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HYDROFORMYLATION OF 1-HEXENE UNDER MILD CONDITIONS CATALYZED BY VARIOUS μ-PYRAZOLATO DIRHODIUM(I) COMPLEXES

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Summary

The selective hydroformylation reaction of 1-hexene into the corresponding aldehydes has been achieved under very mild conditions of pressure and temperature by various catalyst precursors of the type [Rh_2(μ-pyrazolato)$_2$(CO)$_2$$L_2$] where L = $P(OR)_3$ or PPh_3. The electronic effects of the ligands, which play an essential role in the reaction rates, are discussed.

Introduction

Many studies have recently been carried out on the hydroformylation reaction [1]. They concern the discovery of new catalyst systems as well as the elucidation of the behaviour of the complexes during the catalytic cycle. Kalck *et al.* [2] have recently shown the fast reaction rates obtained at 5 bars and 80 °C with dinuclear thiolato-bridged rhodium(I) complexes of the type $\{Rh_2(\mu\text{-SBu}^t)_2(CO)_2[P(OR)_3]_2\}$. Some evidence has been presented concerning the retention of the dinuclear structure during the catalytic cycle [2]. Furthermore, Oro *et al.* [3] have observed that some pyrazolato-bridged dirhodium complexes allow hydroformylation of 1-heptene under 50 atm of syn gas and at 80 °C.

The present investigation was undertaken in order to test the activity at low pressure of $[Rh_2(\mu\text{-Pz})_2(CO)_2L_2]$ and related complexes and to gain insight into the active species generated by these precursors. Indeed, recent studies on μ-pyrazolato dirhodium [4, 5] or diiridium [6 - 8] complexes have demonstrated the good stability and the flexibility of the six-membered cyclic core $\mathrm{M}\langle\begin{smallmatrix}\mathrm{N}-\mathrm{N}\\ \mathrm{N}-\mathrm{N}\end{smallmatrix}\rangle\mathrm{M}$ since the metal–metal distances range from 2.62 to 3.57 Å. This latter feature seemed interesting to us because of the cooperative effect it could induce on the catalytic activity of the complex.

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Results and discussion

As shown in Table 1 and Fig. 1, the three complexes $[Rh_2(\mu\text{-}Pz)_2(CO)_2L_2]$ (L = PPh_3, $P(OMe)_3$, $P(OPh)_3$) exhibit good catalytic activity. Infrared spectroscopy reveals some differences in the electronic density induced by the phosphorus ligands on the metal atom (see Table 1). Indeed the more basic phosphine is triphenylphosphine, whereas the less basic ligand is triphenylphosphite (ν(CO) = 2010 cm^{-1}). In our case the highest conversion rates were observed for $P(OPh)_3$; these rates decreased when the basicity of the ligand was increased. In our opinion, it would be rash to correlate the basicity or the ν(CO) stretching frequency with the catalytic activity, since in other cases with thiolato-bridging ligands the activity order $P(OMe)_3 > P(OPh)_3 \gg PPh_3$ was found [9]. In the present case we observed the order $P(OPh)_3 > P(OMe)_3 > PPh_3$.

Similarly, the effect of the bridging ligand was investigated: in addition to pyrazolate, the mono- (Me—Pz) and the di-substituted (Me_2Pz) (on one or two *ortho* positions of the nitrogen atoms) were examined. The substitution slightly increased the basicity (see Table 1) since ν(CO) = 2010, 2000

TABLE 1

Selected catalytic and spectroscopic data for pyrazolato-bridged rhodium complexes used in the hydroformylation of 1-hexene

