

more stable than *ortho*-quinoid structures,<sup>33</sup> and there are other experimental and theoretical con-

(33) P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press, Inc., New York, N. Y., 1959, p. 82 ff.

(34) See, for example, (a) W. A. Waters, *J. Chem. Soc.*, 727 (1948); (b) M. J. S. Dewar, *ibid.*, 463 (1949); (c) G. E. K. Branch and D. L.

siderations which may provide some less direct support for this hypothesis.<sup>34</sup>

Yabroff, *J. Am. Chem. Soc.*, **56**, 2568 (1934), for ionization of methoxybenzoic acids in water; (d) P. Mamalis and H. N. Rydon, *Nature*, **166**, 404 (1950), for base-catalyzed decomposition of substituted benzoyl-oxyethyl dimethyl sulfonium iodides.

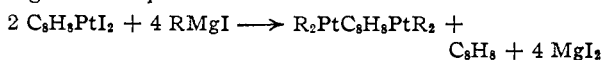
## COMMUNICATIONS TO THE EDITOR

### METAL-OLEFIN COMPOUNDS. II. REACTIONS OF *cis*-DIIDO-(CYCLOÏTATETRAENE)-PLATINUM(II) WITH GRIGNARD REAGENTS<sup>1</sup>

Sir:

Recently a series of compounds containing cyclooctatetraene as a bridging group in a number of binuclear complexes has been reported by Manuel and Stone.<sup>2</sup> The structure of  $(OC)_3FeC_8H_8Fe(CO)_3$  has been determined by Dickens and Lipscomb<sup>3</sup> and confirms the assignment of the cyclooctatetraene to the bridge location in this compound.

In connection with a study of the reactions of platinum-olefin compounds we have isolated a series of platinum(II) alkyl and aryl derivatives in which cyclooctatetraene acts as a bridging ligand between two platinum atoms. The reaction of *cis*-diiodo-(cyclooctatetraene)-platinum(II) with alkyl or aryl Grignard compounds proceeds according to the equation



R = alkyl or aryl group

Similar products were obtained from the reaction of *cis*-diiodo-(cyclooctatetraene)-platinum(II) and alkyl, aryl, or cyclopentadienyl metal compounds.

In a typical preparation 100 ml. of an ether solution containing 50 mmoles of methylmagnesium iodide was added to a suspension of 5.53 g. (10 mmoles) of *cis*-diiodo-(cyclooctatetraene)-platinum(II). The resulting clear solution was stored at room temperature for 4 hours and then hydrolyzed by adding it to an ammonium chloride-ice mixture. The organic phase was separated, dried and evaporated. The resulting dark brown residue was extracted with methylene chloride, decolorized and filtered. The product was separated by evaporation of the solution and addition of *n*-hexane until crystallization commenced. Recrystallization of the product from a methylene chloride-hexane mixture gave 2.0 g. (3.61 mmoles) of  $\mu$ -cyclooctatetraene-di-(bismethylplatinum(II)), I, in the form of yellow needle-shaped crystals decomposing at 161–175°.

*Anal.* Calcd. for  $C_{12}H_{20}Pt_2$ : C, 25.98; H, 3.63; Pt, 70.38; mol. wt., 554.7. Found: C, 25.55; H, 3.70; Pt, 70.02; mol. wt., 427 (ebullioscopically in benzene); 575 (from unit cell dimensions),

(1) For the previous paper in this series, see *J. Am. Chem. Soc.*, **82**, 535 (1960).

(2) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960). This article contains a number of leading references on this subject also.

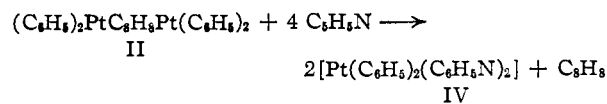
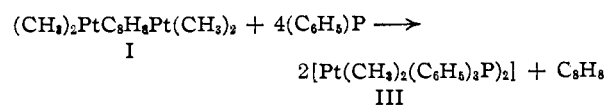
(3) B. Dickens and W. N. Lipscomb, *ibid.*, **83**, 489 (1961).

measured density and assuming four molecules per unit cell).

