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X-Ray Photoelectron Spectroscopic and Infrared Studies of some Rhodium(I) Aminophosphine Complexes. Correlation with Selected Properties in Homogeneous Hydroformylation of 1-Hexene

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X-Ray photoelectron and infrared spectroscopies are used to analyse the electronic displacements on changing the ligands in $RhClCOL_2$ complexes, particularly with $Ph_{3-n}P(N\langle)_n$ (n = 1,2,3) aminophosphines. In the free aminophosphines, a back donation from N to P is shown, whereas in the rhodium complexes an unexpected behaviour is observed, as the electron transfer seems to be from P to N.

By comparing the binding energies of the nitrogen and phosphorus atoms in these complexes and the results obtained in hydroformylation of 1-hexene, a good correlation is found between this electron acceptor property and the normal to branched aldehyde ratio.

Introduction

Among the characteristics of the hydroformylation reaction [1], usually done with cobalt or rhodium catalysts, increasing the selectivity in linear product is one of the aspects which is of great interest from both fundamental and industrial points of view.

The modification of rhodium catalytic activity and selectivity by using phosphine modified catalysts was first achieved by Wilkinson's school [2], and this research area has received much attention in recent years, since the large number of possible combinations offers a promising opportunity to find more active and more selective catalysts.

Two major factors have been used to explain the stereoselective role of these ligands: a geometric factor and an electronic one. In order to obtain more information about this latter point, a study of this stereospecificity has been undertaken on well characterized $RhClCOL_2$ catalysts, where the ligand L is a phosphine or an $Ph_{3-n}P(N\langle)_n$ aminophosphine with which a variation of the electronic distribution is expected in the complexes. The aim of this paper will thus concern the analysis of the infrared and X-ray photoelectron spectroscopic (ESCA) properties of these homogeneous complexes.

TABLE I. Spectroscopic and Catalytic Hydroformylation Data Obtained on Different $RhClCO(phosphine)_2$ Complexes.

Number	1	2	3	4	5	6
Phosphine	PPh_3	PBu_3	P(*o*-tolyl)$_3$	P(*p*-tolyl)$_3$	$(PPh_2–CH_2–)_2$	$PPh_2(CH_2)_3\ PPh_2$
ν_{CO} (cm^{-1})	1960	1953	1965	1970	2062 (w) 2002 (s) 1982 (s)	1958
LWHM C1s (eV)	1.55	1.5	1.65	1.5	1.7	1.5
B.E. P2p (eV)	131.5	131.4	131.9	131.7	131.0	131.55
Conversion	97%	89%	80%	~100%	75%	82%
n/b Ratio	1.2	1.9	0.8	2.5	2.17	1.96

TABLE II. Spectroscopic and Catalytic Hydroformylation Data Obtained on Different RhClCO(aminophosphine)$_2$ Complexes.

Number	7	8	9	10	11	12	13	14
Phosphine	PPh_2NEt_2	$PPh(NEt_2)_2$	$P(NEt_2)_3$	PPh_2NMe_2	$PPh(NMe_2)_2$	PPh_2–N(Me)(Cy)	$PPh(N(Me)(Cy))_2$	$(PPh_2–N(Me)–CH_2–)_2$
ν_{CO} (cm^{-1})	1959	1974	1970	1964	1962	1972	1988	1988
LWHM C1s (eV)	1.7	1.95	1.6	1.6	2.0	1.85	1.95	1.85
B.E. P2p (eV)	132.1	132.3	132.9	132.5	132.5	132.2	132.1	131.65
B.E. N1s (eV)	399.2	398.9	398.85	399.4	399.0	399.0	398.7	398.8
Conversion	78%	42%	29%	86%	18%	76%	23%	80%
n/b Ratio	1.47	1.97	2.07	0.77	1.57	1.60	2.18	2.28

A comparison between these results and the catalytic behaviour of these compounds in hydroformylation of 1-hexene allows us to propose an explanation of the observed stereoselectivities in terms of electronic density variations in the aminophosphine complexes.