Run	Catalyst precursor	$\nu(CO)^a$ (cm^{-1})	Turn-over^b rate (min^{-1})	Selectivity^c in n-heptanal (%)	$\frac{[\text{n-heptanal}]}{[\text{methyl-2-hexanal}]}$
1	$Rh_2(\mu\text{-}Pz)_2(CO)_2(PPh_3)_2$	1980	1.8^d	57.6	1.36
2	$Rh_2(\mu\text{-}Pz)_2(CO)_2\{P(OCH_3)_3\}_2$	1998	3.8^d	58	1.38
3	$Rh_2(\mu\text{-}Pz)_2(CO)_2\{P(OPh)_3\}_2$	2010	6.0^d	73.5	2.77
4	$Rh_2(\mu\text{-}Pz)_2(CO)_4 + 2P(OPh)_3$	2010	7.9^e	75.4	3.07
5	$Rh_2(\mu\text{-}MePz)_2(CO)_4 + 2P(OPh)_3$	2000	7.7^e	74.6	2.93
6	$Rh_2(\mu\text{-}3{,}5\text{-}Me_2Pz)_2(CO)_4 + 2P(OPh)_3$	1995	3.9^e	69	2.25
7	$Rh_2(\mu\text{-}Pz)_2(COD)_2 + 2P(OPh)_3$		20.6^e	70	2.32

Reaction conditions: [Rh] = 0.5 10^{-4} at-g; [alkene]/[Rh] = 800; CO/H_2 = 1/1; total pressure 5 bar at 80 °C; solvent: 20 ml.

[a] Solutions in CH_2Cl_2.

[b] Turnover rate is defined as the ratio of the number of moles of 1-hexene converted to the number of moles of dinuclear species per time unit.

[c] Selectivity in aldehyde (n + i) is greater than 98%.

[d] In toluene solvent.

[e] In n-heptane solvent.

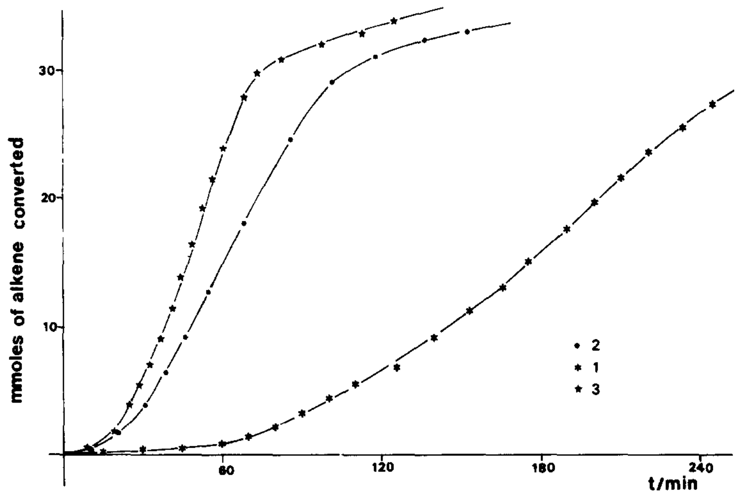

Fig. 1. Hydroformylation of 1-hexene by dinuclear pyrazolato-bridged rhodium complexes: effects of phosphine ligands. Numbers refer to catalytic runs (see Table 1).

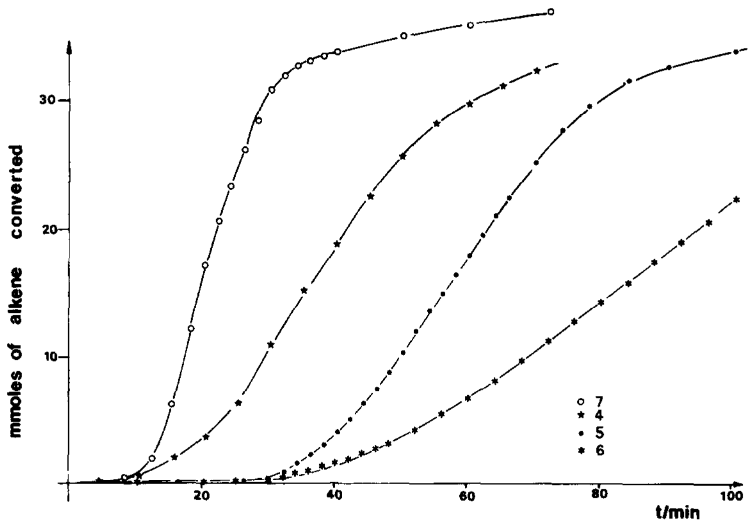

Fig. 2. Hydroformylation of 1-hexene by dinuclear pyrazolato-bridged rhodium complexes: effects of substituents on the bridging pyrazolato ligands. Numbers refer to catalytic runs (see Table 1).