$\mu$ -Cyclooctatetraene - di - (bisphenylplatinum (II)), II,  $(C_6H_5)_2PtC_8H_8Pt(C_6H_5)_2$ , was prepared in a similar manner starting with 2.00 g. (3.6 mmoles) of *cis*-diiodo-(cyclooctatetraene)-platinum (II). Purification of the product gave 1.20 g. (1.49 mmoles) in the form of light yellow plates decomposing at 155–165°.

*Anal.* Calcd. for  $C_{32}H_{28}Pt_2$ : C, 47.86; H, 3.51. Found: C, 47.30; H, 3.54.

The compounds in this series are moderately soluble in chlorinated hydrocarbons and benzene. They react with substituted phosphines and amines displacing the cyclooctatetraene and yielding compounds such as dimethyl-bis-(triphenylphosphine)-platinum(II), III, and di-(phenyl)-di-(pyridine)-platinum(II), IV, as shown below.



*Anal.* Calcd. for  $C_{38}H_{36}P_2Pt$ , III: C, 60.86; H, 4.84. Found: C, 60.34; H, 4.37.

*Anal.* Calcd. for  $C_{24}H_{20}N_2Pt$ , IV: C, 52.04; H, 3.97; N, 5.52. Found: C, 51.44; H, 4.07; N, 5.49.

Compounds I and II added bromine and hydrogen rapidly and the addition was accompanied by the decomposition of the complex.

The absence of absorption bands at 1635 and 1609  $cm^{-1}$  assigned to the C=C stretching frequency<sup>4</sup> in cyclooctatetraene indicates that all of the olefin bonds are coordinated to platinum in compounds I and II. The appearance of a strong absorption band at 1352  $cm^{-1}$  in platinum complexes containing cyclooctatetraene acting as a bridging unit or as a chelated olefin appears to be a characteristic of this series of compounds. In addition it was noted that all of the platinum-cyclooctatetraene complexes displayed an absorption band in the 800  $cm^{-1}$  region of the infrared spectra which has been assigned to a ring deformation frequency in the pure hydrocarbon.<sup>4</sup> The major difference noted in the 800  $cm^{-1}$  band of the hydrocarbon and the compounds studied has been

(4) E. R. Lippincott, R. C. Lord and R. S. McDonald, *ibid.*, **73**, 3370 (1951).

in the relative intensity of this band. In compounds such as  $C_8H_8PtI_2$ , the reduction in intensity is very slight while the intensity of the band is decreased by a factor of 10 to 100 in the binuclear compounds.

The conformation of the cyclooctatetraene in this series of compounds currently is being investigated by X-ray diffraction techniques on single crystals of I.<sup>5</sup> Preliminary results indicate that the crystals are monoclinic with four molecules in a unit cell of a parameters  $a = 10.95 \text{ \AA}$ ,  $b = 11.19 \text{ \AA}$ ,  $c = 10.78 \text{ \AA}$  and  $\beta = 111.2^\circ$ . From characteristic absent reflections the crystals were assigned tentatively to space group  $C2/c$  or  $Cc$ . The shortest Pt-Pt distance was  $4.03 \text{ \AA}$ , as determined from the two-dimensional Patterson function and a least squares refinement on the platinum contribution to the structure factor.

In  $(OC)_3FeC_8H_8Fe(CO)_3$  Dickens and Lipscomb reported an eight membered "chair" configuration for cyclooctatetraene. In compound I the observed Pt-Pt bond distance is in close agreement with the distance one might expect if the cyclooctatetraene retained a "tub" configuration.

Further details on the preparative studies and structure determination will be reported shortly.

We wish to thank the Research Corporation for support.

(5) We wish to acknowledge the support of the Office of Ordnance Research in carrying out the structural studies.

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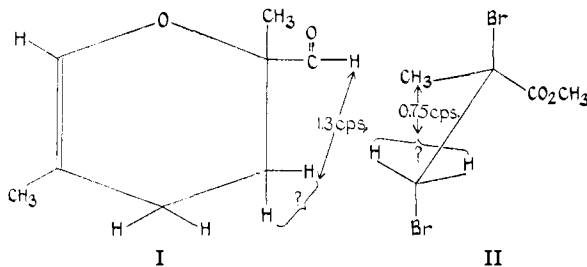
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### LONG-RANGE SPIN-SPIN COUPLINGS IN THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BICYCLO[2.1.1]HEXANES<sup>1</sup>

Sir:

The usual assumption that proton spin-spin couplings are negligibly small over more than three bonds in saturated systems<sup>2</sup> recently has been shown to be unfounded by the discovery of several counter-examples.<sup>3</sup> Thus, the aldehydic proton of



Long-range spin-spin couplings

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the 139th National Meeting in St. Louis, March 21-30, 1961 (abstract page 39-O).

