Journal of Catalysis **199,** 302–308 (2001)
doi:10.1006/jcat.2000.3159, available online at http://www.idealibrary.com on IDEAL®

o-Alkyl-Substituted Triphenyl Phosphines: Activity and Regioselectivity in Rhodium-Catalysed Propene Hydroformylation

H. K. Reinius,*,[1] P. Suomalainen,† H. Riihimäki,‡ E. Karvinen,§ J. Pursiainen,‡ and A. O. I. Krause*

*Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland; †Department of Chemistry, University of Joensuu, FIN-80101 Joensuu, Finland; ‡Department of Chemistry, University of Oulu, Linnanmaa, FIN-90570 Oulu, Finland; and §Neste Chemicals Oy, Technology Centre, P.O. Box 310, FIN-06101 Porvoo, Finland

Received September 25, 2000; revised December 18, 2000; accepted December 18, 2000; published online March 21, 2001

Hydroformylation of propene is the most important hydroformylation process on the industrial scale. Typically, the aim has been the regioselective production of the linear product *n*-butanal. Recently, interest in selective formation of the branched aldehyde, isobutanal, has increased due to its use in the production of polyols, such as neopentyl glycol (2,2-dimethyl-1,3-propanediol). Study was made of the effect of *o*-alkyl-substituted triphenylphosphine ligands on the activity and regioselectivity in rhodium-catalysed propene hydroformylation. In addition, the effect of the process conditions on the activity and regioselectivity was investigated by varying the ligand-to-rhodium ratio (0–40), temperature (353–403 K), and deactivation for some of the ligands. The results suggest that *o*-alkyl-substituted triphenylphosphine ligands enhance the selectivity to isobutanal. However, the activity decreases at the same time. A correlation was found between the ^{31}P-NMR shifts of the ligands and the regioselectivity and activity: as the shift decreases, the regioselectivity to isobutanal increases and the activity decreases. Changes in the process conditions had an effect similar to that in the reaction modified with triphenylphosphine.

Key Words: **hydroformylation; phosphine ligands; isobutanal; effect of process parameters.**

INTRODUCTION

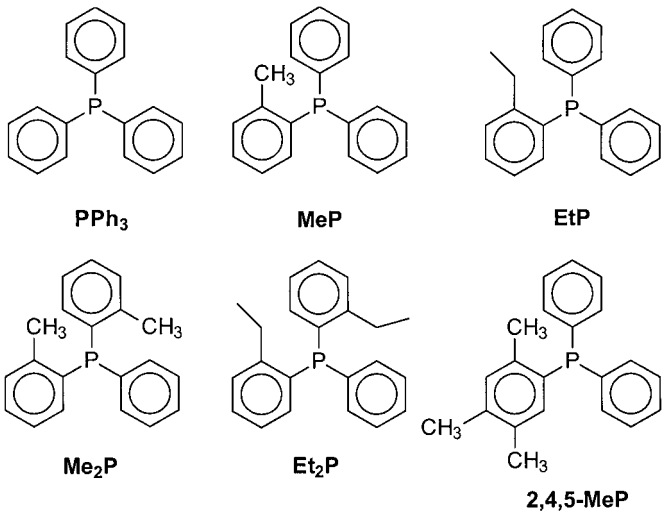
Hydroformylation of propene yielding *n*-butanal and isobutanal is the most important hydroformylation process on the industrial scale, representing approximately 75% of the world consumption of oxo chemicals (1, 2). Propene is also an ideal test substrate for hydroformylation because no double-bond isomerisation can occur and it contains no other functional groups to distort the regioselectivity. Indeed, hydroformylation of propene has been widely studied: as a homogeneous process with phosphine and phosphite ligand modified catalysts (3, 4) even in supercritical carbon dioxide (5), as a heterogeneous process with rhodium dispersed to various carriers (6, 7), and as a two-phase process with a water-soluble ligand modified catalyst (8, 9). The aim in all these approaches has been regioselective production of the linear product *n*-butanal. Recently, interest in selective formation of the branched aldehyde isobutanal has increased due to its use in the production of polyols, such as neopentyl glycol (2,2-dimethyl-1,3-propanediol). Indeed, the production of isobutanal already represents 9% of the world consumption of oxo chemicals and it is expected to increase steadily in the near future (2).

