(η^4-Cyclo-octa-1,4-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium(0) Chemistry: the Role of Molecular Hydrogen in a New Synthetic Route to Cyclo-olefin Ruthenium Complexes

By Paolo Pertici, GianPaolo Simonelli, and Giovanni Vitulli*
(*Istituto di Chimica Organica Industriale, Facoltà di Scienze, Nucleo del CNR,* 56100 *Pisa, Italy*)
Giulio Deganello
(*Istituto di Chimica Generale, Facoltà di Scienze,* 90100 *Palermo, Italy*)
and PierLuigi Sandrini and Angelo Mantovani
(*Cattedra di Chimica, Facoltà di Ingegneria,* 35100 *Padova, Italy*)

Summary The use of (η^4-cyclo-octa-1,5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium(0) as a starting material for the preparation of several cyclo-olefin ruthenium complexes and the influence of molecular hydrogen in these reactions are reported.

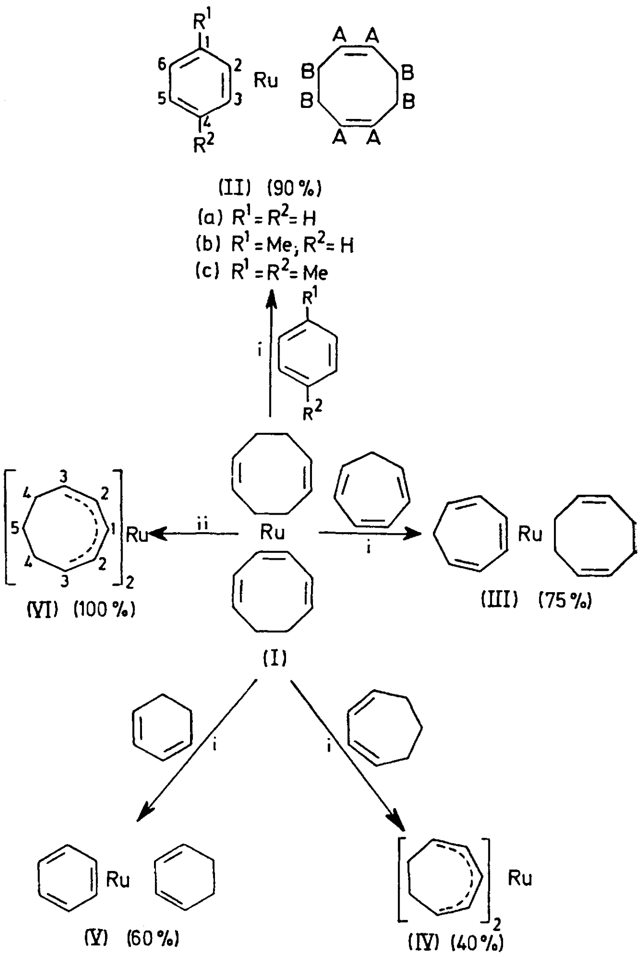
ZEROVALENT cyclo-olefin complexes of transition metals, particularly those not containing carbon monoxide, are very useful compounds in catalysis[1] and preparative chemistry.[2] However, only a limited number of synthetic routes to such species are available.

Recently we reported a new preparative route to cyclo-olefin ruthenium complexes containing only olefins as ligands such as (η^4-cyclo-octa-1,5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium(0), [Ru(C_8H_{12})(C_8H_{10})].[3] The use of this compound as a starting material for the preparation of several cyclo-olefinic ruthenium complexes is now reported, including evidence of the determining role played by molecular hydrogen in these reactions.

[Ru(C_8H_{12})(C_8H_{10})] (I) reacts rapidly under hydrogen at room temperature with cyclo-olefins or aromatic hydrocarbons, producing, in good yields, the η-cyclo-olefin-ruthenium(0) and -ruthenium(II) complexes (II)—(V) (Scheme). In a typical experiment, complex (I) was stirred in benzene at room temperature for *ca.* 5 h, under hydrogen. Evaporation of the benzene and recrystallization of the residue at −78 °C from n-pentane gave (IIa) as light yellow crystals (yield *ca.* 90%). Cycloheptatriene, cyclohexa-1,3-diene, and cyclohepta-1,3-diene are selectively hydrogenated to the cyclomono-olefin.

No ligand displacement reaction takes place in the absence of molecular hydrogen. Under nitrogen, in aromatic or aliphatic solvents, complex (I) isomerizes at *ca.* 100 °C to bis(1—5-η-cyclo-octadienyl) ruthenium (VI) (see Scheme).

Complexes (II)—(VI) were characterized by elemental analysis, and by mass, i.r., and ^{1}H n.m.r. spectral data [τ (C_6D_6); (IIb): 5·13 (5H, s, 2- to 6-H), 6·53 (4H, m, H_A), 7·59 (8H, m, H_B), and 8·2 (3H, s, Me); (IIc): 5·21 (4H, s, 2-, 3-, 5-, and 6-H), 6·64 (4H, m, H_A), 7·58 (8H, m, H_B), and 8·18 (6H, s, 2-Me); (VI): 4·42 (2H, t, 1-H), 6·16 (4H, dd, 2-H), 6·45 (4H, m, 3-H), and 7·49—8·95br (12H, m, 4- and 5-H)] as well as by comparison with authentic samples for (IIa), and (III)—(V).[3]



SCHEME. i, under H_2, 20 °C; ii, under N_2, 100 °C.

Since no cyclo-octatriene was detected in the mother liquor of the reactions, a possible mechanism for the formation of the complexes (II)—(V) from (I) probably involves the hydrogenation of the bonded cyclo-octatriene to a co-ordinatively unsaturated ruthenium complex which undergoes ligand exchange with a new cyclo-olefin. The isomerization of complex (I) to complex (VI) by heating at *ca.* 100 °C under nitrogen can be interpreted in terms of a hydride-transfer mechanism.[4]

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[1] See, for example, A. Carbonaro, A. Greco, and G. Dall'Asta, *J. Organometallic Chem.*, 1969, **20**, 177.

[2] See, for example, D. A. White, *Organometallic Chem. Rev.*, *A*, 1968, **3**, 497.

[3] P. Pertici, G. Vitulli, and L. Porri, *J.C.S. Chem. Comm.*, 1975, 846; J. Mueller and E. O. Fischer, *J. Organometallic Chem.*, 1966, **5**, 275.

[4] E. O. Fischer and W. Frohlich, *Z. Naturforsch.*, 1960, **15b**, 266; A. J. Deeming, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2093.