Contrasting Reactivity of Mono- and Di-nuclear Dihydrido-*trans*-Bisphosphine-rhodium and -iridium Complexes towards Alkenes

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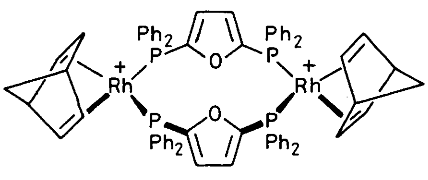
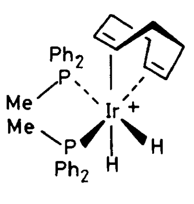
The binuclear rhodium complex $Rh_2{}^{2+}(\mu\text{-P—P})_2(MeOH)_4H_4$, (**2**), P—P = 2,5-bis(diphenylphosphino)furan, is inferior to mononuclear models in hydrogen transfer to 3,3-dimethylbut-1-ene; related mono- and di-nuclear iridium complexes exhibit contrasting chemistry.

Recently we reported[1] that the ligand 2,5-bis(diphenylphosphino)furan formed a range of binuclear rhodium complexes in which two such ligands were either *cis*-or *trans*-related and mixed stereochemistry was not observed. An incentive for the investigation was the potential of binuclear complexes for selective catalysis, but in preliminary experiments complex (**1**) proved to be inferior to mononuclear analogues for effecting alkene hydrogenation, and the reasons for this were investigated.

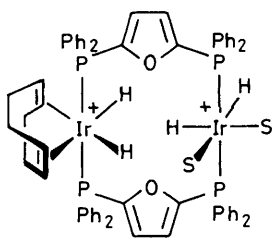
In methanol solution complex (**1**) reacts first to form a solvate and then the dihydrido complex (**2**) under a hydrogen atmosphere.[1] If hydrogen is removed, and 3,3-dimethylbut-1-



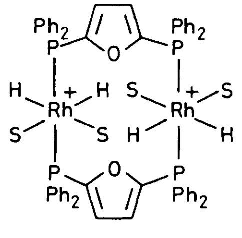
(1)



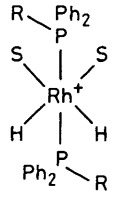
(6)



(7)

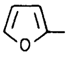


(2)

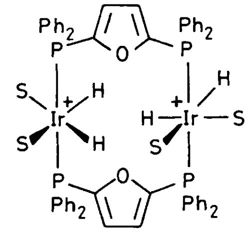


(3)

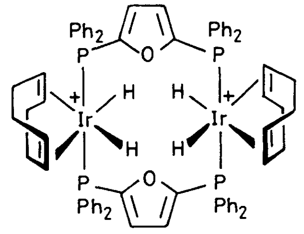
a; R = Me

b; R = 

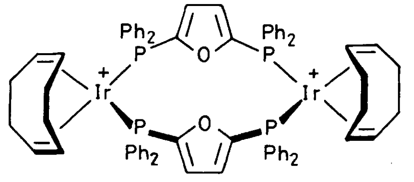
S = MeOH



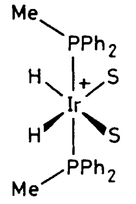
(8)



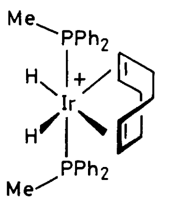
(9)



(4)

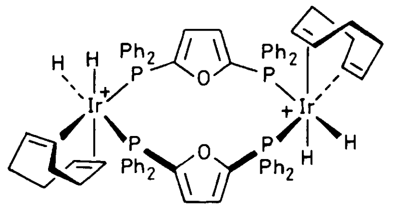


(10)



(11)

S = Me_2CO
Counterion = BF_4^-



(5)

ene† then added [0.077 M, *vs.* 0.007 M (**2**), CD_3OD], the transfer of hydrogen to the alkene may be followed from the diminution of the RhH resonance (δ −21.2, J_{Rh-H} = 24, J_{P-H} = 34 Hz) and the concomitant appearance of a new CH_3 resonance due to 3,3-dimethylbutane (δ 0.90). The reaction is too slow to measure at 0 °C, but can be monitored between 10 and 20 °C. In the absence of alkene the loss of hydrogen from (**2**) occurs sufficiently slowly that it can be ignored. Under identical conditions hydrogen transfer from the corresponding rhodium complex of methyldiphenylphosphine (**3a**) to 3,3-dimethylbut-1-ene occurred much more rapidly, (**3a**) being twenty times more reactive than complex (**2**) at 10 °C. Part of the difference is electronic for it was subsequently found that complex (**3b**) transferred H_2 to 3,3-dimethylbut-1-ene at an intermediate rate, but still four times more rapidly than complex (**2**).