The most effective way to influence the selectivity of the rhodium-catalysed reaction is through a modifying ligand because the stereoelectronic factors of the transition state determine the rate and selectivity of the reaction. Various types of phosphine ligands have been studied since Wilkinson (10) introduced the first rhodium phosphine catalyst. Several studies (11) have been done on the mechanism by which the ligands control the selectivity in hydroformylation. Perhaps the most successful example is the natural biting angle concept of Casey *et al.* (12), according to which the regioselectivity obtained with a diphosphine-modified rhodium catalyst is correlated with the geometry of the ligand. However, a satisfactory explanation of the catalytic results in terms of the properties of the ligands has yet to be provided (11, 13).

Regioselective control to a branched product has been reported in the hydroformylation of 3,3,3-trifluoropropene (14), but in this approach the other end of the alkene was substituted with fluoro groups, changing the polarity of propene, and thus the tailoring of the ligand is easier. In our recent study (15) of propene hydroformylation with triphenylphosphine-type ligands modified with different heteroatom groups ($-SCH_3$, $-N(CH_3)_2$, $-OCH_3$, or $-CF_3$) in the ortho or para position of the phenyl ring, the aim was to enhance the regioselectivity to the branched form, isobutanal. The heteroatom modification did not, however, affect the selectivity, but decreased the conversion markedly, and in some cases the hydroformylation reaction was totally hindered.

[1] To whom correspondence should be addressed. Fax:+358 9 451 2622. E-mail: Heidi.Reinius@hut.fi.

0021-9517/01 $35.00



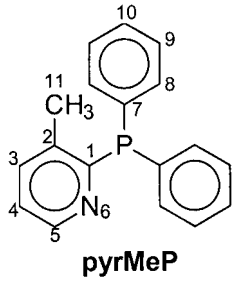
SCHEME 1. Schematic structures of the ligands.

Ancillotti *et al.* (16) showed that, in the hydroformylation of 2-butene with $PtCl_2$(cod)/$SnCl_2$ catalyst, the addition of the *o*-methylphenyldiphenylphosphine (MeP) ligand enhanced the selectivity to the branched aldehyde. To determine whether *o*-alkyl-substituted triphenylphosphine ligands also enhance the selectivity to a branched aldehyde in rhodium-catalysed propene hydroformylation, we synthesised a set of closely related *o*-alkyl-substituted ligands (Scheme 1) differing in their steric properties. In addition, to be able to distinguish the role of the process conditions in the activity and regioselectivity for some of the ligands, we studied the effect of the ligand-to-rhodium ratio, temperature, and deactivation.

EXPERIMENTAL

Ligands

Synthesis and characterisation. The commercial ligand used as reference in the experiments was triphenylphosphine (PPh_3, Fluka, ~99%). All alkyl-substituted ligands (Scheme 1, (17); Scheme 2, (18)) were prepared according to literature methods. NMR spectra were recorded on Bruker AM200 and DPX400 spectrometers at room temperature in $CDCl_3$. ^{1}H NMR: reference $SiMe_4$. $^{13}C\{^1H\}$ NMR: $CDCl_3$ was set to 77.0 ppm. $^{31}P\{^1H\}$ NMR: external standard was 85% H_3PO_4. Exact mass peaks were determined on a Micromass LCT, ESI+.



SCHEME 2. Schematic structure of the pyrMeP ligand; numbering corresponds to the NMR data.

To the best of our knowlegde, a detailed characterisation of (6-methyl-2-pyridyl)diphenylphosphane (pyrMeP, Scheme 2) has never been published before and therefore it is included here. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3 H, H^{11}), 7.11 (dd, $^3J_{H-H} = 6.6$ Hz, $^4J_{H-P} = 4.8$ Hz, 1 H, H^3), 7.33 (d, $^3J_{H-H} = 1.6$ Hz, 4 H, H^8), 7.31–7.35 (m, 6 H, H^9, H^{10}), 7.35 (t, $^3J_{H-H} = 3.8$ Hz, 1 H, H^4), 8.48 (dd, $^3J_{H-H} = 4.6$ Hz, $^4J_{H-P} = 1.4$ Hz, 1 H, H^5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.02 (d, $^3J_{C-P} = 18.2$ Hz, 1 C, C^{11}), 122.55 (s, 1 C, C^4), 128.30 (d, $^3J_{C-P} = 7.4$ Hz, 4 C, C^9), 128.73 (s, 2 C, C^{10}), 134.28 (d, $^2J_{C-P} = 19.6$ Hz, 4 C, C^8), 135.85 (d, $^1J_{C-P} = 7.4$ Hz, 2 C, C^7), 136.85 (d, $^3J_{C-P} = 4.1$ Hz, 1 C, C^3), 138.53 (d, $^2J_{C-P} = 3.4$ Hz, 1 C, C^2), 147.83 (d, $^3J_{C-P} = 3.4$ Hz, 1 C, C^5), 160.50 (d, $^1J_{C-P} = 6.1$ Hz, 1 C, C^1). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ −6.3. TOF MS ES + calcd. for $(M+H)^+$ ($C_{18}H_{16}NP$): 278.1099. Found: 278.1063.

