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A Comparative Study of the 1-Hexene Hydroformylation Either Under Syngas Conditions or with Paraformaldehyde Catalyzed by Rhodium/Diphosphine Systems

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Abstract In order to carry out a comparison, the hydroformylation of 1-hexene to their corresponding aldehydes (heptanal and 2-methyl-hexanal) was studied both under syngas conditions and with paraformaldehyde using the catalytic rhodium/diphosphine precatalysts; the catalytic systems were formed in situ by the addition of one or two equivalents of the corresponding diphosphine, $Ph_2P(CH_2)_n PPh_2$, $n = 2$ (dppe), 3 (dppp) and 4 (dppb), to the carbonyl complex $Rh(acac)(CO)_2$. For the hydroformylation reactions under syngas conditions, the more active systems were the ones containing one equivalent of the diphosphine, which produce trigonal bipyramidal species like $RhH(CO)_2$(diphos). The activity and selectivity of these systems strongly depend on the bite angle of the ligand: when the bite angle increases both parameters are higher (dppb > dppp > dppe). Contrary to these results, for the reaction with paraformaldehyde, the systems containing two equivalents of the diphosphine ligand, which produce the cationic square planar species $[Rh(diphos)_2]^+$, were more active than those containing one equivalent; the reaction rate decreases with the enlargement of the carbon chain of the bridge between the two phosphorous atoms of the diphosphine (dppe > dppp > dppb). These results may be explained by a higher steric effect on the metal center, which probably produces a decreasing of the rate of the CH_2O oxidative addition reactions. For both reactions, these effects were explained through DFT calculations of the corresponding resting states.

Keywords Rhodium · Diphosphines · Hydroformylation · Syngas · Paraformaldehyde · 1-Hexene

1 Introduction

The olefin hydroformylation under syngas conditions (OXO Process) is a well known synthetic tool for a wide range of organic molecules of high commercial value, and it is also one of the largest scale applications of homogeneous catalysis in industry, being $RhH(CO)(PPh_3)_3$ the more used precatalyst [1–5]. This reaction has been also studied extensively by using rhodium-*diphosphine* systems as precatalysts; a comprehensive review dealing with recent advances in homogeneous hydroformylation of olefins with rhodium complexes containing diphosphine ligands has been published by Van Leeween and Claver [6]. Another route to carry out the hydroformylation of olefins is by the use of paraformaldehyde (CH_2O) instead of syngas, although this reaction has been poorly investigated [7–12]. Recently, some of us reported the reaction of a series of olefins with CH_2O to their corresponding aldehydes, under argon atmosphere in the presence of rhodium-phosphine catalytic systems, and found that the one formed by the addition of two equivalents of 1,2-bis(diphenylphosphino)ethane (dppe) to the complex $Rh(acac)(CO)_2$ was the most active precatalyst, obtaining an linear/branched ratio (l/b) close to 2; the active species was considered

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to be $[Rh(dppe)_2]^+$ [13]. In the present work, we present a comparative study of the hydroformylation of 1-hexene under syngas conditions and with paraformaldehyde catalyzed by $Rh(acac)(CO)_2$/diphosphine systems, including ab-initio DFT calculations of the assumed resting state of both processes.

2 Experimental

All manipulations were conducted with rigorous exclusion of air using a vacuum line, an argon-filled Schlenck line and/or an argon-filled glovebox. Complex $Rh(acac)(CO)_2$ was prepared by a published procedure [14]. 1-Hexene and solvents were purified by known procedures and distilled at reduced pressure before using.

