a) M. F. Lappert and J. S. Poland, *Advan. Organometal. Chem.*, **9**, 397 (1970); (b) J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 1872 (1969).

(3) (a) P. Hong, N. Nishi, K. Sonogashira, and H. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 514 (1973).

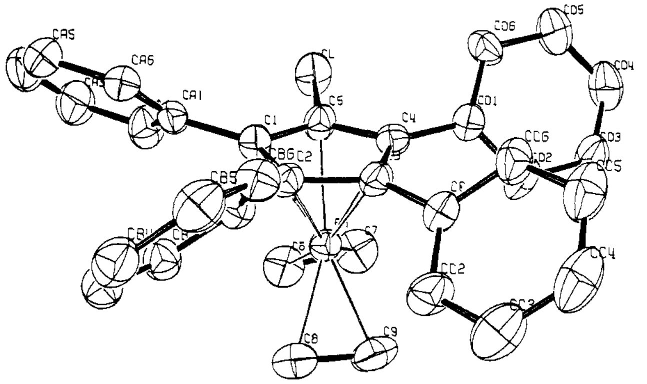
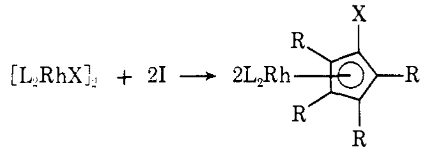


Figure 1. The molecular geometry of $[h^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$.



(1)

IIa, $R = C_6H_5$; L_2 = COD; X = Cl
b, $R = C_6H_5$; L_2 = COD; X = Br
c, $R = C_6H_5$; $L_2 = (C_2H_4)_2$; X = Cl
d, $R = C_6H_5$; $L_2 = (CO)_2$; X = Cl
e, R = H; L_2 = COD; X = Cl

stituted *pentahapto*cyclopentadienyl derivatives is in contrast to those presently available[4] which often require many laborious steps.

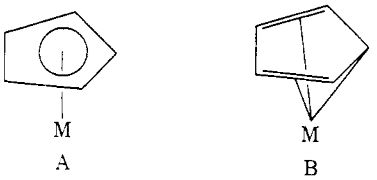
Compound I may also form *pentahapto*cyclopentadienyl derivatives by means of hydride abstraction (presumably from the solvent). This occurs in the reaction of Ib with $Fe_2(CO)_9$ in toluene to produce the familiar $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$. Ia forms the tetraphenyl analog of this dimer when treated with $Fe_2(CO)_9$ in hexane at room temperature.[5] However, at 124° in octane, Ia reacts with $Fe_2(CO)_9$ to form a yellow compound, III, whose formula is $[C_5(C_6H_5)_4H]Fe(CO)_3$. Complete characterization has not been possible yet and may require an X-ray structure determination. However, analytical, mass spectroscopic, infrared, and nmr data suggest a monomeric structure containing a *pentahapto*-tetraphenylcyclopentadienyl group having one phenyl group linked to the iron *via* an acyl group in the ortho position.

The crystal structure of IIc has been determined. Crystals of $[h^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$ are monoclinic, space group $P2_1/n$, $a = 15.846\ (2)$, $b = 10.593\ (2)$, $c = 16.081\ (2)$ Å, $\beta = 104.95\ (1)°$, and $Z = 4$. Data collection (Mo K$\bar{\alpha}$ radiation, Syntex P$_1$-Autodiffractometer) yielded 4285 symmetry independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 55°$ and $I > 2\sigma(I)$. The structure was solved using standard heavy-atom and difference Fourier techniques. Unit-weighted full-matrix least-squares refinement, employing anisotropic thermal parameters for the 35 nonhydrogen atoms, has resulted in a conventional R of 0.059. The analysis shows that the crystal contains discrete $[h^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$ molecules in which the Rh atom is π bonded to the substituted cyclopentadienyl ring and two ethylene ligands (Figure 1). Although the cyclopentadienyl ring is bonded to the rhodium atom in a *pentahapto* fashion, the bond lengths around the five-membered ring show some similarities with those of a σ-bonded cyclopentadienyl ring, namely two short (1.409 (8, 4, 4)[6] Å) and three long (1.451 (8, 7, 10) Å) carbon–carbon bonds (Table I). The Rh-C bonds seem to be of three types based on their lengths. The ring carbon to which the chlorine atom is attached is bonded to the Rh atom at a distance of 2.177 (6) Å, while the pairs (C_1, C_2) and (C_3, C_4) have average Rh-C bond lengths of 2.300 (6, 4, 4) and 2.259 (6, 10, 10) Å, respectively. The cyclopentadienyl ring is folded by 4.2° about the C_1–C_4 vector such that C_5 is brought closer to the Rh atom. The four carbon atoms of the cyclopentadienyl ligand involved in the two short C–C bonds are each bonded to a phenyl ring at an average distance of 1.491 (8, 3, 7) Å, while the fifth carbon of the cyclopentadienyl ring is bonded to the chlorine at a distance of 1.726 (7) Å. The four phenyl rings are all planar (maximum deviation from any of the respective least-squares mean planes is 0.012 Å) with an average C–C bond distance of 1.396 (10, 8, 29) Å. The dihedral angles between the least-squares mean planes of the cyclopentadienyl ring and those of the four phenyl rings range from 45 to 54°. The two nearly parallel ethylene ligands are each π bonded to the rhodium with the four Rh–C distances averaging 2.115 (8, 10, 19) Å. The molecule has approximate $C_s(m)$ point symmetry excluding the tilts of the phenyl rings.