Cone angle (θ) calculations. Gaussian 94 (19) and Sybyl (20) programs were used in modelling of the ligands. For geometric optimisations at the Hartree–Fock level, the 3-21G* basis set was used. Estimation of steric size of the prepared phosphine ligands was estimated by Tolman's cone angle method. Cone angle determinations were done with the metal(dummy atom)–phosphorus distance 2.28 Å and the van der Waals radii of hydrogen 1.2 Å.

Hydroformylation

Propene hydroformylation experiments were carried out in a 250-ml autoclave (Berghof) equipped with a sampling system. The experiments were done in semibatch mode so that synthesis gas pressure was kept constant during the experiment. The rhodium precursor was $Rh(NO_3)_3$ (Fluka). In a typical experiment the autoclave was charged with the rhodium precursor (0.02 mmol calculated as rhodium), acetone (310 mmol, Merck, >99%), internal standards decane (7 mmol, Fluka, >98%) and hexane (12 mmol, Riedel de Häen, >99%), and the respective phosphine. If not otherwise stated, the ligand-to-rhodium ratio was 10 : 1 on a molar basis. The system was flushed with nitrogen, pressurised with propene (0.1 or 0.2 MPa, Aga, 99.8%), heated to the reaction temperature (353–403 K) with continuous stirring, and then pressurised to the reaction pressure (1 MPa) with a 1 : 1 molar ratio of H_2 and CO (MG, 99.997%). At least nine samples were taken for analysis in each experiment: one of the fresh reaction mixture, one immediately after pressurising with H_2 and CO, which was considered as the starting point of the reaction, six during the experiment, and one after the reaction.

A disposable inner Teflon reactor was used to avoid the accumulation of rhodium on the reactor walls. Furthermore, the purity of the system was checked with blank runs

before each experiment. The products were analysed with a Hewlett Packard 5890 GC equipped with a capillary column (HP-1, 1.0 μm $\times$ 0.32 mm $\times$ 60 m) and a flame-ionisation detector. Products were quantified by the internal standard method. In addition, the aldehydes were identified by GC-MS analysis.

In the deactivation experiments, the rhodium precursor, phosphine, acetone, and internal standards (hexane and decane) were charged into the autoclave. The system was flushed with nitrogen, heated to 373 K, and pressurised with H_2 and CO to 1 MPa. The reactor was left overnight (12 h) under synthesis gas pressure at 373 K. It was then rapidly cooled with ice, the pressure released, propene fed, and the standard hydroformylation test performed.

Conversion, selectivity, and i/n ratio were calculated on a molar basis. Conversion was calculated with respect to propene and selectivity with respect to aldehydes. The i/n ratio of the aldehydes was defined as the amount of branched product divided by the amount of linear product. The formation of propane was not detected in any of the experiments.

The initial rates of aldehyde formation were calculated according to the equation

$$r_{\text{initial,ald.}} = \frac{n_{\text{tot}}}{n_{\text{Rh}}} \frac{dX}{dt} \qquad [1]$$

in which n_{tot} is the amount of propene in the beginning of the experiment and dX/dt is calculated by fitting a polynomial function to a curve presenting propene conversion as a function of time and then calculating the derivative of the polynomial function at time zero.

Propene, hydrogen, and carbon monoxide concentrations in the liquid phase during the reaction were estimated by calculating the phase equilibrium of the reaction with Soave's modification of the Redlich–Kwong equation of state (21).

RESULTS

Effect of Alkyl-Substituted Ligand

When unmodified rhodium is used as a catalyst in propene hydroformylation, *n*-butanal and isobutanal are formed in a roughly equal amount. Typically, if a ligand is added to the reaction mixture, the regioselectivity of the reaction changes to favour *n*-butanal. Table 1 shows the presence of this effect when PPh_3, MeP, EtP, or 2,4,5-MeP is introduced to the mixture. However, with MeP, EtP, and 2,4,5-MeP ligands the decrease in the selectivity to isobutanal is less drastic when compared to that with PPh_3. Interestingly, with Me_2P and Et_2P the selectivity is even slightly on the side of isobutanal. Figure 1 shows the regioselectivity as a function of time. The i/n ratio stayed more or less constant with the ligands MeP, EtP, and 2,4,5-MeP. The downward slope and thereafter rapid increase in the i/n ratio with ligands Me_2P and Et_2P most probably reflect analytical discrepancies at the beginning of the reaction due to the small amount of products in these experiments (less than 3% propene conversion).