Experimental

Preparation of Homogeneous Catalysts

PPh_3, PBu_3, $P(o\text{-tolyl})_3$, $P(p\text{-tolyl})_3$, PPh_2–$(CH_2)_2$–PPh_2 and PPh_2–$(CH_2)_3$–PPh_2 are commercial products. The aminophosphines were prepared by a procedure described elsewhere [3] and $Rh_2Cl_2(CO)_4$ was prepared from $RhCl_3 \cdot 3H_2O$ (Strem Chemicals) by reaction of carbon monoxide at 100 °C [4]. Displacement of carbon monoxide from $Rh_2Cl_2(CO)_4$ in a benzene solution at room temperature was used to obtain the complexes $RhClCOL_2$ [5]:

$$Rh_2Cl_2(CO)_4 + 4L \rightarrow 2RhClCOL_2 + 2CO$$

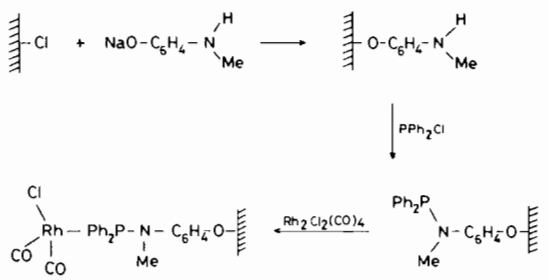
Caution had to be taken to add the stoichiometric quantity of L in the case of aminophosphines, as a complete removal of CO could be observed with an excess of some of these ligands. In each case, yields up to 80% were obtained upon evaporation of the solvent, washing with petrol, and drying under vacuum. With $P(NEt_2)_3$, $RhClCO[P\text{-}(N(Et)(Et))_3]_2$ was isolated in low yield.

In Tables I and II are reported the values of the infrared carbonyl stretching frequencies of 14 complexes prepared by this method (Nujol mulls, KBr discs, Perkin-Elmer 257). All these complexes exhibit only one carbonyl band, indicating a *trans* coordination of the phosphines, except for complex 5, for which the three bands were attributed by Hieber and Kummer [6] to a *cis* configuration of the bidentate.

Preparation of Supported Catalysts

On silica

A silica (PBS 300–300 m^2/g) was chlorinated by reaction of triethoxychloropropylsilane according to the British Petroleum procedure [7]. The aminophosphine rhodium complex was then grafted to the support by the following sequence:



On 5 g of chlorinated silica (1 matg Cl/g), we added successively 50 ml of ethanol, 0.8 g (20 mmol) of NaOH, 3.5 g (10 mmol) of paraaminophenol sulfate and 20 ml of water. The mixture was stirred under nitrogen at 80 °C for 12 h. The solid was washed with water and ethanol after cooling, and dried under vacuum.

In a Schlenk tube containing 4 g of this supported amine, we added 40 ml of anhydrous toluene and 0.78 ml (5 mmol) of triethylamine. A solution of 1.1 g (5 mmol) of chlorodiphenylphosphine was slowly added at 0 °C for 30 min. Stirring was continued for 6 hours at room temperature. After several washings with toluene, ethanol, water and finally absolute ethanol, the solid was dried under vacuum (P content = 0.814 atg/g [8]).

To graft the metal, bridge splitting of the dimer $Rh_2Cl_2(CO)_4$ (0.198 g, 0.6 mmol) by 1.5 g of the aminophosphine supported silica was carried out in benzene (10 ml) during 12 hours at room temperature. The supported catalyst was then washed with benzene until the filtrate remained colourless, and dried under vacuum (ESCA: P2p = 133.0 eV; N1s = 399.8 eV; Ref. B.E. C1s = 285.0 eV or Si2p = 104.0 eV).

On polymer

The above procedure was used to support the same aminophosphine on a Merrifield resin (Fluka polymer, 2% divinylbenzene, 3.5 mmol Cl/g) (P content = 1.8 matg/g). Subsequent reaction with $Rh_2Cl_2(CO)_4$ gave a complex, polymer–O–C_6H_4–N(Me)P $Ph_2RhCl(CO)_2$ whose infrared spectra exhibited 2 carbonyl bands at 1990 and 2078 cm^{-1} (ESCA: P2p = 132.9 eV; N1s = 399.5 eV; Ref. B.E. C1s = 285.0 eV).

