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Preliminary communication

BIDENTATE P,N LIGAND-MODIFIED RHODIUM(I) COMPLEXES: THE IMPACT OF NITROGEN LIGANDS ON ISOMERIZATION CAPABILITY*

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Summary

Chlororhodium(I) complexes containing cyclic aminophosphonites $\mathrm{Ph}\underline{\overline{\mathrm{P\quad N}}}\mathrm{R}$ (R = H, Me) catalyze the hydrogenation of 1-hexene. Isomerization is an important side reaction and is explained by the formation of hydridorhodium(I) species which result from the $\geqq$NR induced HCl abstraction from rhodium(III) dihydrides.

Extensive work on rhodium(I) diphosphine complexes including mechanistic aspect [1] and practical applications [2] has been carried out in the last years. Conversely, bidentate phosphorus—nitrogen ligands have been much less examined. Roundhill and his co-workers concluded from a study of IrCl(CO)PN complexes where PN are *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline and *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine that the dimethylamino arm of the ligands does not modify markedly the basicity of the metal center. The higher rate of hydrogenation registered for these complexes compared to $\mathrm{IrCl(CO)(PPh_3)_2}$ may arise from an increased facility for dissociation of the nitrogen moiety to give a coordinatively unsaturated intermediate and from promotion of the insertion step by the free amine [3].

Much more flexible phosphorus-nitrogen ligands 1 are available from the reaction of dichlorophenylphosphine and diethanolamines [4]. We have reported on the synthesis and structure of rhodium(I) complexes containing 1 [5]. Noteworthy was the occurrence of a N—H. . .Cl hydrogen bond in complexes 2, 3a which affects the reactivity patterns. On the other hand, reaction of 1b with $\mathrm{[Rh(CO)_2Cl]_2}$, $\mathrm{[Rh(C_2H_4)_2Cl]_2}$ or $\mathrm{[Rh(cod)Cl]_2}$ gives rise to complexes where the $\geqq$NMe arm of the ligand is reversibly (i.e. 4) or

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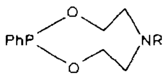
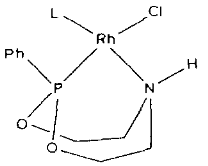
*Dedicated to Prof. Jack Halpern on the occasion of his 60th birthday.

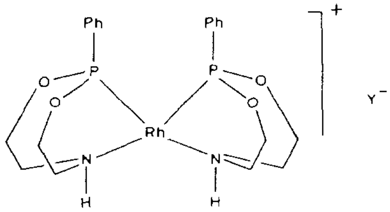
not (i.e. **5**) bonded to the rhodium(I) center [6]. This communication describes results on the comparative behavior of complexes **2b** and **4b** in hydrogenation and isomerization of 1-hexene.



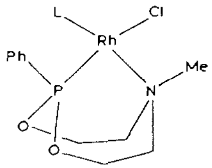
(**1a**, R = H;
1b, R = Me)



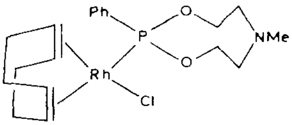
(**2a**, L = CO,
2b, L = C_2H_4)



(**3a**, Y^- = Cl^-,
3b, Y^- = ClO_4^-,
3c, Y^- = $[Rh(cod)Cl_2]^-$)



(**4a**, L = CO,
4b, L = C_2H_4)



(**5**)

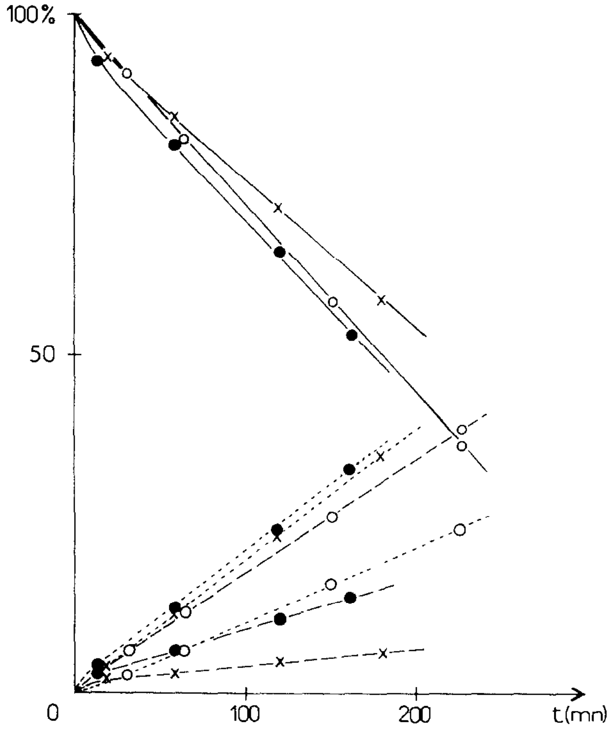


Fig. 1. The hydrogenation of 1-hexene in toluene/ethanol (1/1) ○, complex **4b**; ●, complex **2b**; X, complex **6**; (——), 1-hexene; (- - - -), hexane; (— — —), *cis*- and *trans*-2-hexenes.

