

### RHODIUM COMPLEXES OF CYCLO-OLEFINS

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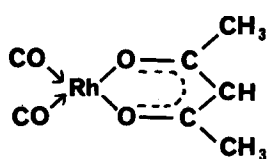
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The ability of metal ions to promote molecular rearrangements in organic substrates containing olefinic groups or strained rings is well known.<sup>1,2</sup> An unusual rearrangement of 1,3,5-cycloheptatriene to a rhodium complex of bicyclo {2.2.1}hepta-2,5-diene (norbornadiene) under the influence of dicarbonyl (pentane-2,4-dionato)rhodium (I) has been reported<sup>3</sup> but more recent work<sup>4</sup> has indicated that the norbornadiene complex (II; R=H) arises from norbornadiene present as an impurity in the cycloheptatriene. We have also reinvestigated this rearrangement and our results, which differ in several respects from those reported previously, are summarised below.

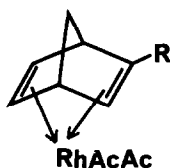
We find that the conversion of  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  into (I; 94%), m.p. 154-155°, is complete after 2 hr. heating under reflux with acetylacetone and barium carbonate in 60-80° petroleum ether. Treatment of cycloheptatriene with (I) in boiling 60-80° petroleum ether as described previously<sup>3</sup> gave 14-24% of crystalline material<sup>5</sup>, m.p. 83-83.5, M (mass spec) 308. This product differs from that obtained by previous workers<sup>3,4</sup> i.e. (II; R=H), m.p. 176-177, M 294. The n.m.r. spectrum of the new compound ( $\text{CCl}_4$ ) showed the presence of a methyl group at  $\tau$  8.35, a methylene group at  $\tau$  8.8 (fine splitting), two multiplets at 6.15 (3H) and 6.55 (2H) as well as signals due to the acetylacetone ligand ( $\tau$  4.88, S, 1H and 8.18, S, 6H). A related product  $(\text{C}_8\text{H}_{10})_2\text{Rh}_2\text{Cl}_2$  (69%), m.p. 145-147°, was obtained when commercial cycloheptatriene and  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  were heated in hexane for 1 hr.

Careful purification of cycloheptatriene (Nester-Faust 24" spinning band column) gave material which failed to react with either (I) or  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  implicating an impurity in the cycloheptatriene. Addition of either toluene<sup>6</sup>

or ethylbenzene to the purified cycloheptatriene had no effect. The active impurity therefore appeared to be a  $C_8H_{10}$  hydrocarbon. The preparation of cycloheptatriene involves pyrolysis of norbornadiene and results in a number of by-products including benzene (i.e. formal loss of carbene). We considered therefore, possible impurities arising from carbene attack on  $C_7H_8$  hydrocarbons and capable, either directly or on rearrangement, of giving rise to a product containing a methyl group. An attempt was made to prepare the rhodium complex of 7-methylcycloheptatriene by reaction with (I) in boiling 80-100 petroleum ether. Slow reaction occurred (i.r. monitoring of carbonyl band) over 70 hr. but only a trace (< 5%) of material still containing a carbonyl group was isolated.



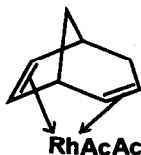
(I)



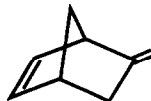
(II)



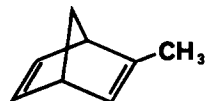
(III)



(IV)



(V)



(VI)

Reaction of (I) with 1,3,5-cyclooctatriene in boiling hexane gave (III; 99%), m.p. 128-129<sup>o</sup>, which clearly differed from the unidentified complex. The product (IV; 90%), m.p. 173-174<sup>o</sup>, from (I) and bicyclo{3.2.1}octa-2,6-diene in boiling hexane was also the complex of the unrearranged olefin. Finally the reaction of 5-exo-methylene-2-norbornene (V) with (I) was investigated. Transition metals are known to catalyse 1,3-hydrogen shifts<sup>7</sup> and it was hoped that the conversion (V→VI) would occur in situ. When (V) and (I) were heated in n-hexane (60 hr.) the desired product (II; R=Me) was obtained only if a trace of Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> (ca. 2% by wt. of I) was added. The product (48%), m.p. 83-83.5<sup>o</sup>, was identical to that obtained previously from cycloheptatriene.

G.l.c. analysis<sup>8</sup> of our Shell sample<sup>5</sup> of cycloheptatriene demonstrated the presence of (V; ca. 3-5%) or its endocyclic isomer (VI) and the absence of norbornadiene. Thus cycloheptatriene does not react with (I) under the conditions reported above and the product is derived from an impurity in commercial cycloheptatriene.

#### R E F E R E N C E S

- <sup>1</sup> T.J. Katz and S.A. Cerefice, J. Amer. Chem. Soc., 1969, 91, 6519.
- <sup>2</sup> W.G. Dauben, M.G. Buzzolini, C.H. Schallhom and D.L. Whalen, Tet. Let., 1970, 787.
- <sup>3</sup> F. Bonati and G. Wilkinson, J. Chem. Soc., 1964, 3156.
- <sup>4</sup> B.E. North and M. Rosenblum, J. Organometallic Chem., 1970, 21, 445.
- <sup>5</sup> We have obtained the same product from three batches of cycloheptatriene, The best yields were obtained from a Shell sample at least 7 yr. old, whereas two recent batches from Koch-Light gave lower yields. We also

found that a trace of  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  was necessary to give the best yields.

<sup>6</sup> Commercial cycloheptatriene contains ca. 5% toluene.

<sup>7</sup> F.G. Cowherd and J.L. von Rosenberg, J. Amer. Chem. Soc., 1969, 91, 2157.

E. Bertele and P. Schudel, Helv. Chim. Acta, 1967, 50, 2445.

<sup>8</sup> A 2 metre x  $\frac{1}{8}$ " (O.D.) column packed with 15% polyethylene glycol 20 M on silanised (HMDS) 90-100 mesh Chromosorb W.