Table I. Selected Bond Lengths (Å) in $[h^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$

Rh–C_1 = 2.296 (6)	C_1–C_2 = 1.405 (8)
Rh–C_2 = 2.303 (6)	C_2–C_3 = 1.461 (8)
Rh–C_3 = 2.268 (6)	C_3–C_4 = 1.413 (9)
Rh–C_4 = 2.249 (6)	C_4–C_5 = 1.445 (8)
Rh–C_5 = 2.177 (6)	C_5–C_1 = 1.446 (9)
Rh–C_6 = 2.115 (8)	C_6–C_7 = 1.423 (12)
Rh–C_7 = 2.105 (8)	C_8–C_9 = 1.427 (12)
Rh–C_8 = 2.134 (8)	
Rh–C_9 = 2.105 (8)	C_5–Cl = 1.726 (7)

As in the case of metal acetylene and metal butadiene derivatives, two extreme bonding models can be envisioned for *pentahapto*cyclopentadienyl metal derivatives. A is the familiar symmetrical π-type model. B



is the hitherto unreported localized type where the ring is bonded to the metal by two olefin π bonds and one σ-alkyl bond. The structure reported here is unique because of the appreciable contribution of the B form. Further studies are planned to investigate the interesting questions this structure raises about the bonding modes of halogen substituted cyclopentadienyl derivatives.[6a]

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(4) (a) M. L. H. Green in "Organometallic Compounds," Vol. II, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London 1968; (b) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **92**, 3239 (1970).

(5) D. Cashman and F. J. Lalor, *J. Organometal. Chem.*, 32, 351 (1971).

(6) The first number in parentheses is the estimated standard deviation of an individual bond length. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.

(6a) NOTE ADDED IN PROOF. We have recently solved the structure of (h^5-C_5Cl_5)RhCOD, COD = 1,5-cyclooctadiene, and find bond localization of type B in the C ring. A more detailed discussion of this type of localization and that discussed by Bennett, *et al.*, *Nature* (*London*), 201, 1318 (1964), will follow.

Fortunately the insertion reactions of diazocyclopentadienes provide an easy route to these compounds.

Acknowledgment. We gratefully acknowledge the advice and interest of Professor H. C. Clark in whose laboratories the preparative work was conducted.

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[7] National Research Council of Canada Scholarship Awardee, 1970–1973.

[8] National Research Council of Canada Postdoctoral Fellow, 1972–1974.

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Effect of Ethyl Iodide on the Photodimerization of Acenaphthylene[1]

Sir:

Heavy-atom solvents have been shown to produce large increases in the quantum yields of dimerization and cycloaddition of acenaphthylene. These effects have been attributed to an increase in the rate of intersystem crossing resulting from spin-orbit coupling induced by the heavy-atom solvent.[2-6] Most of the work to date has involved heavy-atom solvents containing bromine. In all cases, the magnitudes of the quantum yields of dimerization and cycloaddition have been limited solely by the amount of bound bromine present in the solvent. However, the proposed mechanism for these reactions predicts that there should be an upper limit for these quantum yields when sufficient spin–orbit perturbation is present.[6,7] We wish to report the first evidence that this limit may be reached in the presence of a heavy-atom solvent.