Complexes 2a and 4a are inactive for hydrogenation of 1-hexene. A comparison of the catalytic activity of 2b, 4b and RhCl(PPh$_3$)$_3$ (6) is shown in Fig. 1. The results show that the rate of 1-hexene hydrogenation decreases in the order 2b > 6 > 4b. However, and significantly, the rate of 1-hexene isomerization increases more steeply from 6 to 2b and 4b. This is also reflected in Table 1 in the values of initial rate constants and times required for the production of 15% hexane and 2-hexenes.

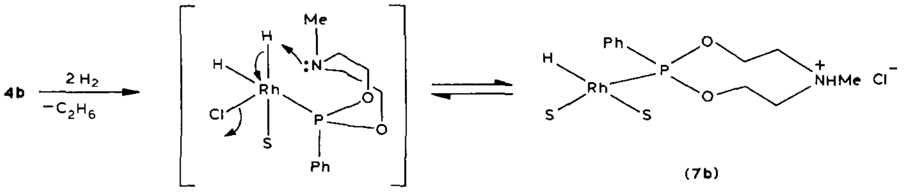
TABLE 1

HYDROGENATION AND ISOMERIZATION OF 1-HEXENE [a]

Complex	Additive (equiv.)	t_1 [b]	t_2 (% *trans*) [c]	t_3 [d]	k [e]	k_h [f]	k_i [g]
4b		140	88 (63)	180	5.1	1.8	3.2
2b		70	180 (65)	180	8.4	4.5	3.9
6		75	—	275	5.0	3.0	1.9
4b		—	(71) [h]	—	3.0	—	3.0
2b		—	(79) [h]	—	3.0	—	3.0
4b [h]	Et$_3$N (1.5)	86	72 (63)	135	7.7	3.3	4.3
2b [h]	Et$_3$N (1.5)	43	36 (81)	80	14.2	6.6	7.5
6	Et$_3$N (1.5)	58	78 (71)	125	9.1	5.5	3.5
4b	Et$_3$N (7.5)	48	40 (62)	80	11.2	5.8	6.4
4b	HClO$_4$ (1.5)	248	40 (45)	135	7.4	0.5	6.8
2b	HClO$_4$ (1.5)	—	—	—	0.9	0.1	0.8

[a] Reaction conditions: 1-hexene, 1.68 mol l^{-1}; complex, 4.5×10^{-3} mol l^{-1}; internal standard (2-methylpentane), 6.9×10^{-1} mol l^{-1}; solvent, 1/1 PhMe/EtOH, 7.7 ml; temperature, 30°C; pH$_2$, 1 bar. [b] Time (min) for the production of 15% hexane. [c] Time (min) for the production of 15% 2-hexenes and amount of *trans*-2-hexene at that time. [d] Time (min) for the consumption of 50% 1-hexene. [e] Initial rate constant (× 10^5 in units of s^{-1}) for hexene consumption. [f] Initial rate constant (× 10^5 in units of s^{-1}) for hexane production. [g] Initial rate constant (× 10^5 in units of s^{-1}) for 2-hexenes production. [h] Isomerization reaction with removal of hydrogen from the apparatus and initial *trans*-2-hexene content.

Complexes 2b, 4b are per se not active for 1-hexene isomerization. The active isomerization catalysts are therefore generated in the presence of molecular hydrogen. This formation is rapid since no induction period is observed. Furthermore, subsequent removal of hydrogen from the reaction apparatus yielded solutions which still isomerized 1-hexene. The initial rates of isomerization are very similar to those observed under hydrogenation conditions (Table 1). It is well known that Group VIII monohydride complexes are active for isomerization [7]. In fact, addition under hydrogen of excess triethylamine to an acetonitrile solution of 4b led to the formation of Et$_3$NHCl and a solvated hydridorhodium species. The formation under hydrogen of rhodium monohydride complexes from 2b, 4b may arise from intramolecular assistance from the basic ⋝NR (R = H, Me) arm of the P,N ligand for HCl elimination, e.g.:



(7b)

(1)

Addition of triethylamine to the catalyst system prior to hydrogenation increases the rate of isomerization and hydrogenation in all cases. Noteworthy is the larger increase in isomerization power for **2b** and **6** than for **4b**. This could be explained by the higher extent of deprotonation (4 → 7) in the case where **1b** is used (i.e., higher basicity and availability, as there is no extra stabilization of the Rh—N bond).

Addition under hydrogen of perchloric acid to solutions of **2b** and **4b** suppresses hydrogenation. Isomerization of 1-hexene only occurs with **4b**. In fact, this reaction is also observed for **4b** + 1.5 $HClO_4$ in the absence of hydrogen, but not for **2b** + 1.5 $HClO_4$.

The above observations indicated that bidentate phosphorus-nitrogen ligands are not suitable ligands for hydrogenation at least when associated with rhodium centers. The isomerization capability induced by the nitrogen moiety of these ligands will explain the low n/iso (~1.5—2) observed in hydroformylation of 1-hexene.

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