The cationic iridium compound (**4**) was readily prepared by standard procedures.[2] It reacted rapidly with H_2 [0.007 M (**4**) in 1:1 CD_2Cl_2–$(CD_3)_2CO$, −78 °C] to give a colourless solution whose ^1H n.m.r. spectrum showed a new set of resonances in the IrH region (δ −12 to −15) consistent with two pairs of hydridometal bonds, one of each pair being *trans* to alkene and the other *trans* to P [*e.g.* (**5**) or a mixture of related diastereoisomers] by comparison with the corresponding methyldiphenylphosphine complex (**6**).[3] On warming to 0 °C, a new species with IrH triplet resonances (δ −13.25 and −27.1, J_{P-H} = 16 Hz) was produced. A somewhat different result was obtained when hydrogenation of complex (**4**) was carried out at 20 °C in $(CD_3)_2CO$. Examination of the ^1H n.m.r. spectrum in the MH region immediately the solution became colourless showed that both the high-field and low-field resonances contained two triplets (δ −13.10, −13.16; −27.09, −27.16, J_{P-H} = 16 Hz in each case). This spectrum is ascribed to the presence of complexes (**7**), (**8**), and (**9**). After leaving the solution under hydrogen for several hours only the species at δ −27.09 remained and must therefore be the solvate (**8**).‡ In a separate experiment, it was

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† The choice was dictated by the ease of monitoring its reduction by ^1H n.m.r. (CMe_3) and the lack of competing isomerisation.

‡ Attempted isolation of this solvate complex leads to a new species with six inequivalent Ir–H resonances in the region δ −25 to −28 (trimer?) whose structure is under investigation.

shown that addition of cyclo-octa-1,5-diene (COD) to a solution of complex (**8**) in acetone [0.01 M in (**8**), 0.16 M in COD, 20 °C] causes slow displacement of solvent ($t_{1/2}$ *ca.* 75 min) to form the cyclo-octadiene complex (**9**) (δ − 13.16) with small amounts of the mixed complex (**7**) evident at intermediate times.

The results for binuclear complexes are very different from those reported by Crabtree and co-workers for related mononuclear complexes[3] which were confirmed under the precise conditions of our experiments. Thus complex (**6**) is rapidly and cleanly transformed into solvate (**10**) on warming from −78 to 20 °C. The latter reacts very readily with cyclo-octadiene (fast at −30 °C)[3] to give (**11**) which is never observed in the absence of an excess of dialkene. Reaction is presumably initiated by solvent dissociation.[4]

We have demonstrated that a *trans*-locked rhodium complex[5] only transfers H_2 slowly to alkenes and that the reaction patterns of an iridium analogue are anomalous. The results lend weight to the argument[6] that the kinetically significant intermediates in homogeneous hydrogenation have *cis*-bisphosphine stereochemistry.

We thank the S.E.R.C. for support and Johnson–Matthey for a generous loan of platinum metal salts. Professor L. M. Venanzi very kindly provided details of unpublished work. We thank a referee for useful comments.

Received, 19th March 1984; Com. 362

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4 O. W. Howarth, C. H. McAteer, P. Moore, and G. E. Morris, *J. Chem. Soc., Dalton Trans.*, 1981, 1481.

5 Rhodium complexes containing a normally rigid *trans*-chelating ligand have been reported, (*cf.* J. S. Reed and L. M. Venanzi, *Helv. Chim. Acta*, 1977, **60**, 2804) with catalytic activity more than tenfold less than corresponding triphenylphosphine complexes; L. M. Venanzi, P. S. Pregosin, and M. L. M. Pasquier, unpublished work.

6 J. M. Brown and A. R. Lucy, preceding communication.