and 1995 cm^{-1} respectively. However, due to the presence of methyl groups in close vicinity to the rhodium atoms, the steric hindrance of the bridging ligand plays an important role. Figure 2 gives evidence for the decrease in activity of $[Rh_2(\mu\text{-}Me_2Pz)_2(CO)_2\{P(OPh)_3\}_2]$ which, according to the basicity ($\nu(CO) = 1995\ cm^{-1}$), should exhibit about the same activity as $[Rh_2(\mu\text{-}Pz)_2(CO)_2\{P(OMe)_3\}_2]$ ($\nu(CO) = 1998\ cm^{-1}$).

Interestingly, this study revealed that the catalytic species generated from the addition of two equivalents of $P(OPh)_3$ to the cyclooctadiene precursor $[Rh_2(\mu\text{-}Pz)_2(COD)]$ provided the best catalytic performances when compared to the $[Rh_2(\mu\text{-}Pz)_2(CO)_2L_2]$ prepared complexes. Figure 2 shows not only a shorter induction period but also a very high rate of conversion.

In all the cases studied, the complexes $[Rh_2(\mu\text{-}Pz)_2(CO)_2L_2]$ were found after catalysis and identified by IR and in some cases by ^{31}P NMR. As in the case of the $[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2L_2]$ complexes, the full catalytic cycle presumably involves dinuclear species. In order to understand the specific behaviour of the cyclooctadiene precursor, we suggest that an undetected species $[(CO)_2Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$ can be produced at the beginning of the reaction by carbonylation of the $[(COD)Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$ complex. Indeed, in the case of $[(COD)Rh(\mu\text{-}Cl)_2Rh(COD)]$ it was previously shown that addition of two equivalents of triphenylphosphite gave rise to formation of the $[(COD)Rh(\mu\text{-}Cl)_2Rh\{P(OPh)_3\}_2]$ complex [10]. By reaction of this latter complex with the pyrazolate anion we were able to isolate the compound $[(COD)Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$. However, the direct addition of triphenylphosphite to $[Rh_2(\mu\text{-}Pz)_2(COD)_2]$ did not permit to us to isolate the proposed complex. Furthermore, carbonylation under atmospheric conditions of the complex $[(COD)Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$ gave exclusively, as shown by IR spectroscopy, the complex *trans*-$[Rh_2(\mu\text{-}Pz)_2(CO)_2\{P(OPh)_3\}_2]$. Presumably the asymmetric complex $[(CO)_2Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$ could be an intermediate.

We have shown elsewhere [9] that the first step of the catalytic cycle for the complex $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ should be the activation of dihydrogen leading to a mixed rhodium complex $[L(CO)Rh^{I}(\mu\text{-}SR)_2Rh^{III}(CO)L(H)]_2$. In the present case, we propose that in a H_2/CO atmosphere the cyclooctadiene ligand was substituted by two CO ligands, whereas oxidative addition of di-hydrogen occurred on the second metal center, so that the μ-pyrazolate asymmetric complex could either follow a slightly different catalytic cycle or lead more rapidly to the dihydride species. Further work is in progress in order to test the validity of our hypothesis and to examine the activity of various nitrogen donor-atoms as bridging ligands in dirhodium systems.

Experimental

All solvents and reactants were distilled or saturated with nitrogen, and stored and used under nitrogen atmosphere.