TABLE 1

Results of Propene Hydroformylation with *o*-Alkyl-Substituted Triphenylphosphines[a]

Ligand	Cone angle, θ	^{31}P-NMR shift	Initial rate,[b] mol/(mol$_{\text{Rh}}$ s)	$S_{\text{isobutanal}}$, %	$S_{n\text{-butanal}}$, %
PPh_3	149°	−3.30	53	36	64
MeP	151°	−10.7	30	43	57
EtP	169°	−14.2	20	46	54
Me_2P	158°	−19.0	3	53	47
Et_2P	194°	−23.5	2	51	49
2,4,5-MeP	159°	−11.8	20	45	55
No ligand	n.a.	n.a.	1	50	50

[a] 373 K, $p_{\text{total}} = 1$ MPa, propene/Rh = 2250, L/Rh = 10.
[b] Initial rate for aldehyde formation.

The initial aldehyde formation rates (Table 1) were considerably lower with all the *o*-alkyl-substituted ligands (2–30 mol mol$_{\text{Rh}}^{-1}$ s^{-1}) than with the PPh_3 ligand (53 mol mol$_{\text{Rh}}^{-1}$ s^{-1}). In fact, the initial rates of aldehyde formation with Me_2P and Et_2P were so low (3 and 2 mol mol$_{\text{Rh}}^{-1}$ s^{-1}, respectively) that we abandoned the idea of testing the effect of process conditions with these two ligands.

Effect of Process Conditions

On the industrial scale, an excess of ligand is required to ensure the activity of rhodium in the long run. However, the excess of ligand also decreases the activity because of stabilisation of the species that must dissociate the ligands during the catalytic cycle (22). The effect of an excess

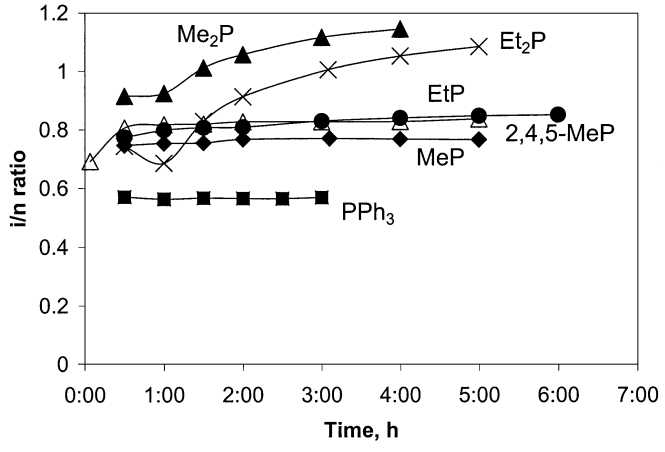


FIG. 1. Regioselectivity of propene hydroformylation as a function of time with *o*-alkyl-substituted triphenylphosphines (373 K, $p_{\text{total}} = 1$ MPa, propene/Rh = 2250, L/Rh = 10).