Catalytic Reactions

1-hexene and benzene were purified by distillation under nitrogen over calcium hydride and stored under nitrogen. The hydroformylation of 1-hexene was carried out under pressure in a 300 ml stainless steel autoclave. In a typical experiment, 0.0378 mmol of catalyst in benzene solution (10 ml) and 1-hexene (5 ml) were introduced in the autoclave under nitrogen. The reactor was filled at room temperature with a 1/1 mixture of CO and H_2 at 25 atm. The temperature was then quickly raised to 80 °C with the aid of a circulating water bath. The autoclave was supplied with a double jacket, so that the stabilisation at 80 ± 1 °C could be reached within 5 min. After 15 hours under magnetic stirring, the reaction products were monitored by gas chromatography (Girdel 3000) using a capillary column of squalane, which allowed good separation of the aldehydes. Olefin conversion was determined by taking benzene as an internal standard. Selectivities are expressed by the ratio n/b (normal/branched aldehydes), the term branched including both 2-methyl-1-hexanal and 2-ethyl-1-pentanal, this latter product being observed in some cases.

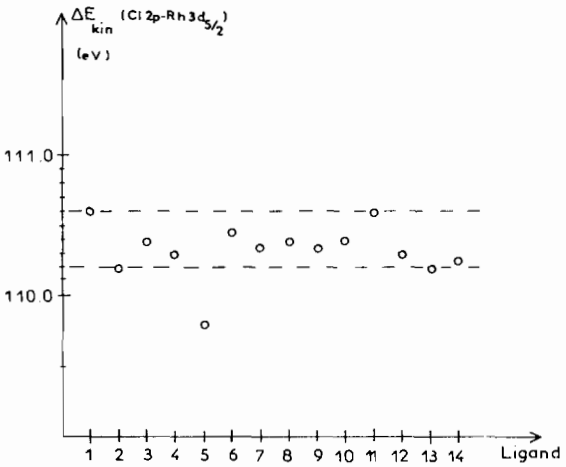


Fig. 1. Difference between kinetic energies of $Cl2p_{3/2}$ and $Rh3d_{5/2}$ ESCA lines *versus* the nature of L in $RhCoCl(L)_2$ complexes. The average value of $\Delta E_{Kin}(Cl2p_{3/2} - Rh3d_{5/2})$ is 110.4 eV except for the complex *cis*-$RhCOCl(L_5)_2$.

X-ray Photoelectron Spectra

The photoelectron spectra were obtained by using an AEI ES 200 B spectrometer. The excitation source was an Mg X-ray anode. The pressure in the sample chamber during the irradiation of the samples was less than 5×10^{-8} Torr. The complexes and the aminophosphines, as powders, were pressed on an indium foil. The aminophosphines 7, 8 and 9, liquid at room temperature, were cooled at ≅ –80 to –100 °C under dry nitrogen before their introduction into the spectrometer.

The full width at half height (FWHM) of the carbon 1s line was about 1.4 ± 0.1 eV for the free aminophosphines. The binding energies were therefore given relative to the C1s binding energy (285 eV) as a reference. But, for the rhodium complexes, C1s lineshape depended upon the nature of the phosphines bound to the rhodium metal (Tables I and II), so that C1s binding energy could not be taken as a reference. Thus the $Rh3d_{5/2}$, P2p and N1s binding energies were corrected for charging shifts by requiring the observed Cl2p binding energy to be 198.2 eV. It is clear, from Fig.1, that the different aminophosphines do not strongly modify the Rh–Cl bond in the studied complexes. These results are in accordande with the studies of Walton *et al.* [9], who showed that the binding energy $Rh3d_{5/2}$ in Rh(I) complexes was not very much affected by the nature of the ligands: the slope of the straight line B.E. ($Rh3d_{5/2}$) *versus* ν(Rh–Cl) is much less for Rh(I) or Rh(II) complexes than for Rh(III) complexes.

TABLE III. ESCA Results on the Free Aminophosphines $Ph_{3-n}P(N\langle^{R_1}_{R_2})_n$[a].

n	0	1	2	3
B.E. P2p (eV) experimental	131.0[b]		131.3 ± 0.2	
B.E. P2p (eV)[c] calculated	131.2	131.5	131.8	132.1
B.E. N1s (eV)	–	399.2	398.9	398.5

[a] R_1, R_2 = Me, Et or Cy. [b] Numerous values were found in the literature for the binding energy of P2p in the phosphine PPh_3. The values quoted by B. J. Lindberg and J. Hedman (*Chem. Scripta.*, *7*, 155 (1975)) vary from 130.6 to 131.9. If this last value, too high, is eliminated, an average value of 131.1 is obtained. The average of the results from W. L. Jolly (*Coord. Chem. Rev.*, *13*, 47 (1973)) was 131.3 eV. The result found in this work is very similar. [c] See text for the evaluation of B.E. (P2p).

