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ISOLATION OF A METALOCYCLIC INTERMEDIATE IN $[Ir(CO)_3Cl]_2$-CATALYZED REARRANGEMENT OF 1,3-BISHOMOCUBANE[1]

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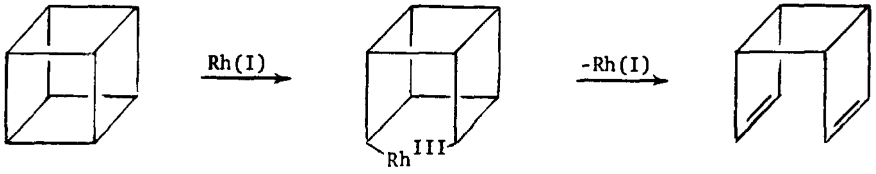
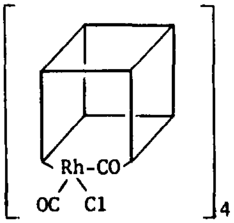
Metal catalyzed isomerization of strained cyclobutane derivatives has been the focus of considerable research in recent years. Yet, the mechanism of this process still evokes some controversy.[2,3] Thus, e.g., the Rh(I)-catalyzed rearrangement of cubane and related compounds has been explained, on the one hand, by the capability of the metal to remove the symmetry constrains on the "thermally forbidden" concerted mechanism of the reacting system via interaction with the d orbitals of the catalyst. On the other hand, it was implied that conversion of cubane (1) into *syn*-tricyclooctadiene (3) follows a stepwise mechanism 1 → 2 → 3.



1 2 3

Support of the latter mechanism that is indeed favored by most researchers, has been found in the formation of an isolable acyl-rhodium complex 5 in the reaction of 1 and $[Rh(CO)_2Cl]_2$ (4) in which the metal inserts into a C-C bond of the substrate.[4] However, neither 5 nor any of its analogs derived from other strained cyclobutane derivatives[5] can be regarded as a reaction intermediate in the metal assisted valence isomerization, since their thermolysis leads to carbonyl compounds rather than to the rearranged hydrocarbons.[6]

We now wish to report a 1,3-bishomocubane (6) transformation to dicyclopentadiene (2) in which a true metalocyclic intermediate (9) can be isolated and further converted into the final diene.



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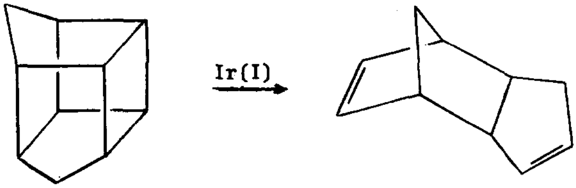

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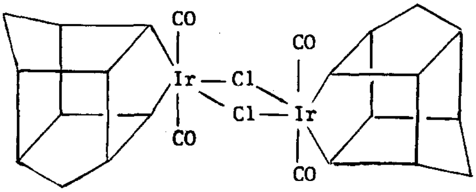
On heating a mixture of 0.75 mmol of 6 and 0.16 mmol of $[Ir(CO)_3Cl]_2$ (8) in 3 mL dry benzene at 120°C (pressure tube) under N_2, CO is evolved and a colorless precipitation is formed along the walls of the reaction vessel. After 48 h the shiny organo-iridium compound was hand-separated from some gray starting $[Ir(CO)_3Cl]_2$ with the aid of a microscope to yield 19% of an analytically pure sample of mp (dec) 260 - 262°C. (The remaining insoluble material was a mixture of 8 and 9). Elementary analysis indicated a 1:1 adduct of empirical formula $C_{12}H_{12}ClIrO_2$ [Calcd: C, 34.7; H, 2.9; Cl, 8.5. Found: C, 35.0; H, 3.2; Cl, 9.0]. Owing to the extreme insolubility of the complex in solvents that do not lead to its decomposition, structure elucidation by NMR spectroscopy was not possible. The electron impact mass spectrum (at 70 eV), however, is highly indicative. A distinguished molecular ion[7] (*m/e* starting from 828) and $[M-nCO]^{+\cdot}$ fragments (n = 1 - 4) with the theoretical isotope patterns prove that the complex is a dimer of elementary formula $C_{24}H_{24}Cl_2Ir_2O_4$. By virtue of the very strong IR bands (Nujol) at 1998 and 2050 cm^{-1} and complete absence of metal-acyl absorptions we concluded that all the CO groups are metal-carbonyls. This has been verified by comparing the ratio of relative intensities of $[M]^{+\cdot}$: $[M-nCO]^{+\cdot}$, (n = 1 - 4) deduced from the EI-mass spectrum of