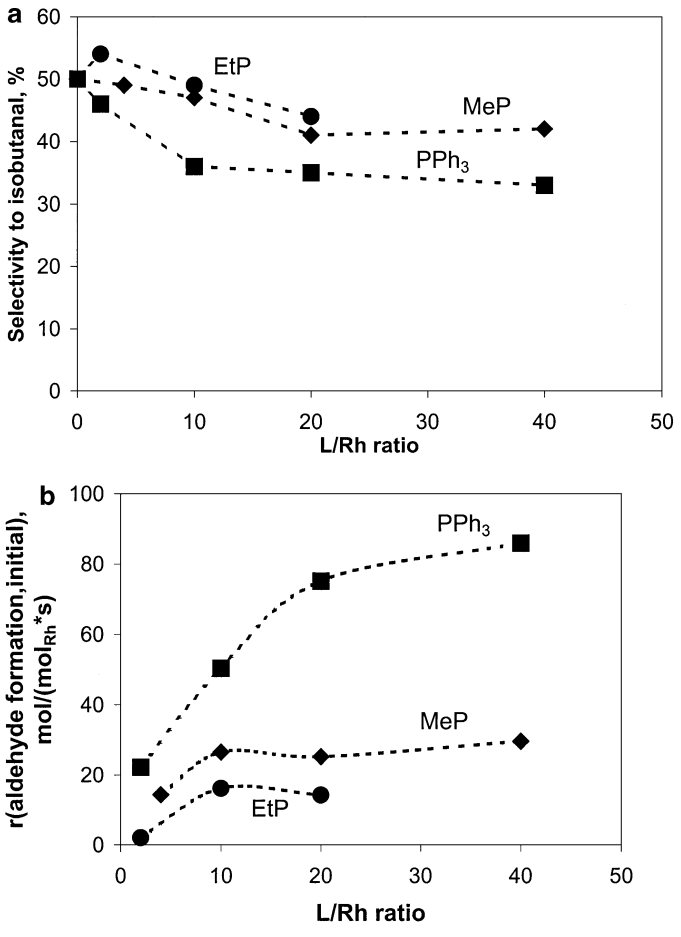


FIG. 2. Effect of L/Rh ratio on (a) selectivity to isobutanal and (b) initial aldehyde formation rate with MeP, EtP, and PPh_3 ligand modified reactions (373 K, $p_{total} = 1$ MPa, propene/Rh = 3200).

of the ligand on the rate and regioselectivity depends on the type of phosphorus ligand (23). Figure 2 shows the effect of the L/Rh ratio on the selectivity to isobutanal and on the initial rate of aldehyde formation when the catalyst was modified with MeP, EtP, and PPh_3. With all ligands the selectivity to isobutanal decreases as the L/Rh ratio increases, but the differences in selectivity between the ligands remain. In the MeP-modified reaction, however, it appears that the selectivity would stabilise at L/Rh ratios greater than 20. The effect of the L/Rh ratio on the initial aldehyde formation rate is similar for the three ligands; at low L/Rh ratios the rate increases with L/Rh and at higher L/Rh ratios it stabilises or even decreases slightly. The induction period effect cannot totally be ruled out, especially at low L/Rh ratios, even though the product distribution stayed constant during the whole experiment, indicating that the active complex stays unaltered during the run.

In the case of α-alkenes the selectivity to the branched form is increased with temperature (22). As Fig. 3 shows, the selectivity to isobutanal is enhanced with both MeP- and PPh_3-modified catalysts and the difference in the selectivity of the ligands is preserved at all temperatures tested. Even though, in general, an increase in temperature should mean an increase in the reaction rate, above 373 K the initial aldehyde formation rates started to drop. Possible cause seems to be the vaporisation of the reactants at high temperature because the phase equilibrium calculations show ($p_{total} = 1$ MPa) that at 403 K the liquid phase contains 30% less propene and 17% less H_2 and CO relative to the concentrations at 373 K. The possible decomposition of the active complex caused by the higher temperature could be ruled out because the initial aldehyde formation rate with PPh_3 at 423 K under higher synthesis gas pressure (6 MPa) was almost 3 times higher (320 mol mol_{Rh}^{-1} s^{-1}) than that at 373 K (120 mol mol_{Rh}^{-1} s^{-1}).

Deactivating Treatment

Some ligand-modified rhodium catalysts are rather easily deactivated at elevated temperatures (24). To be able to compare the stabilising effect and deactivation

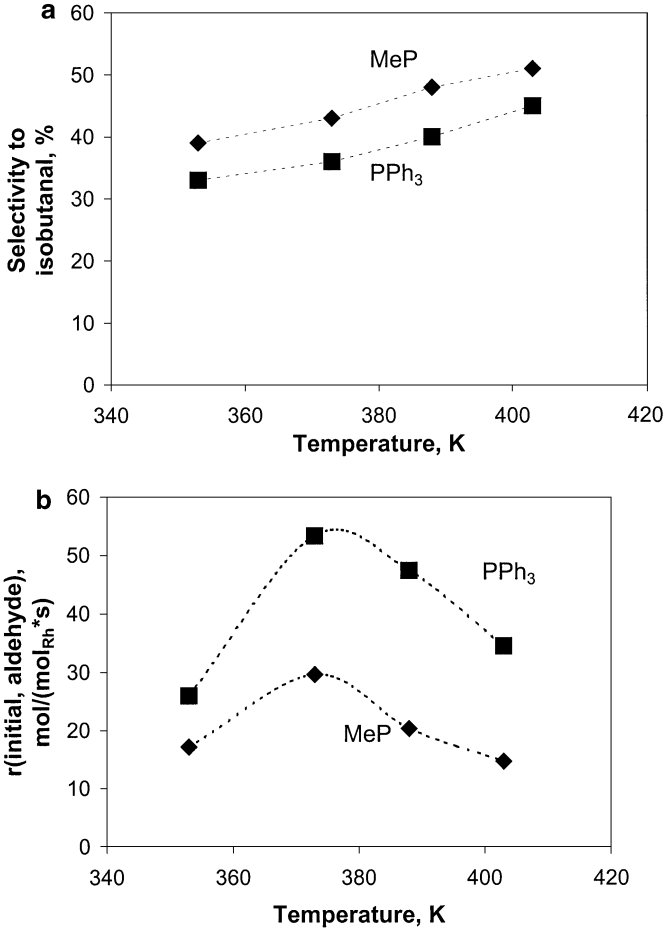


FIG. 3. Effect of temperature on (a) selectivity to isobutanal and (b) initial aldehyde formation rate with MeP and PPh_3 ligand modified reactions ($p_{total} = 1$ MPa, propene/Rh = 2250, L/Rh = 10).