Results and Discussion

Spectroscopic Studies on the Aminophosphines Complexes

Electron donor–acceptor properties of aminophosphines in Tolman's scale

The very commonly used term of basicity which represents the ability of a ligand L to withdraw or to release the electronic density of a metal atom can be evaluated by the carbonyl ligand stretching frequency A_1 in complexes $Ni(CO)_3L$. This method was described by Tolman [10]: the greater the electron donor properties of the ligand L, the greater the electron density on the metal; so, the metal can back-donate more to the antibonding molecular orbital of CO, thus decreasing the bond order and the ν_{CO} stretching vibration.

In order to have a good agreement between our results and Tolman's scale, we used his method [10] to measure the stretching frequency ν_{CO} of the complexes $Ni(CO)_3L$, with $Ni(CO)_3PPh_3$ as a reference. All the studied aminophosphines have basicities between those of PBu_3 and PPh_3 (Fig. 2a). While very small effects are observed by changing the alkyl group substituted on the nitrogen atom, the number n of aminosubstituents bound to phosphorus is of greater importance: when n increases by one unit, ν_{CO} decreases by a nearly constant increment (~3 cm^{-1}). Moreover, it is shown in Fig. 2a that the donor character of an aminophosphine is about the same as that of an ethyl substituent. In regard to the electronegativity of the nitrogen atom, this result could seem quite surprising; nevertheless, the following ESCA studies on the free aminophosphines will confirm this fact.

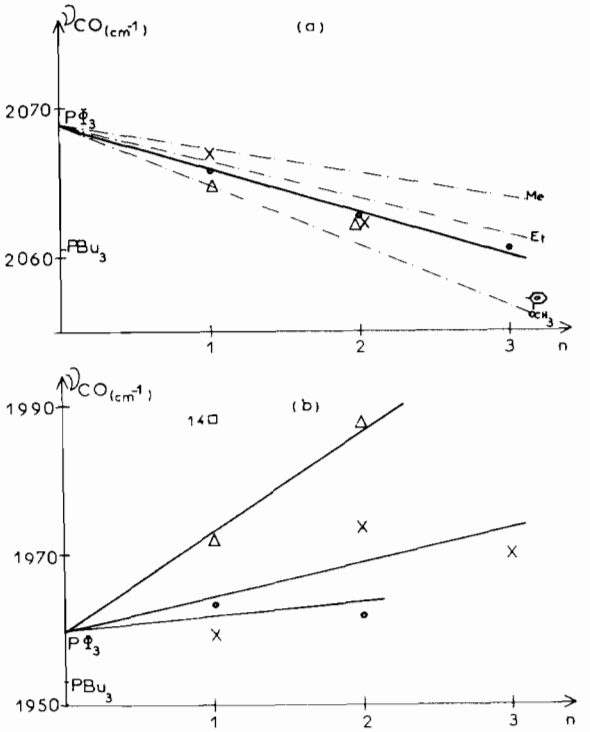


Fig. 2. Effect of successive replacement of Ph by amino groups on ν_{CO} for a) $Ni(CO)_3[PPh_{3-n}(N\langle)_n]$ (A_1 band). For the effect of replacement of Ph by Me, Et or *o*-anisyl see Tolman [10]. b) $RhCOCl[PPh_{3-n}(N\langle)_n]_2$. The complex $RhCOCl[P(NMe_2)_3]_2$ has not been isolated. O = $-N\langle^{Me}_{Me}$, X = $-N\langle^{Et}_{Et}$, Δ = $-N\langle^{Me}_{Cy}$

ESCA spectra of free aminophosphines

The data obtained on these ligands are summarized in Table III, which shows that a methyl, ethyl or cyclohexyl substituent on the nitrogen atom has practically no influence on either P2p and N1s binding energies, neither does the number n of aminosubstituents on P2p binding energy.

If one evaluates the partial charge q(P) of phosphorus according to Pauling's method [11], the theoretical binding energy of P2p level can be predicted by the relation found by Hedman *et al.* [12]: B.E. (P) – B.E. (P^o) = 0.9 + 1.84 q(P) with B.E. (P^o) = 130.1 eV. Similar results are obtained in the case of nitrogen by the use of a plot B.E. (N1s) = f(q(N)) previously depicted by Nordberg *et al.* [13].