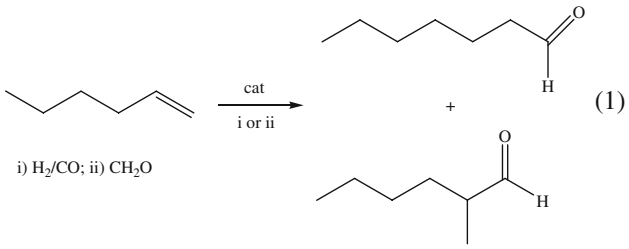
The catalytic reactions were carried out in a high pressure reactor, supplied by Parr Instrument, which was provided with arrangements for sampling of liquid contents, automatic temperature and pressure control and variable stirrer speed. In a typical experiment, a solution of the precatalyst, 1-hexene, paraformaldehyde (if it is the case), the internal standard (1.0 mL) and the solvent (total volume 30 mL) was placed in the reactor. The solution was carefully deoxygenated with argon, charged with 3 bars of a 1:1 mixture of CO and H_2 or argon for hydroformylation under syngas conditions or with formaldehyde, respectively, and the reactor heated to the desired temperature. The reaction was followed by taking liquid samples at regular intervals of time, which were analyzed by using gas chromatography. Each reaction was repeated at least twice in order to ensure reproducibility of the results. Gas chromatographic analyses were performed in a 3300 Series VARIAN instrument fitted with a flame ionization detector (FID) and a 2 m 20% SP-2100 on a 0.1% carbowax 100/120 Supelcoport column, using N_2 as carrier gas and n-heptane (for hydroformylation of 1-hexene) or cycloheptane (for hydroformylation with paraformaldehyde) as internal standard. The results were quantified with a VARIAN 4400 microcomputer.

All the reactions were carried out at low conversions (close to 10%) in order to determine their initial rates [15]. The data of the hydroformylation of 1-hexene were plotted as molar concentration of the corresponding products (heptanal and 2-methylhexanal) versus time yielding straight lines, which were fitted by conventional linear regression programs; initial rates of the reaction were obtained from the corresponding slopes.

The optimized energy calculations for $RhH(CO)_2$(diphos) and $[Rh(diphos)_2]^+$ complexes were carried out using simplified $H_2P(CH_2)_nPH_2$ diphosphine analogues in order to have a better calculation level. These calculations were performed with the Gaussian 98 computational package by using the B3LYP [16–18] hybrid method of density functional theory (DFT); the optimizations were performed with the 6-31+G(d, p) basis sets [19–22].

3 Results and Discussion

In order to carry out a comparison, the hydroformylation of 1-hexene to their corresponding aldehydes (heptanal and 2-methyl-hexanal) was studied either under syngas condition or with paraformaldehyde (Eq. 1) by using Rh/diphosphine precatalyst. The catalytic systems were formed in situ by the addition of one or two equivalents of the corresponding diphosphine to the dicarbonyl rhodium complex $Rh(acac)(CO)_2$, where diphosphine = 1,2-bis(diphenylphosphino) ethane [dppe, $Ph_2P(CH_2)_2PPh_2$], 1,3-bis(diphenylphosphino) propane [dppp, $Ph_2P(CH_2)_3PPh_2$] and 1,4-bis(diphenylphosphino)butane [dppb, $Ph_2P(CH_2)_4PPh_2$].



(1)

For the hydroformylation reactions under syngas conditions, the systems containing one equivalent of the diphosphine ligand produce the trigonal bipyramidal species $RhH(CO)_2$(diphos), which were more active than those containing two equivalents, as reported before by some of us for the dppe system [23]; the results are showed in Table 1. As it can be observed, both the reaction rate and the selectivity, measured as the linear to branch ratio (l/b), increase with the enlargement of the carbon chain of the bridge between the two phosphorous atoms of the diphosphine (dppb > dppp > dppe) which may be explained by the bite angle of the corresponding diphosphine. The trigonal bipyramidal complexes $RhH(CO)_2$(diphos) have four isomers, two in which the phosphorus

Table 1 Hydroformylation of 1-hexene under syngas conditions catalyzed by the $RhH(CO)_2$(diphos) systems

Diphosphine	Bite angle (°)	10^5 r_i (Ms^{-1})	TOF (h^{-1})	l/b
dppe	85	(0.94 ± 0.09)	20 ± 2	2.9
dppp	91	(4.43 ± 0.21)	94 ± 4	3.1
dppb	98	(6.23 ± 0.28)	132 ± 6	3.7

Conditions: [Rh] = 1.7 mM, [1-hexene] = 0.5 M, T = 80 °C, $p(H_2/CO)$ = 3 atm, solvent = toluene. r_i = initial rate; TOF = turnover frequency; l/b = linear to branched ratio