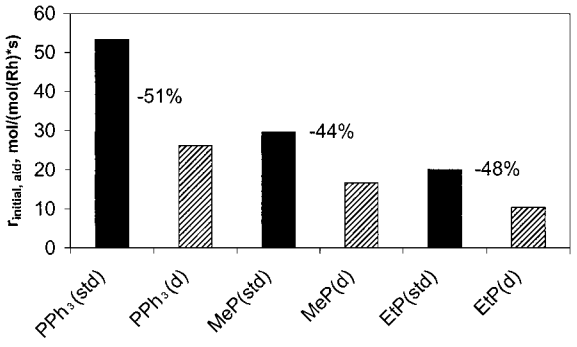


FIG. 4. Effect of deactivating pretreatment on initial aldehyde formation rate in PPh_3-, MeP-, and EtP-modified reactions (■ standard test; ▨ tests with deactivating pretreatment, 373 K, $p_{total} = 1$ MPa, propene/Rh = 2250, L/Rh = 10).

pattern of the MeP and EtP ligand modified reactions with those of PPh_3, we compared the initial aldehyde formation rates obtained from the standard experiments (373 K, $p = 1$ MPa, L/Rh = 10) with those obtained from the experiments where a deactivating pretreatment was done. As Fig. 4 shows, the deactivation pattern is more or less the same for the three ligands—the initial activity drops to about half. However, MeP and EtP performed slightly better than PPh_3 (decrease 44, 48, and 51%, respectively). In the deactivation tests the regioselectivities remain unaltered when compared to the respective non-deactivated tests with all three ligands.

DISCUSSION

Ancillotti *et al.* (16) found that, in the hydroformylation of 2-butene with a platinum catalyst modified with MeP or tris(*o*-methylphenyl)phosphine ligand, the selectivity to the branched form increased while the activity decreased relative to the PPh_3-modified catalyst. Our studies show, in a similar way, that *o*-alkyl-substituted triphenylphosphines applied in the rhodium-catalysed hydroformylation of propene enhance the selectivity to isobutanal. The regioselectivity of the hydroformylation reaction is determined by the stereoelectronic factors of the catalytically active complex. Electronically, the *o*-alkyl-substituted ligands do not differ much from PPh_3 because the modification is obtained through a nonpolar alkyl group. This suggests that the difference in the selectivity could be due to the steric stress created by the alkyl group. However, the cone angles (Table 1), which are commonly used to measure the steric stress created by the ligand, do not correlate with the regioselectivity.

The electronegativity of the substituents on phosphorus and the angles between the substituents are the two most important variables determining ^{31}P-NMR shifts, and hence the shift reflects the stereoelectronic state of the phosphorus atom (25). Indeed, there are clear correlations between the ^{31}P-NMR shifts of these closely related ligands and the regioselectivity and activity of the reaction (Fig. 5). As the shift decreases, the selectivity to isobutanal increases and the activity decreases. Apparently, then, the stereoelectronic factors of the catalytically active complex correlate with the regioselectivity and activity. In their unpublished studies on the complex formation of these *o*-alkyl-substituted ligands (Scheme 1) with $Rh_2(\mu\text{-}Cl)_2(CO)_4$, Suomalainen *et al.* (17) found that two *o*-alkyl-substituted ligands coordinate in a monodentate fashion to rhodium, in the manner the PPh_3 ligand does. However, an interesting finding was that the *o*-alkyl groups in the complex are rotated so that they are facing each other and, thus, blocking one side of the complex. Furthermore, the crystal structures of the complexes showed that the *o*-alkyl substituents are very close to the metal centre. In such structures the alkyl groups are in close contact with the coordinating reactants during the catalytic cycle and this would appear to direct the insertion of propene as well as the subsequent hydrogen insertion so that the formation of isobutanal is as favoured as the formation of *n*-butanal.