The conclusions can be drawn as follows:

(i) In the case of phosphorus, a good correlation between the calculated and the experimental values is obtained when n = 0, but with the amino groups, the phosphorus atom is less positively charged as

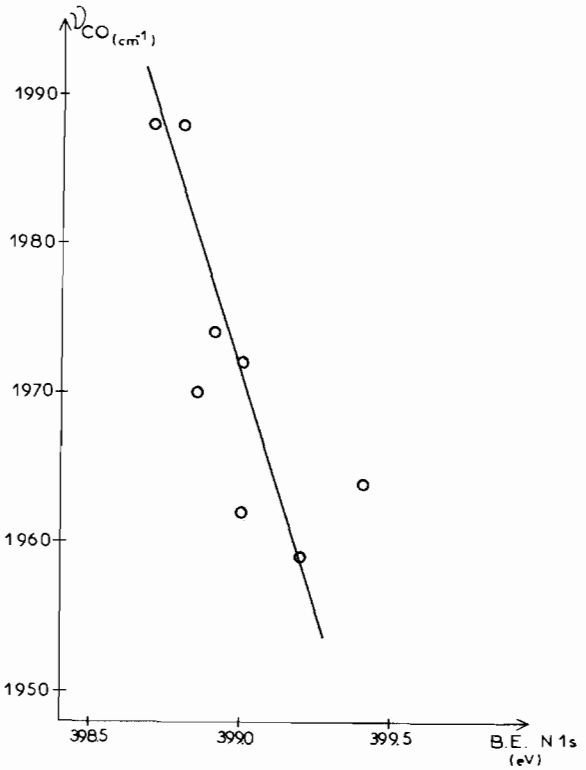


Fig. 3. Dependence of the IR CO stretching frequency of the Rh(I) complexes on the nitrogen 1s binding energy.

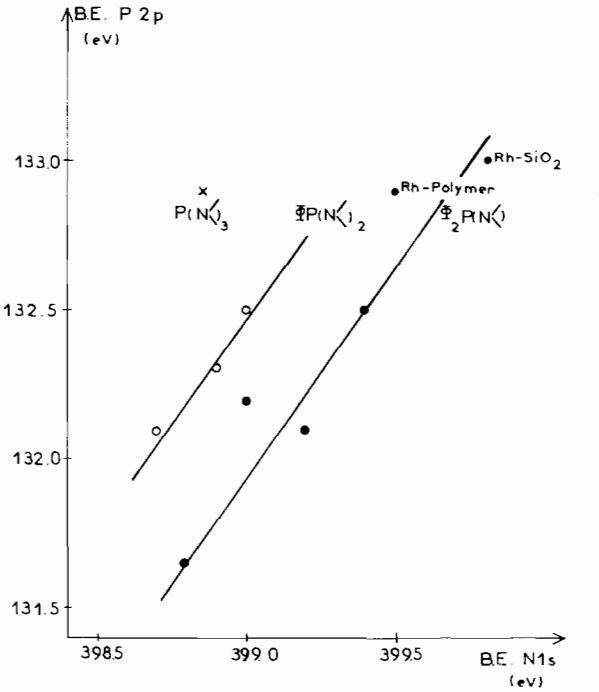


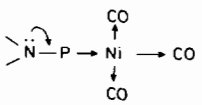
Fig. 4. Plot of the binding energy P2p against the binding energy N1s.

could be expected from the electronegativity difference between P and N.

(ii) The nitrogen atom has a very small partial negative charge, increasing with n.

These results have to be compared with those obtained by nmr spectroscopy by Ewart *et al.* [14] who showed that a $p\pi$–$d\pi$ back donation from the $p\pi$ filled orbital of the nitrogen atom to the $d\pi$ empty orbital of phosphorus occurs: this electronic displacement reinforces the donor character of the phosphorus to the detriment of the nitrogen atom.

This interpretation is completely in agreement with the above observations and in the case of $Ni(CO)_3L$ complexes, the strong π acceptor property of the three CO ligands assists the global electronic transfer:



Infrared and ESCA studies of $RhClCOL_2$ complexes

Fig. 2b shows the values of ν_{CO} in the rhodium aminophosphine complexes. The comparison of Figs. 2a and 2b shows that the carbonyl stretching frequencies change oppositely in the cases $Ni(CO)_3L$ and $RhClCOL_2$; therefore, a classification of the basicity of these ligands based on ν_{CO} cannot be transposed *a priori* to all types of complexes.

