Paramagnetic Intermediates in Oxidative Coupling Reactions. Molecular Orbital Calculations as an Aid to Rational Organometallic Synthesis

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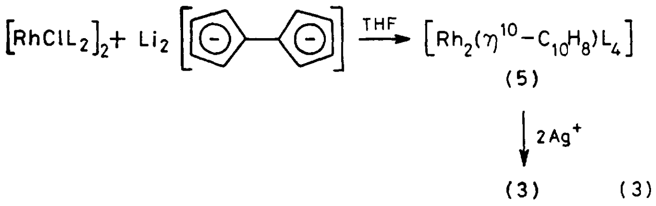
Summary Oxidation of (η^5-C_5H_5)Rh(PPh_3)$_2$ by silver ion results in coupling of cyclopentadienyl ligands to give fulvalene–dirhodium(II) complexes; semi-empirical MO calculations give insight into the reaction sequence and allow a rational extension to the coupling reaction of a co-ordinated allyl ligand to give a hexa-1,5-diene complex.

PARAMAGNETIC organometallic species have been detected or implicated in an increasing number of catalytic processes.[1] However, aside from radical initiation of chain reactions, the role of such species in a reaction sequence often remains unclear. We have isolated a series of thermally stable 17-electron cobalt complexes exemplified by (**1**) (equation 1).[2] In contrast, attempts to synthesize similar rhodium complexes resulted in oxidative coupling of the cyclopentadienyl ligand to give violet rhodium(II) fulvalene complexes (**3**) (equation 2).

$$CoCpL_2 + AgBF_4 \xrightarrow{THF} \underset{(\mathbf{1})}{[CoCpL_2][BF_4]} + Ag \qquad (1)$$

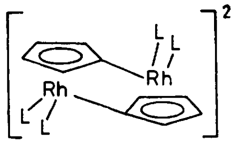
$$\underset{(\mathbf{2})}{4RhCpL_2} + 4AgBF_4 \xrightarrow{THF} \underset{(\mathbf{3})}{[Rh_2(\eta^{10}\text{-}C_{10}H_8)L_4][BF_4]_2} + \underset{(\mathbf{4})}{2[RhCpHL_2][BF_4]} + 4Ag \qquad (2)$$



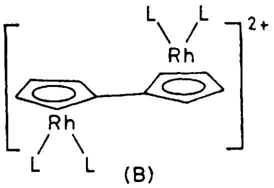
$$RhCpL_2 + HBF_4 \longrightarrow (4) \qquad (4)$$

Cp = η^5-C_5H_5; L = PPh_3; THF = tetrahydrofuran

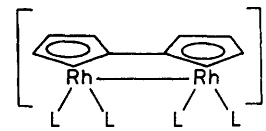
When a brown solution of (**2**) is treated with 1 equiv. of silver ion, the colour changes immediately to blue-violet. Adding hexane to the mixture causes (**3**) and the hydride complex (**4**) to coprecipitate quantitatively. Because (**3**) and (**4**) were difficult to separate, analytically pure samples were prepared by the alternative syntheses† in equations (3) and (4).[3,4] That (**3**) may be prepared from the fulvalene dianion, and the fact that in the ^{13}C n.m.r. spectra the rhodium–carbon coupling constants are small (*ca.* 3 Hz) and equivalent, strongly argue against an $\eta^5:\eta^1$ structure such as (A). While we cannot clearly distinguish between structures (B) and (C) at this time, we tend to favour (C), similar to that found for titanocene derivatives.[5]



(A)