(2) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapt. 3; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapt. 6; M. Karplus, *J. Am. Chem. Soc.*, **82**, 4431 (1960).

(3) D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

methacrolein dimer (I) has been found to be split into a doublet ( $J = 1.3 \text{ cps}$ ) by one of the two  $\beta$ -hydrogens, four single bonds away. Similarly, one of the non-equivalent methylene protons of methyl  $\alpha,\beta$ -dibromoisobutyrate (II) couples with the  $\alpha$ -methyl group ( $J = 0.75 \text{ cps}$ ). We wish to report the first example of long-range spin-spin couplings of this type in rigid molecules, where the coupled protons occupy readily definable positions in space.<sup>4</sup>

The n.m.r. spectrum<sup>5</sup> of *exo*-5-chlorobicyclo-[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide (III)<sup>6</sup> (see Fig. 1A) shows this long-range coupling with startling clarity. Peaks at 327 (broad), 173, 109 and 82 cps. of relative intensity 1:2:4:9 correspond to NH, bridgehead, methylene and *t*-butyl protons, respectively. The two doublets at 229 and 150 cps. form a typical AB pattern ( $J \cong 7 \text{ cps}$ ), and must arise from the two protons on the one carbon bridges. From the values of the chemical shifts for these peaks,<sup>7</sup> the former may be assigned to the *endo* proton on the chlorine-bearing carbon ( $C_6$ ) and the latter to the *endo* proton  $\alpha$  to the amide group ( $C_5$ ). It appears, then, that these two distant protons, at opposite corners of a folded cyclobutane ring, are responsible for this clear AB pattern. The extreme simplicity of this analysis is made possible by the apparent equivalence of the two methylene protons *cis* to the chlorinated bridge and those *cis* to the amide bridge, and by the fact that all the remaining 1,2-coupling constants (between the bridgehead protons and those on  $C_2$ ,  $C_3$ , and the *endo*  $C_5$  and  $C_6$  positions) are either zero or else very small.<sup>8</sup>

In order to strengthen these arguments, the  $\alpha$ -deuterioamide IV has been prepared and its n.m.r. spectrum examined (see Fig. 1B). The results are in accord with expectations. Thus, the proton at  $C_5$  is now unsplit, the  $C_6$  proton has vanished (indicating essentially complete deuteration), and the remainder of the spectrum is unchanged.

We also have examined the epimeric amides V and VI, in which the  $C_6$  proton or deuteron occupies an *exo* position, with the results shown in Fig. 1C and 1D. Not unexpectedly, the upper and lower pairs of methylene protons in these compounds are no longer equivalent, so that they now give rise to a complex  $A_2B_2$  pattern. Significantly, the 7 cps. long-range coupling no longer appears, demonstrating its rather special geometrical requirement. In the case of V, the bridgehead hydrogens are split into a doublet ( $J \cong 2 \text{ cps}$ ) by the single *exo*  $C_6$  proton. Interestingly, the  $C_6$  proton itself, in its new configuration, is shifted downfield to a position about the same as that of the  $C_5$  proton. Once

(4) For calculations of the shapes of bridged molecules of the type used in this study, see C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960).

(5) All spectra were taken at 60 Mc. in  $CDCl_3$  with tetramethylsilane (0 cps.,  $\tau = 10$ ) as an internal standard.

(6) The syntheses of all compounds discussed in this paper, as well as evidence for their configurations, will be described in detail in a forthcoming publication.

(7) L. M. Jackman, ref. 2, Chapt. 4; Figs. 1A and C give peak positions in both cps. and  $\tau$  values, while Figs. 1B and 1D show  $\tau$  values only.

(8) These fortunate but unexpected observations emphasize the limitation of the correlation of coupling constants with dihedral angles, as treated by M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).