Thus, in $RhClCOL_2$ compounds the back donation of the lone pair of electrons on nitrogen seems to be absent, since in all cases the carbonyl stretching vibration increases with the number of amino groups.

Some results on the ESCA characterization of rhodium complexes have already been published [9, 15–20], but no work has been done on aminophosphine rhodium complexes. A first observation can be made about the evolution of the N1s binding energy (Fig. 3): as the ν_{CO} frequency increases, the N1s binding energy decreases, indicating an increasing electronic density on the nitrogen atom, which confirms the lack of $p\pi$–$d\pi$ back donation from N to P.

Thus, the aminophosphines must be considered as electron acceptor ligands in these rhodium complexes. This hypothesis is confirmed by the study of the relative evolution of the binding energies of P2p and N1s in these compounds, plotted in Fig. 4, about which the following comments can be made:

1) According to these curves, it is clear that the electronic density increases on the phosphorus and nitrogen atoms on increasing the number n.

2) The presence of 3 series of curves is probably due to the influence of the aromatic systems on the phosphorus, whose effect cannot be ascertained unambiguously, as it would be necessary to determine the C1s binding energies of the aromatic part.

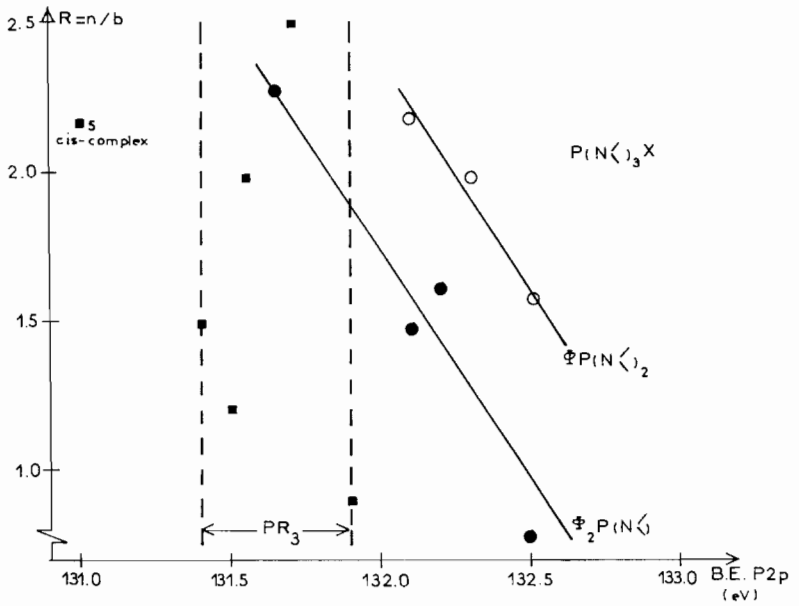
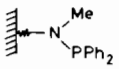


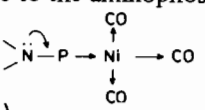
Fig. 5. Plot of the n/b aldehyde ratio against the binding energy P2p.

3) The order of electronic affinity according to the nature of the substituent of the nitrogen atom is N(Me)(Cy) > NEt_2 > NMe_2, and is identical to the conclusions that we could obtain from the infrared data on $RhClCOL_2$ aminophosphine complexes (Fig. 2b).

4) Finally, the values obtained on two aminophosphine–rhodium complexes supported on silica and polymer are in accordance with these results. These complexes were grafted on a support containing



All the experimental spectroscopic data and their consequences obtained on the complexes $Ni(CO)_3L$ and $RhClCOL_2$ can be summarized in the following schemes where we can notice the electronic displacements due to the aminophosphine groups:



(β) $N \leftarrow P \leftarrow Rh \leftarrow CO$

(α) The high π acceptor properties of the three CO ligands around the nickel atom dictate the whole electronic transfer.

(β) It is the high electronegativity of nitrogen which dictates the whole electronic transfer.

Correlation with Selective Properties in Hydroformylation of 1-Hexene

The above results describing the electronic transfers in the aminophosphine–rhodium complexes are of a great interest for the study of the catalytic behaviour of these compounds in the homogeneous hydroformylation of olefins.