As shown in Fig. 5, the decrease in activity is more drastic than the increase in the selectivity as a function of ^{31}P NMR shift. Before the *o*-alkyl-substituted ligands can be incorporated in industrially viable catalysts, the activity will have to be increased. Since the ^{31}P NMR shift reflects both the electronic and steric properties of the ligand, the question arises whether the activity is lower because the alkyl groups block one side of the complex or because of the electronic state of the phosphorus atom. We suspected that the decrease in activity with the *o*-alkyl-substituted ligands was due to the steric effect of the alkyl groups rather than the low activity of the rhodium centre. To test this hypothesis, we synthesised and tested in propene hydroformylation a ligand, pyrMeP (Scheme 2), closely resembling MeP in structure (methyl group in ortho position;

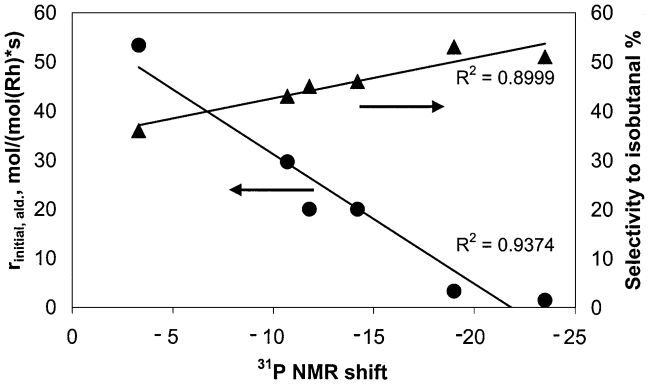


FIG. 5. Correlation between the ^{31}P NMR shifts of the ligands and the regioselectivity and activity of propene hydroformylation.

cone angle 151°, the same as in MeP), but having a higher ^{31}P-NMR shift (−6.3 vs −10.7). Indeed, the regioselectivity achieved with pyrMeP ($S_{isobutanal}$: 42%) was similar to that achieved with MeP ($S_{isobutanal}$: 43%), but the initial aldehyde formation activity was even lower than that of MeP (20 and 30 mol mol_{Rh}^{-1} s^{-1}, respectively). Usually, the reaction rates obtained with pyridyl-modified compounds are higher than the rates of their phenyl analogues, which has been attributed to the electron-withdrawing capasity of the pyridyl ring causing the CO molecule to be less strongly bonded to the rhodium centre and thus facilitating alkene coordination (26). However, in the case of *o*-pyridyl groups the reaction rates have been reported (27, 28) to be lower compared to their phenyl analogues even though the electron-withdrawing capasity of the ortho nitrogen should be stronger than that of meta or para nitrogen. Thus, it seems that ligands containing 3- or 4-pyridyls and an *o*-alkyl group would have been a better alternative than the tested 2-pyridyl (pyrMeP) where the ortho nitrogen (27) is not as inert as the para or meta nitrogens.

Changes in the process conditions for the *o*-alkyl-substituted ligands induced changes in regioselectivity similar to those found in the PPh_3-modified reaction. Although the ligand-to-rhodium ratio has an influence on the regioselectivity, as also shown by Diéguez *et al.* (13), within the range of L/Rh ratios we tested the selectivities of the MeP- and EtP-modified catalysts to isobutanal were constantly higher than the selectivity of PPh_3. The deactivation pattern of the MeP and EtP ligands was similar to that of PPh_3: the activity decreased but the regioselectivity remained unaltered. Apparently, the *o*-alkyl-substituted ligands deactivate by the same mechanism as proposed (11, 29, 30) for PPh_3. To summarise, it appears that even though the process conditions have an effect on the regioselectivity, the conditions selected for comparison are not the cause of the higher selectivity to isobutanal with the MeP- and EtP-modified catalysts when compared to those with PPh_3.

CONCLUSIONS

We have shown that, in the rhodium-catalysed hydroformylation of propene, *o*-alkyl-substituted triphenylphosphine ligands enhance the selectivity to isobutanal. Unfortunately, the activity decreases drastically as the selectivity increases. A correlation was found between the ^{31}P-NMR shifts of these closely related ligands and the regioselectivity and activity: as the shift decreases the regioselectivity to isobutanal increases, while the activity decreases. The regioselectivity and activity seem to be controlled through the steric properties of the active complex in which one side of the complex is blocked by the alkyl substituents. The behaviour of the *o*-alkyl-substituted ligands closely resembles that of PPh_3: changes in the process conditions (L/Rh ratio, temperature, and deactivation) induce a pattern of changes similar to those induced by PPh_3.

ACKNOWLEDGMENTS

The authors wish to thank Ms. Johanna Suutari for performing part of the hydroformylation experiments. The funding from Neste Chemicals Oy and the National Technology Agency of Finland (Tekes) is gratefully acknowledged.