The complexes $[Rh_2(\mu\text{-}Pz)_2(CO)_2L_2]$ where $L = PPh_3$, $P(OPh)_3$ were prepared according to literature methods [4].

The complex $[Rh_2(\mu\text{-}Pz)_2(CO)_2\{P(OCH_3)\}_2]$ was similarly obtained. Analysis found: C: 25.85%, H: 3.45%, N: 8.56%; calculated for $C_{14}H_{24}N_2O_8P_2Rh_2$: C: 26.11%, H: 3.76%, N: 8.70%.

The complexes $[Rh_2(\mu\text{-}Me_xPz)_2(CO)_2\{P(OPh)_3\}_2]$ ($x = 1$ or 2) were prepared *in situ* by adding a stoichiometric amount ($P/Rh = 1$) of $P(OPh)_3$ to $[Rh_2(\mu\text{-}Me_xPz)_2(CO)_4]$ [4].

The complex $[(COD)Rh(\mu\text{-}Pz)_2Rh\{P(OPh)_3\}_2]$ was synthesized by adding 5 ml of a methanolic solution of sodium pyrazolate (prepared from HPz (8.2 mg; 0.12 mmol) and NaOH (0.12 mmol) to a suspension of $[(COD)\text{-}Rh(\mu\text{-}Cl)_2Rh\{P(OPh_3\}_2$ [10] (60 mg; 0.06 mmol) in methanol (20 ml). The suspension was stirred for 30 min and then filtered and washed with methanol. Analysis found: C: 55.93%, H: 4.69%, N: 4.62%; calculated for $C_{50}H_{48}N_4O_6\text{-}P_2Rh_2$: C: 56.19%, H: 4.53%, N: 5.24%.

Each catalytic experiment was carried out in a 150 ml stainless steel magnetically stirred autoclave from the Sotelem Co., using a procedure previously described [11], which was slightly modified; for instance rhodium complexes were introduced, either as well-defined dinuclear disubstituted complexes of the type $[Rh_2(\mu\text{-}Pz)_2(CO)_2L_2]$ where L = PPh_3, $P(OCH_3)_3$, $P(OPh)_3$, in toluene solution, or as n-heptane solutions of dinuclear tetracarbonyl or dicyclooctadiene rhodium complexes containing the stoichiometric amount (P/Rh = 1) of required phosphine or phosphite as well.

After the run, the composition of the solution was determined by gas phase chromatography on an Intersmat IGC 131 apparatus equipped with a 6 m X 1/8 in column of OV-17 on Chromosorb W.H.P.

Infrared spectra were recorded on a Perkin-Elmer 783 IR spectrophotometer.

Each experiment was repeated twice; after five runs a blank experiment was performed and no catalytic activity was noted. Moreover, no decomposition of the rhodium complexes on the walls of the autoclave was observed.

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References

1 I. Tkatchenko, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon Press, Oxford, 1982, pp. 115 - 157.

2 P. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern and A. Thorez, *J. Chem. Soc., Chem. Commun.*, (1983) 511.

3 R. Uson, L. A. Oro, M. T. Pinillos, M. Royo and E. Pastor, *J. Mol. Catal.*, *14* (1982) 379.

4 R. Uson, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organometall. Chem.*, *205* (1981) 247.

5 R. Uson, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organometall. Chem.*, *206* (1981) C14.

6 L. A. Oro, M. T. Pinillos, M. Royo and E. Pastor, *J. Chem. Res.*, (1984) 206.

7 G. W. Bushnell, D. O. K. Fjeldsted, S. R. Stobart and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, (1983) 580.

8 K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood and M. J. Zaworotk, *Organometallics*, *2* (1983) 1447 and references therein.

9 P. Kalck, J. M. Frances and A. Thorez, unpublished results.

10 L. M. Haines, *Inorg. Chem.*, *9* (1970) 1517.

11 J. M. Frances, A. Thorez and P. Kalck, *Nouv. J. Chim.*, *8* (1984) 213.