9 with those obtained from the mass spectrum of the acyl-rhodium complex 10.[6,8] While the successive loss of the four carbonyl groups in 9 gives rise to fragments of comparable or even increasing abundances (ratios $[M]^{+\cdot}$: $[M-nCO]^{+\cdot}$ are 1:1.6/1.6/1.8/21.0), the fragment ions that arise from loss of one or two carbonyls from the molecular ion of 10 are 20 times more abundant than $[M-3CO]^{+\cdot}$ or $[M-4CO]^{+\cdot}$ ($[M]^{+\cdot}$: $[M-nCO]^{+\cdot}$ - 1:0.2/0.2/0.01/0.01).



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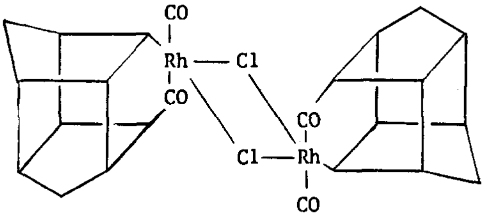

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Unlike homocuabne that rearranges by iridium tricarbonyl chloride dimer (8) at 80°C to a mixture of norsnoutane, tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene and tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene (but forms no isolable iridium complex)[9], 1,3-bishomocubane (6) does not lead to any isomerization products below 200°C. However, on heating a mixture of 6 and 8 or the crystaline iridium complex 9 to 265°C, dicyclopentadiene (7) and its dissociation product - cyclopentadiene - are formed in nearly quantitative yield. Both 7 and monomeric cyclopentadiene proved to react with 8 to give complexes that differ from 9.

Finally, it should be recalled that the insoluble iridium compound obtained from norbornadiene and $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ has been suggested as the intermediate in Ir(I)-catalyzed dimerization of norbornadiene.[10] However, only its secondary transformation products were well defined and could be converted into norbornadiene dimer.

REFERENCES AND NOTES

(1) This study is part of a joint research project of the Hebrew University of Jerusalem and the Technical University of Berlin. Financial support by the Israel Commission for Basic Research of the Israel Academy of Sciences and Humanities and by the Fonds der Chemischen Industrie - Frankfurt, is gratefully acknowledged.

(2) F.D. Mango, Coordin. Chem. Rev., 15, 109 (1975).

(3) J. Halpern, Advan. Organometal. Chem. 15, 705 (1977).

(4) L. Cassar, P.E. Eaton and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).

(5) Even non-cage compounds form well defined acyl-rhodium complexes. See e.g., J. Halpern, M. Sohn and J. Blum, Proc. 43rd Annual Meeting, Isr. Chem. Soc., 22 (1975)

(6) See e.g., J. Blum, C. Zlotogorski and A. Zoran, Tetrahedron Lett., 1117 (1975).

(7) The absence of tri- or poly-nuclearic species was confirmed also by the FI- and CI-spectra.

(8) Unlike the rhodium derivative of cubane 5, that has been proposed to be a tetramer (reference 4), complex 10 proved to be a dimer (lowest mass of molecular ion pattern 652). Some further physical data for 10 are given in reference 6.

(9) L.A. Paquette, R.A. Boggs and J.S. Ward, J. Am. Chem. Soc., 97, 1118 (1975).

(10) A.R. Fraser, P.H. Bird, S.A. Bezman, J.R. Shapley, R. White and J.A. Osborn, J. Am. Chem. Soc., 95, 597 (1973).

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