Particularly, a variation of the normal/branched aldehyde ratio should be obtained on varying the nature of the ligand, as has been previously observed with a rhodium-on-charcoal catalyst modified by phosphites or phosphines [21] or in cobalt systems [22]. To check this possibility, all the complexes have been tested in the catalytic hydroformylation of 1-hexene under the same conditions (80 °C, 25 atm) and the conversion and selectivities measured after 15 hours. The results obtained (Table II) show that the n/b aldehydes ratio can be greatly modified from 0.77 to 2.28 as the reaction is done either with the ligand PPh_2NMe_2 or $PPh_2-\underset{\displaystyle Me}{\underset{|}{N}}-(CH_2)_2-\underset{\displaystyle Me}{\underset{|}{N}}-PPh_2$. A variation of activity is also noticed, as the conversion decreases with an increase of the number n of aminogroups on the phosphorus. This experimental result can be explained if one considers the catalytic scheme of Wilkinson [2], as the rate determining step of the process is the oxidative addition of hydrogen on the acylrhodium complex:

$$Rh(I)COL_2(COR) \overset{H_2}{\rightleftharpoons} Rh(III)H_2COL_2(COR) \longrightarrow Rh(I)HCOL_2 + R-C(=O)H$$

This addition rate is enhanced when the phosphine contains more phenyl groups [23], as a possible electronic delocalisation in the aromatic ring(s)

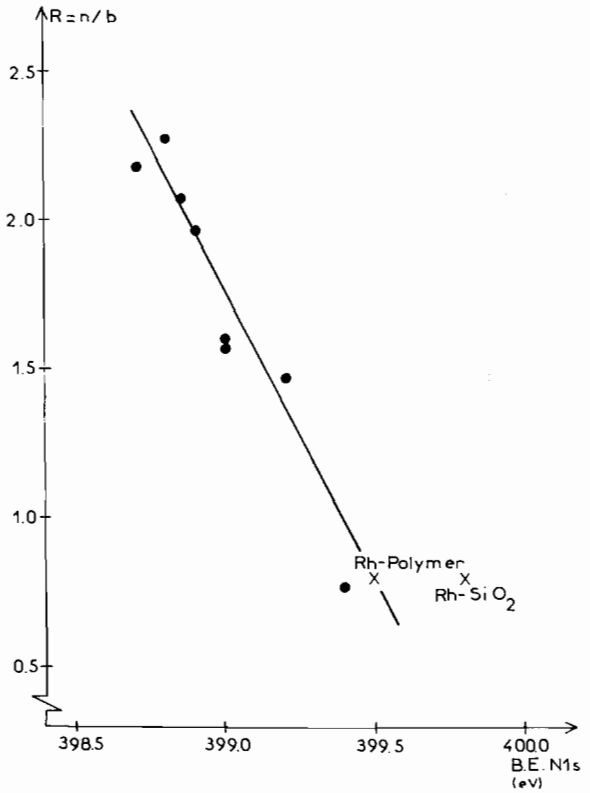
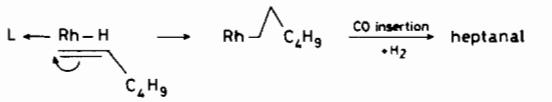


Fig. 6. Plot of the n/b aldehyde ratio against the binding energy N1s.

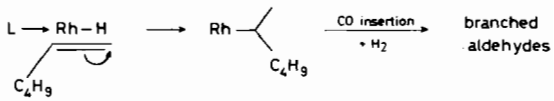
favours the reversible step Rh(I) ⇄ Rh(III). Therefore, the activity decreases in the order $PPh_2(N\langle) > PPh(N\langle)_2 > P(N\langle)_3$.

Comparison between the observed selectivities and the binding energies of P2p and N1s are plotted in Figs. 5 and 6. These curves clearly show that for the same aminophosphine series (Fig. 5) there is linear relationship between the n/b ratio and the binding energy of the phosphorus atom, but this does not seem to be the case with phosphines of type PR_3. The most interesting result is obtained in Fig. 6, where all experimental data n/b = f(B.E. N1s) are on the same straight line: the more the electronic density on the nitrogen atom increases, the more the selectivity in normal aldehyde is favoured (the same conclusion can be deduced if one plots the n/b ratio against the $\nu_{C=O}$ stretching frequencies). The corresponding values obtained on the supported catalysts are in accordance with these relations, but have to be considered with caution as some loss of rhodium was observed in both cases. The analogy observed between these last curves and those depicted in the preceeding ESCA studies (Fig. 4) demonstrates that the selectivity in hydroformylation of 1-hexene under our experimental conditions on $RhClCOL_2$ catalysts strongly depends upon electronic factors when L is an aminophosphine.

