Rhodium(I)-catalysed Dismutation of Electron-rich Olefins: Rhodium(I) Carbene Complexes as Intermediates

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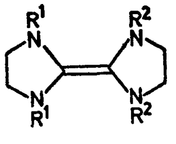
Summary Dismutation of two different electron-rich olefins C_2X_4 and C_2Y_4 proceeds only in the presence of an additive, compounds such as $L(Ph_3P)_2RhCl$ ($L = Ph_3P$ or CO) being particularly effective; carbene complexes $L(Ph_3P)Rh(CX_2)Cl$ and $L(Ph_3P)Rh(CY_2)Cl$ are isolable intermediates and the active catalysts.

Dismutation of olefins, both hetero- and homo-geneously catalysed by transition-metal complexes, is a topic of current interest.[1] A mechanism involving a cyclobutane intermediate has been suggested,[2] but appears untenable.[3] A concerted mechanism has been suggested,[3] and is supported by kinetic data,[4] in which the σ- and π-bonds of the two olefins are broken to give a tetramethylene–metal complex with each methylene group sp^3-hydridized.[3] We now provide definitive evidence for a metal carbene-complex intermediate in the catalysed dismutation of *electron-rich* olefins by rhodium(I) complexes; and the first characterisation of rhodium(I) carbene complexes is described. (For a review on carbene complexes see ref. 5, for data on the new compounds see footnote to the Table.)

Contrary to the hypothesis of electron-rich olefin dissociation into nucleophilic carbenes,[6] a cross-over reaction between (Ia) and (Ib) to give (Ic) was found not to take place on heating the two olefins in xylene under reflux for 2 h.[7] We confirm this, but find that dismutation does take place, with the formation of crossed product (Ic), under the same conditions except for the presence of a catalytic amount of a rhodium(I) complex (see Table). Catalysis by organic compounds is under investigation.



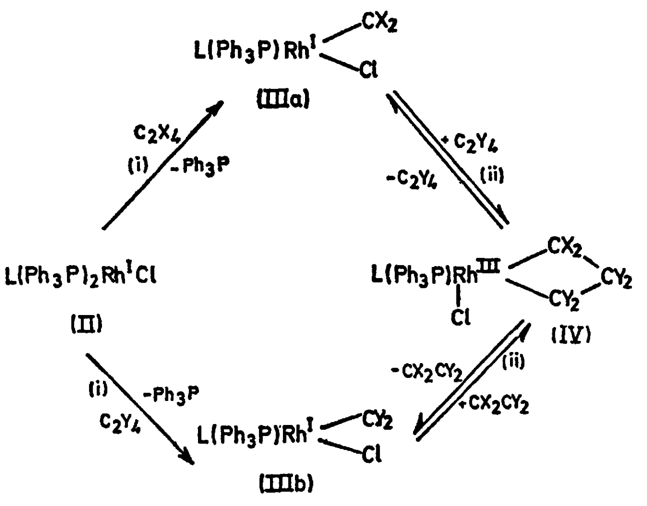
(I)

a; $R^1 = R^2 = Ph$
b; $R^1 = R^2 = p\text{-}MeC_6H_4$
c; $R^1 = Ph, R^2 = p\text{-}MeC_6H_4$

For catalysis by $L(Ph_3P)_2RhCl$ ($L = Ph_3P$ or CO) (II) of the dismutation: $C_2X_4 + C_2Y_4 \rightleftharpoons 2CX_2{:}CY_2$, we suggest the following simplified mechanism (see Scheme). Evidence rests on: (a) the demonstration of step (i) {see ref. 8 for *trans*-$Et_3P(Cl_2)PtC[N(Ph)CH_2]_2$, (V), obtained from (Ia) and $(Et_3PPtCl_2)_2$} for C_2X_4 or C_2Y_4 = (Ia) or (Ib); (b) the characterisation of the appropriate complexes (III) prepared as in step (i); (c) the catalytic activity of (III) (see Table); and (d) the conversion:

$$(IIIa) \xrightarrow{(Ib)} (IIIb)$$

for L = Ph_3P. Additionally, (e) the oxidative addition step (ii) seems plausible because other oxidative addition reactions of (III) can be demonstrated,[9] and (f) (V), which is known to be unreactive with regard to oxidative addition,[8] is not a dismutation catalyst (see Table). Dicarbene complexes $L(Cl)Rh(CX_2)(CY_2)$ are also possible intermediates (some, L = CO, have been isolated[10]) but we cannot yet distinguish between 2-C- and 3-C-situations.



Scheme

The transition state involved in the formation of (IV) from (III) may be as shown in (VI) or (VII) with the former more likely. Thus, for (VI), electron-rich olefins and Rh^I are good nucleophiles and C_{carb} is an electrophilic centre; the covalency changes (α) and (β) in (VI) or (VII) need not be synchronous; in that event, (α) probably precedes (β).

Table

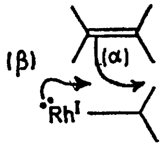
Dismutation of (Ia) *and* (Ib) *to give* (Ic)[a]

Compound	Concentration (mole %)	Yield of mixed olefin (%)[b]
$(Ph_3P)_3RhCl$	1·8	50
$(Ph_3P)_2Rh(Cl)C[N(Ph)CH_2]_2$[c]	1 (0·5)	40 (17)
$(Ph_3P)_2RhClC[N(p\text{-}Me{\cdot}C_6H_4)CH_2]_2$[c] ..	1	40
$(Ph_3P)_2RhCOCl$	1	40
$(Ph_3P)_2(OC)Rh(Cl)C[N(Ph)CH_2]_2$[c] ..	1	40
trans-$Et_3P(Cl)_2PtC[N(Ph)CH_2]_2$, (V) ..	1	0

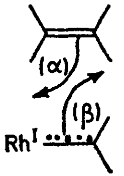
[a] Olefins (*ca.* 2 × 10^{-2} M) in boiling xylene for 2 h, under an atmosphere of nitrogen.

[b] Statistically, the maximum yield of mixed olefin is 50%; the quoted yields by ^1H n.m.r. integration (of ring methylene protons in a MeCN solution of the dinitrate salts) are reproducible to at least ±5%.

[c] New carbene complexes $L(Ph_3P)RhClC\{N(R)CH_2\}_2$ (i)—(iii) are characterised by: i.r., $\nu_{C=O}$, $\nu_{C\cdots N}$, ν_{Rh-Cl} (Nujol mull); n.m.r., $\delta(CH_2)$ ($CDCl_3$); m.p.; additional data: (i) L = Ph_3P, R = Ph; —, 1498(s), 285(w, broad) cm^{-1}, τ 7·0; 194—195° d; orange crystals; ^{31}P n.m.r. shows *trans*-configuration. (ii) L = CO, R = Ph; 1973(vs), 1495(s), 299(w) cm^{-1}; τ 5·7; 193—195° d, yellow crystals. (iii) L = PPh_3, R = p-Me·C_6H_4; —, 1513(s), 298(w, broad) cm^{-1}; τ 7·0; 191—192° d, yellow crystals.



(VI)



(VII)

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