Five-, Six-, and Seven-membered Rhodacycloalkanes from $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ and $BrMg–[CH_2]_n–MgBr$ (n=4, 5, or 6). Occurrence of Carbon–Carbon σ-Bond Cleavage in the Preparation of the Rhodacyclopentane Derivative

By Pietro Diversi, Giovanni Ingrosso, and Antonio Lucherini

(Istituto di Chimica Organica Industriale, Università di Pisa, Via Risorgimento 35, 56100 *Pisa, Italy)*

Summary Reactions of $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (**1a**) with the di-Grignard reagents $BrMg–[CH_2]_n–MgBr$ (**2**; n = 5 or 6) led to the rhodacycloalkanes (**3**) and (**4**), respectively; reaction of (**1a**) with (**2**); (n = 4) gave the rhodacyclopentane (**6**) and the rhodium(I)–ethylene complex (**5**).

Metallocycloalkane derivatives have been postulated to be involved in a number of transition-metal-catalysed reactions, such as olefin metathesis,[1] isomerization of strained carbocyclic rings,[2] [2 + 2] cycloaddition of olefins,[3] and oligomerisation of 1,3- and 1,2-dienes.[4] While rhodium compounds are known to act as catalysts in many of these reactions, only a few rhodacycloalkanes have been reported.

In this connection we now report some results obtained in a study of the cyclodialkylation of the rhodium complex (**1a**) with the αω-di-Grignard reagents (**2**).

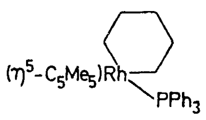
Thus, the cyclic rhodium compounds (**3**) and (**4**) were prepared by the reaction of (**1a**) with the appropriate di-Grignard reagent (molar ratio 1 : 3) in diethyl ether at room

$[RhX_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$

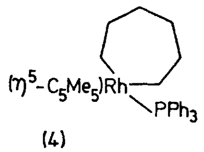
(1): a; X = I
b; X = Br
c; X = Cl

$BrMg\text{-}[CH_2]_n\text{-}MgBr$

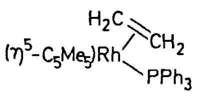
(2), n = 4, 5, or 6



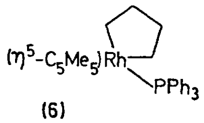
(3)



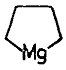
(4)



(5)



(6)



(7)

temperature. They are orange red crystalline diamagnetic compounds which were characterized by elemental analysis, molecular weight determination, and mass spectrometry.

On reaction with Br_2, in Et_2O at −78 °C, (**3**) and (**4**) gave 1,5-dibromopentane and 1,6-dibromohexane, respectively, in addition to (**1b**) [equation (1)].

$$(\mathbf{3}) \text{ or } (\mathbf{4}) \xrightarrow{Br_2} (\mathbf{1b}) + Br{-}[CH_2]_5{-}Br \text{ or } Br{-}[CH_2]_6{-}Br \quad (1)$$

Treatment of ethereal solutions of (**3**) and (**4**) with dry HCl, at room temperature, yielded (**1c**) and mixtures of the corresponding n-alkanes and n-alkenes [equations (2) and (3)].

$$(\mathbf{3}) \xrightarrow{HCl} (\mathbf{1c}) + n\text{-}C_5H_{12} + n\text{-}C_5H_{10} \quad (2)$$

$$(\mathbf{4}) \xrightarrow{HCl} (\mathbf{1c}) + n\text{-}C_6H_{14} + n\text{-}C_6H_{12} \quad (3)$$

In the solid state, (**3**) and (**4**) decomposed at 160 °C under argon; no carbon–carbon bond cleavage was observed, the only volatile products being n-pentenes and n-hexenes from (**3**) and (**4**), respectively. Similar decomposition modes have been observed in the case of some platinum(II) metallocycles.[5]

The reaction of (**1a**) with (**2**; $n = 4$), carried out under the same experimental conditions as above, gave an oily residue after filtration and removal of solvent. Extraction of this residue with pentane, and chromatography on neutral alumina, led to a mixture of (**5**) (yield, 40%) and (**6**) (*ca.* 10%). Ethylene was detected in the reaction mixture by g.l.c. The same results were obtained employing magnesacyclopentane (**7**) as the alkylating agent, under the above conditions.

Pure (**5**) was obtained as orange needles by crystallization from pentane, and was characterized by its ^1H n.m.r., i.r., and mass spectra, and by elemental analysis. These data were found to be identical with those of a specimen prepared on reaction of bis(ethylene)(η^5-pentamethylcyclopentadienyl)rhodium(I), $[Rh(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$, with PPh_3, in refluxing toluene. The structure of (**5**) has been unambiguously established by single-crystal *X*-ray analysis.[6]

Efforts to isolate (**6**) have so far been unsuccessful, leading invariably to samples contaminated by (**5**). The mass spectrum showed in addition to the characteristic fragmentation pattern of (**5**) a peak at *m/e* 556 corresponding to the parent peak of (**6**). Reactions with HCl or Br_2 gave products containing the tetramethylene unit, while no C_4 derivatives could be detected when pure (**5**) was treated with HCl or Br_2. The similarity in the reactivity of (**6**), (**3**), and (**4**) towards HCl and Br_2, together with mass spectrometric evidence, strongly suggest for (**6**) a rhodacyclopentane structure.

The method of preparation of (5) and the simultaneous evolution of ethylene strongly suggest that the metallocyclopentane derivative (6) is the precursor of (5) undergoing carbon–carbon σ-bond cleavage. Similar fragmentations have been suggested[7] to take place, but no case of stable olefin complexes resulting from them has been reported as yet.

The fact that carbon–carbon σ-bond rupture is not observed in the case of (**3**) and (**4**) stresses the importance of the ring size in determining the properties of rhodacycloalkanes.

Finally, our findings may be of relevance to the mechanism of olefin metathesis.

We thank Professor F. Calderazzo for helpful discussions and reading the manuscript, and C.N.R. (Rome) for financial support.

(*Received*, *2nd November* 1976; *Com.* 1220.)

[1] R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, 1975, **4**, 155.

[2] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.

[3] A. R. Fraser, P. H. Bird, S. A. Bezman, I. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 597; R. Noyori, T. Ishigami, N. Hyashi, and H. Takaya, *ibid.*, p. 1675; M. J. Doyle, J. McMeeking, and P. Binger, *J.C.S. Chem. Comm.*, 1976, 376.

[4] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1975, vol. II; D. R. Coulson, Amer. Chem. Soc. Boston Meeting, April 9—14, 1972, p. B 135; R. J. De Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381; G. Ingrosso, L. Porri, G. Pantini, and P. Racanelli, *ibid.*, 1975, **84**, 75; P. Diversi, G. Ingrosso, A. Immirzi, W. Porzio, and M. Zocchi, *ibid.*, in the press; A. Giarrusso, P. Gronchi, G. Ingrosso, and L. Porri, *Makromol. Chem.*, in the press; G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1976, **98**, 3373.

[5] J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.* 1976, **28**, 6521.

[6] W. Porzio and M. Zocchi, unpublished data.

[7] J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6529; R. H. Grubbs; and T. K. Brunck, *ibid.*, 1972, **94**, 2538.