In order to discuss this point, it seems reasonable to take as a support the mechanism proposed by Wilkinson *et al.* [2], who suggest that the stereoselective process should be the direction of the insertion of the olefin on the hydride $RhH(CO)_2L_2$, a very labile species formed *in situ* from the starting chloride. According to the direction of this addition, two different alkyl complexes can be formed and give subsequently either normal or branched aldehydes. We can assume that at least in part, the direction of addition will depend on the polarity of the Rh–H bond: the linear aldehyde formation should be favoured when the electronic density on the metal atom is reduced by the ligands:



A lower acceptor ability of a ligand causes an increase of electronic density on the metal atom and hence produces more branched aldehydes:



If we assume that the steric environment is approximately the same for the aminophosphines studied in this work [25], a good selectivity should be obtained when the ligands have a pronounced acceptor ability. The ESCA and IR results are in total agreement with this hypothesis, as the most selective catalysts have the highest electronic densities on both phosphorus and nitrogen atoms, thus favouring the linear alkyl–metal intermediate in the catalytic process.

These results are also in accordance with the studies of Pruett and Smith [21], who have shown that phosphites are more efficient than phosphines for the formation of linear product in the hydroformylation of 1-octene on Rh/charcoal catalysts. If one considers that phosphites have an acidic character (as compared to phosphines), their behaviour is quite the same as that observed with the aminophosphine ligands.

In contrast with this, no relationship could be detected between the selectivity and the binding energy of the phosphorus atom in complexes containing PR_3 groups (Fig. 5). It is highly probable that this absence of correlation is due to the fact that in these cases the phosphorus atom is directly bound to the alkyl substituents, which can generate substantial steric hindrance during the approach of the alkene: both steric and electronic effects should explain these untractable results. However, in the case of bulky ligands, like $P(o\text{-tolyl})_3$, the steric effect must provide the highest contribution to the value of the selectivity, as a 0.8 n/b ratio is obtained, where it is as

high as 2.5 with P(p-tolyl)$_3$, for a difference of only 0.2 eV between the binding energies of P2p in the rhodium complexes.

Moreover, as the presence of isomers of 1-hexene has been detected at the end of the reaction, the observed results might be explained by a mechanism in which some part of the branched aldehydes could arise from these isomeric olefins, as was previously shown by Haag and Whitehurst [24]. Kinetic studies are now in progress to check this possibility, which anyway might be related to the spectroscopic results, as the isomerisation extent is probably dependent on the electronic density on the surrounding ligands.

Conclusion

The comparative study of the selectivity during the hydroformylation of 1-hexene on homogeneous and supported catalysts and the binding energy of the nitrogen and the phosphorus atoms in the aminophosphine rhodium complexes has shown a linear relationship between the binding energies and the selectivities to normal aldehyde. This result is in perfect accord with the hypothesis that the stereoselective process in the reaction scheme should be governed by the stereochemistry of the insertion reaction of the olefin on the hydride, during which the partial charge on the Rh atom would play a predominant role. In aminophosphine complexes, the electronegativity of the nitrogen atom is strong enough to withdraw some partial charge from the metal and avoid back donation from the phosphorus to the rhodium atom. With phosphine rhodium complexes the lack of relationship between the binding energy of the phosphorus atom and selectivity can be explained by the proximity of the alkyl groups, in which case the selectivity is also dependent on steric effects. This last aspect and the isomerizing properties of the aminophosphine rhodium complexes will be the subject of further studies in order to confirm the catalytic role of the nitrogen atom in these ligands.

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25 From one Referee's comment, the observation that $\nu_{C=O}$ in $RhClCOL_2$ complexes increases when one replaces Ph by bulkier NR_2 groups (Fig. 2b) could be explained on the basis of rehybridization caused by angle deformation at nitrogen, which are imposed by steric constraints, particularly in $RhClCO[PPh(NMeCy)_2]_2$. An X-ray structure determination and Tolman's cone angle measurements (C. A. Tolman, *Chem. Revs., 77*, 313 (1977)) will be done to solve this interesting problem. Nevertheless, our results (Figs. 5 and 6) seem to indicate that electronic factors play a predominant role for normal aldehyde selectivities with aminophosphines as ligands.