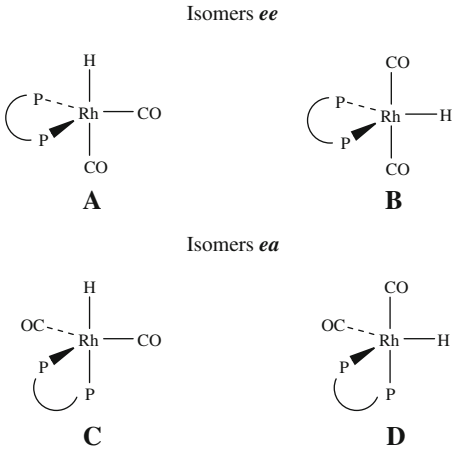
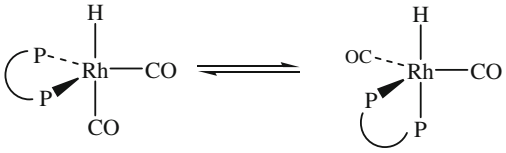


Fig. 1 Possible isomers of complexes $RhH(CO)_2$(diphos) [diphos = $Ph_2P(CH_2)_nPPh_2$, $n = 2$, 3 and 4]

atoms are in *equatorial* plane (*ee*) and two where one phosphorus atom is in the *axial* position and the other is in the *equatorial* one (*ae*), as showed in Fig. 1.

In order to determine the stability of these four isomers, theoretical DFT-calculations were performed for each Rh-diphosphine complex with the $RhH(CO)[H_2P(CH_2)_nPH_2]$ models ($n = 2$, 3 or 4) using the STO/6-31+G(d, p) extended basis. In Table 2 are listed the calculated energies of these four isomers for each complex. As it may be observed, for the two *ee* isomers, the *A* configurations, which present the hydride ligand in the *axial* site, were the most stable ones; van Leeuwen et al. [24] reported X-ray structures for complexes $RhH(CO)(thixantphos)(PPh_3)$ and $RhH(CO)(p\text{-}CH_3O\text{-}thixantphos)(PPh_3)$ in which the hydride ligand is in the *axial* position (bite angles are 109.3 and 111.7°, respectively). Also for the *ea* isomers, the *C* structures containing the hydride ligand in the *axial* position were the most stable ones. Brown and Kent [25] found that the *ee* and *ea* structures are in equilibrium as shown in Eq. 2 and that the ratio between both isomers depends on the bite angle of the disphosphine; when the bite angle of the disphosphine is between 100 and 120°, the *ee* coordination is preferred over the *ae* one, showing a positive effect on the activity and selectivity. We proposed that when the number of carbon atoms between the two phosphorus atoms is incremented, and consequently the bite angle of the diphosphine (see Table 2), the equilibrium in Eq. 2 is slightly displaced toward the *ee* configuration, and therefore the catalytic activities and selectivities are somewhat higher. In fact, the differences between the energies (1 Hartree = 627.51 Kcal) of the structures *C* and *A* decrease in the order $n = 2$ (46.5 Kcal) > $n = 3$ (12.3 Kcal) > $n = 4$ (3.5 Kcal), which is in agreement with the proposal of Brown and Kent [25].



(2)

On the other hand, for the hydroformylation of 1-hexene with paraformaldehyde, the systems containing two equivalents of the diphosphine ligand, which produce the cationic square planar species $[Rh(diphos)_2]^+$, were more active than those containing one equivalent, as it was reported before by some of us for the dppe system [13]; in Table 3 are shown the initial rate and selectivity results. Contrary to the results obtained for the olefin hydroformylation under syngas conditions, the reaction rate of the hydroformylation of 1-hexene with paraformaldehyde decreases with the enlargement of the carbon chain of the bridge between the two phosphorous atoms of the diphosphine (dppe > dppp > dppb). These results could be explained by both electronic and steric effects. Theoretical DFT-calculations performed for the three cationic Rh-bis(diphosphine) complexes using the corresponding $H_2P(CH_2)_nPH_2$ models ($n = 2$, 3 or 4) and the STO/6-31 + G(d, p) extended basis, allowed us to optimize the corresponding structures, which are shown in Fig. 2. As it

Table 3 Hydroformylation of 1-hexene with paraformaldehyde catalyzed by the $[Rh(diphos)_2]^+$ systems