One will observe from the data in Figure 1 that the quantum yield of dimerization increases very rapidly as the concentration of ethyl iodide is increased from 0 to 10 mol %.[8] Further increases in the concentration of heavy-atom solvent, however, result in a gradual decrease in the quantum yield of dimerization. This behavior may be attributed to two competing processes, namely intersystem crossing from the first excited singlet to the first excited triplet, and deactivation of this triplet to the ground state. Heavy-atom solvents appear to have a far greater influence on the initial intersystem crossing rate of acenaphthylene than on any of the nonradiative intercombinational transitions that follow intersystem crossing. However, if the rate of intersystem crossing is sufficiently large, the quantum yield for this process should approach unity. Under these conditions, effects on other intercombinational processes such as deactivation of the triplet state should become important. The data conform very well with this description.

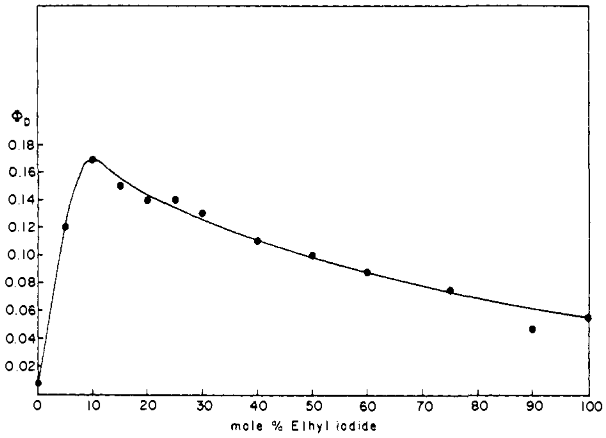

Figure 1. The dependence of Φ_D on the concentration of ethyl iodide.

Figure 2 represents the reciprocal of the quantum yield of dimerization as a function of the ethyl iodide concentration.[9] The observed linear relationship is predicted if one considers the following simplified mechanism

$$\begin{aligned}
\mathrm{A} + h\nu &\xrightarrow{I_a} {}^1\mathrm{A}\\
{}^1\mathrm{A} &\xrightarrow{k_{ic}} \mathrm{A}\\
{}^1\mathrm{A} &\xrightarrow{k_{isc}} {}^3\mathrm{A}\\
{}^1\mathrm{A} + \mathrm{Q} &\xrightarrow{k'_{isc}} {}^3\mathrm{A} + \mathrm{Q}\\
{}^3\mathrm{A} + \mathrm{A} &\xrightarrow{k_2} \mathrm{A}_2\\
{}^3\mathrm{A} + \mathrm{A} &\xrightarrow{k_q} 2\mathrm{A}\\
{}^3\mathrm{A} + \mathrm{Q} &\xrightarrow{k'_q} \mathrm{A} + \mathrm{Q}\\
{}^3\mathrm{A} &\xrightarrow{k_d} \mathrm{A}
\end{aligned}$$

where A = acenaphthylene and Q = ethyl iodide. Using the steady-state approximation, one obtains the quantum yield of dimerization, Φ_D.

$$\Phi_D = \left\{\frac{k_{isc} + k'_{isc}[\mathrm{Q}]}{k_{ic} + k_{isc} + k'_{isc}[\mathrm{Q}]}\right\} \times \left\{\frac{k_2[\mathrm{A}]}{k_2[\mathrm{A}] + k'_q[\mathrm{Q}] + k_q[\mathrm{A}] + k_d}\right\}$$

The first term in this expression is the quantum yield of intersystem crossing, Φ_{isc}, which should approach unity

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[1] Photochemical Reactions. IX. For part VIII, see D. O. Cowan and W. W. Schmiegel, *J. Amer. Chem. Soc.*, **94**, 6779 (1972).

[2] D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281 (1970).

[3] B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).

[4] J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970).

[5] B. F. Plummer and D. M. Chihal, *J. Amer. Chem. Soc.*, **93**, 2071 (1971).

[6] B. F. Plummer and W. I. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 306 (1972); *J. Amer. Chem. Soc.*, **95**, 6709 (1973).

[7] D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6286 (1970).

[8] Irradiations were performed on a merry-go-round apparatus using a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel. A combination of Corning CS-O-52 and CS-7-37 filters was used which produced a narrow band around 365 nm. Irradiation times varied from 8 to 20 hr depending on the quantum yields of the samples. Each sample was degassed with five freeze–thaw cycles before the irradiation. The extent of conversion (<10%) was determined by measuring the optical density of acenaphthylene at 340 nm. The incident light intensity was measured by actinometry with ferrioxalate. At the concentration of acenaphthylene (0.1 *M*) that was used, virtually all of the light was absorbed.

[9] The following parameters were derived by a least-squares treatment of data: slope (M^{-1}), 1.02 ± 0.03; intercept, 4.8 ± 0.2; correlation, 0.997. From the slope, the following rate ratio is obtained: $k'_q/k_2 = 0.10$.