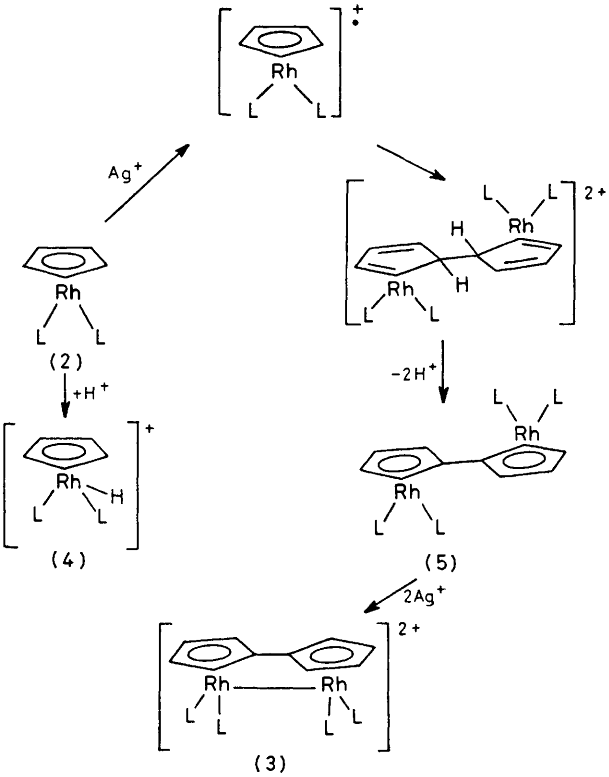


(B)



(C)

Semi-empirical MO calculations[6] reveal that the highest occupied molecular orbital (HOMO) of (**2**) is relatively high-lying and, although primarily metal d-orbital in character, contains significant contribution from a carbon p-orbital in the cyclopentadienyl group. Removing one electron from the HOMO may be looked upon as resulting



SCHEME

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† N.m.r. data: (**3**) ^1H (CD_2Cl_2) δ 3·9 (m, 4H), 6·1 (m, 4H), and 7·3 (m, 60H); ^{31}P (p.p.m. from H_3PO_4), 33·6 (d, *J* 193 Hz); ^{13}C proton-decoupled (p.p.m. from Me_4Si) 83·0 (d, *J ca.* 2), 92·9 (d, *J ca.* 3), 102·4 (d, *J ca.* 2), 129·1 (t, *J* 5·3), 131·4 (s), and 133·6 (t, *J* 6·0); (**5**) ^1H (C_6D_6) δ 4·3 (m, 4H), 5·1 (m, 4H), 6·8 (m. 36H), and 7·5 (m, 24H); (**6**) ^1H [$(CD_3)_2CO$] δ 2·4 (m, 4H), 3·7 (m, 4H), 3·8 (m, 18H), and 5·2 (m, 2H).

in a metal-stabilized carbon radical. Coupling two such radicals followed by deprotonation would give (**5**) (Scheme). Protonating unchanged (**2**) would leave silver ion remaining to oxidize (**5**) further to (**3**). Why the cobalt complexes do not couple is unclear.

Hoping to extend the oxidative coupling reaction to allyl ligands,[7] we carried out MO calculations which revealed that the HOMO of $Rh(\eta^3\text{-}C_3H_5)(PH_3)_2$ is relatively low lying and nearly pure metal-d-orbital in character, but that of $Rh(\eta^3\text{-}C_3H_5)(PH_3)_3$ is much higher-lying with significant p-orbital contribution on each of the outside carbon atoms of the allyl group. Accordingly $Rh(\eta^3\text{-}C_3H_5)[P(OPr^i)_3]_2$[8] was isolated unchanged after treatment with silver hexafluorophosphate in THF for several hours, but similar treatment of $Rh(\eta^3\text{-}C_3H_5)[P(OMe)_3]_3$ resulted in immediate precipitation of silver metal and the subsequent isolation of the hexadiene complex $[Rh(\eta^4\text{-}C_6H_{10})[P(OMe)_3]_2[PF_6]$, (**6**).†

$$[Rh(\eta^4\text{-}C_6H_{10})[P(OMe)_3]_2[PF_6]$$

(**6**)

Thus the information derived from relatively simple molecular orbital calculations can lead to rational syntheses of new organometallic complexes.

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