Diphosphine	Bite angle (°)	10^5 r_i (Ms^{-1})	TOF (h^{-1})	l/b
dppe	85	(4.70 ± 0.06)	100 ± 2	1.7
dppp	91	(1.65 ± 0.05)	35 ± 1	2.1
dppb	98	(1.15 ± 0.03)	24 ± 1	2.2

Conditions: [Rh] = 1.7 mM, [1-hexene] = 0.5 M, $[CH_2O]$ = 0.6 M, T = 130 °C, solvent = 1,4-dioxane. r_i = initial rate; TOF = turnover frequency; l/b = linear to branched ratio

Table 2 Optimized total energies (Hartrees) for the isomers of the model complexes $RhH(CO)_2$(diphos); diphos = $H_2P(CH_2)_nPH_2$, $n = 2$, 3, 4

Isomers	*ee*		*ea*	
Diphosphine	A	B	C	D
$H_2P(CH_2)_2PH_2$	−5652.577804	−5652.566418	−5652.651962	−5652.631610
$H_2P(CH_2)_3PH_2$	−5691.739688	−5691.718893	−5691.759286	−5691.736758
$H_2P(CH_2)_4PH_2$	−5730.864990	−5730.847905	−5730.870544	−5730.848999

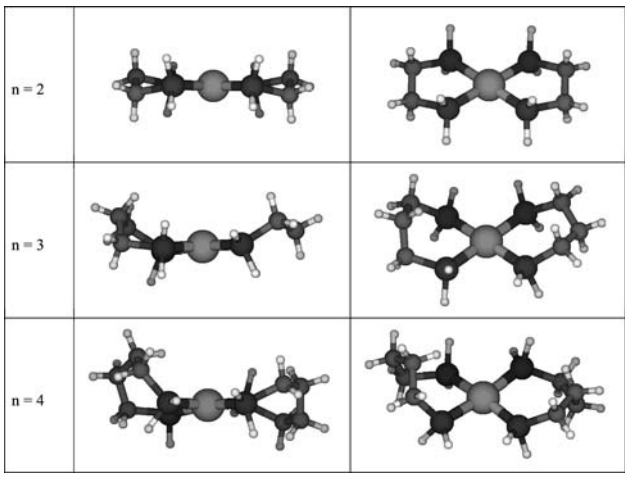


Fig. 2 Optimized geometry for complexes $[Rh(diphos)_2]^+$ [diphos = $HP(CH_2)_nPH_2$, $n = 2, 3, 4$]

Table 4 Optimized total energies (Hartrees) of the model complexes $[Rh(diphos)_2]^+$; diphos = $H_2P(CH_2)_nPH_2$, $n = 2, 3, 4$

Diphosphine	Energy
$H_2P(CH_2)_2PH_2$	−6186,5508
$H_2P(CH_2)_3PH_2$	−6264,7716
$H_2P(CH_2)_4PH_2$	−6342,9806

can be observed in Table 4, the stability of the $\{Rh[H_2P(CH_2)_nPH_2)]_2\}^+$ complexes increases in the order $n = 2 < n = 3 < n = 4$, indicating that the system with $n = 2$ is the most active. Moreover, when the bite angle of the disphosphine increases, a higher distortion of the square planar geometry of the corresponding complex is produced and therefore exists a major steric impediment; this should slow down the rate of activation of the paraformaldehyde addenda, which occurs probably through an oxidative addition reaction, and therefore decreases the hydroformylation rate of the system.

4 Conclusions

The systems $RhH(CO)_2$(diphos) and $[Rh(diphos)_2]^+$ showed to be the active precatalyst for the hydroformylation of 1-hexene to its corresponding aldehydes (heptanal and 2-methyl-hexanal) under syngas conditions or with paraformaldehyde, respectively. Although the hydroformylation of α-olefins under syngas conditions have been studied in detail, the present work have allowed us to explain through DFT calculations of the resting states why the catalytic activity of the process under syngas slightly increases with the enlargement of the carbon chain in a series of bidentated diphenylphosphines (dppb > dppp > dppe). This effect is contrary to the one observed in the reaction employing paraformaldehyde, a reaction that has been less studied. For the hydroformylation reactions under syngas conditions, the increasing of the activity was explained by the bite angle of the corresponding diphosphine, whereas for the reaction with paraformaldehyde the decreasing of the reaction was explained by both electronic and steric effects.

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