cis-Bis(trimethylgermyl)tetracarbonylruthenium

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Summary *trans,trans,trans*-Cyclododeca-1,5,9-triene reacts with *cis*-bis(trimethylgermyl)tetracarbonyl-ruthenium to form 1—5-η-6,7,8-trihydropentalenylruthenium complexes by ring contraction.

The ability of transition-metal complexes to isomerise olefins is well established. Moreover, there is ample precedent for formation of complex organic molecules from the interaction of simple hydrocarbons with transition-metal compounds. We now describe a reaction involving the reverse of the latter process, namely, ring contraction of a cyclic polyolefin.

Over a period of hours in refluxing heptane *trans,trans,-trans*-cyclododeca-1,5,9-triene (CDT) reacts with *cis*-bis-(trimethylgermyl)tetracarbonylruthenium (I) to yield a mixture of products, separable by chromatography, among which are the compounds (II) (ν_{CO}: 2004 and 1949 cm^{-1}) and (III) (ν_{CO}: 2041, 1988, 1979, and 1943 cm^{-1}).† The

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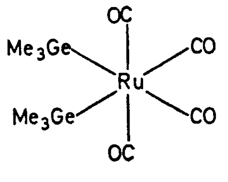
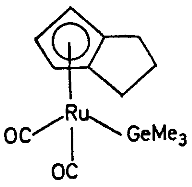
† Satisfactory elemental analyses were obtained for all new compounds.

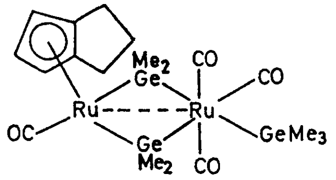
structural assignments are consistent with mass, i.r., and ^{1}H n.m.r. spectroscopic data. Thus both (II) and (III) have, in addition to the expected molecular ion, ions at *m/e* 105 attributable to $C_8H_9^+$, and ^{1}H n.m.r. signals characteristic of the co-ordinated 1—5-η-6,7,8-trihydropentalenyl ligand; for (II) τ 5·02 (2H, d, $J_{\mathrm{HH'}}$ 2·3 Hz), 5·19 (1H, t, $J_{\mathrm{HH'}}$ 2·3 Hz), and 7·64 (6H, m), and for (III) at τ 5·49 (2H, d, $J_{\mathrm{HH'}}$ 2·5 Hz), 6·34 (1H, t, $J_{\mathrm{HH'}}$ 2·5 Hz), and 7·22 (6H, m). The presence of inequivalent bridging dimethylgermyl groups in (III) is indicated by signals at τ 8.96 (6H, s) and 9·11 (6H, s), while terminal trimethylgermyl signals in (II) and (III) occur at τ 9·60 (9H, s) and 9·63 (9H, s), respectively.



(I)



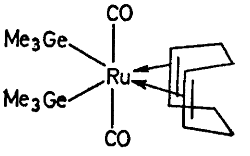
(II)



(III)

That the 1—5-η-6,7,8-trihydropentalenyl ligand did not arise *via* an impurity in the heptane solvent was established by g.l.c., which revealed the absence of any C_8 hydrocarbon, and by refluxing (I) in the solvent alone, when neither (II) nor (III) was formed. The CDT was shown by g.l.c. to be free of any hydrocarbon impurities.

The 1—5-η-6,7,8-trihydropentalenyl ligand is not unknown. Reactions of $Re_2(CO)_{10}$ with cyclo-octa-1,5-diene[1] or of $Mn_2(CO)_{10}$ with cyclo-octatetraene[2] afford the appropriate 1—5-η-6,7,8-trihydropentalenyl-tricarbonylmetal complex. Complexes (II) and (III) can also be obtained from the reaction of cyclo-octa-1,5-diene with (I), when *cis*-bis(trimethylgermyl)-*trans*-dicarbonyl(cyclo-octadiene)ruthenium (IV) is an additional product.



(IV)

The mechanism by which CDT undergoes ring contraction on reaction with (I) to form (II) and (III) is not clear. Investigation of volatile reaction products did not reveal the presence of any C_4 hydrocarbons, and only traces of trimethylgermane. The reaction of cyclo-octa-1,5-diene with (I) does provide some indication, however, of the most probable course. It was shown that (IV), containing co-ordinated cyclo-octa-1,5-diene, is a mutual precursor of (II) and (III) formed in that reaction. It therefore seems likely that CDT reacts with (I) to give a transitory π-complex, which then undergoes loss of a C_4 fragment with formation of the trihydropentalenyl ligand. The affinity of transition metals in low oxidation states for the cyclopentadienyl form of co-ordination with hydrocarbons appears to be great enough in this case to effect an unusual transformation.

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[2] T. H. Coffield, K. G. Ihrman, and W. Burns, *J. Amer. Chem. Soc.*, 1960, **82**, 4209.