REFERENCES

1. Beller, M., Cornils, B., Frohning, C. D., and Kohlpaintner, C. W., *J. Mol. Catal. A: Chem.* **104**, 17 (1995).
2. Bizzari, S. N., Fenlon, S., and Ishikawa-Yamaki, M., "CEH, SRI International," May 1999.
3. Hjortkjaer, J., and Toromanova-Petrova, P., *J. Mol. Catal.* **50**, 203 (1989).
4. Trzeciak, A. M., and Ziólkowski, J. J., *J. Mol. Catal.* **34**, 213 (1986).
5. Guo, Y., and Akgerman, A., *Ind. Eng. Chem. Res.* **36**(11), 4581 (1997).
6. Srinivas, G., and Chuang, S. C., *J. Catal.* **144**, 131 (1993).
7. Rode, E. J., Davis, M. E., and Hanson, B. E., *J. Catal.* **96,** 574 (1985).
8. Bahrmann, H., Bach, H., Frohning, C. D., Kleiner, H. J., Lappe, P., Peters, D., Regnat, D., and Herrmann, W. A., *J. Mol. Catal. A: Chem.* **116**, 49 (1997).
9. Schroeder, M. G., Kamer, P. C. J., and van Leeuwen, P. W. N. M., *J. Mol. Catal. A: Chem.* **134**, 243 (1998).
10. Wilkinson, G., *J. Chem. Soc. A* 3133 (1968).
11. Frohning, C. D., and Kohlpaintner, C. W., *in* "Applied Homogeneous Catalysis with Organometallic Compounds" (B. Cornils and W. A. Herrmann, Eds.), p. 34. VCH, Weinheim, 1996.
12. Casey, C. P., Whiteker, G. T., Melville, M. G., Petrovich, L. M., Gavney, J. A. Jr., and Powell, D. R., *J. Am. Chem. Soc.* **114**, 5535 (1992).
13. Diéguez, M., Pereira, M. M., Masdeu-Bultó, A. M., Claver, C., and Bayón, J. C., *J. Mol. Catal. A: Chem.* **143**, 111 (1999).
14. Fuchikami, T., and Ojiama, I., *J. Am. Chem. Soc.* **104**, 3527 (1982).
15. Suomalainen, P., Reinius, H. K., Riihimäki, H., Laitinen, R. H., Jääskeläinen, S., Haukka, M., Pursiainen, J. T., Pakkanen, T. A., and Krause, A. O. I., *J. Mol. Catal. A: Chem.*, in press.
16. Ancillotti, F., Lamiand, M., and Marchionna, M., *J. Mol. Catal.* **63**, 15 (1990).
17. Suomalainen, P., Riihimäki, H., Jääskeläinen, S., Haukka, M., Pursiainen, J., and Pakkanen, T. A., to be published.
18. Drent, E. I. T., GB Patent 2 240 545 A, 1991.
19. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al- Lahman, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzales, C., and Pople, J. A., "Gaussian 94." Gaussian, Inc., Pittsburgh, PA, 1995.
20. "Sybyl 6.03." Tripos Associates, St. Louis, MO.
21. Reid, R. C., Prausnitz, J. M., and Poling, B. E., "The Properties of Gases and Liquids," McGraw-Hill, New York, 1988.
22. Falbe, J., "New Synthesis with Carbon Monoxide." Springer-Verlag, New York, 1980.

23. Bergounhou, G., Neibecker, D., and Réau, R., *J. Chem. Soc., Chem. Commun*. 1370 (1988).
24. Reinius, H., and Krause, A. O. I., *J. Mol. Catal. A: Chem*. **158**(2), 499 (2000).
25. Tolman, C. A., *Chem. Rev.* 313 (1976).
26. Buhling, A., Elgersma, J. W., Nkrumah, S., Kamer, P. C. J., and van Leeuwen, P. W. N. M., *J. Chem. Soc.* Dalton Trans. 2143 (1996).
27. Buhling, A., Kamer, P. C. J., and van Leeuwen, P. W. N. M., *J. Mol. Catal. A: Chem*. **98**(2), 69 (1995).
28. Reinius, H. K., Laitinen, R. H., Krause, A. O. I., and Pursiainen, J. T., *Stud. Surf. Sci. Catal.* **130**, 551 (2000).
29. Abatjoglou, A. G., Billig, E., and Bryant, D. R., *Organometallics* **3**, 923 (1984).
30. Moser, W. R., Papile, C. J., and Weininger, S. J., *J. Mol. Catal.* **41**, 293 (1987).