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Rhodium-Catalyzed Nonisomerizing Hydroformylation of Methyl Oleate Applying Lactame-Based Phosphoramidite Ligands

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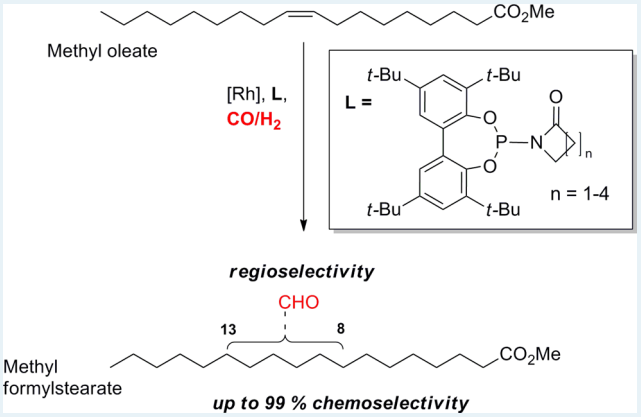
Supporting Information

ABSTRACT: The rhodium-catalyzed hydroformylation of methyl oleate (MO) with new monodentate phosphoramidite ligands **1a**–**d** is investigated here. The ligands are characterized by lactam rings of different size (four- to seven-membered rings). In mild conditions (synthesis gas pressure: 30 bar, 80 °C), the rhodium catalysts based on the P-azetidinone phosphoramidite **1a** gave within 6 h complete conversion and produced mainly methyl 9- and 10-formylstearate (MFS) with 99% chemoselectivity. In the hydrolysis test, phosphoramidite **1a** was also the most stable. This was additionally confirmed by density functional theory calculations.



KEYWORDS: *hydroformylation, methyl oleate, nonisomerizing, phosphoramidite, rhodium*

INTRODUCTION

The homogeneously catalyzed hydroformylation of olefins is one of the most important industrially applied transformations of olefins into aldehydes.[1] Up to now, required starting material is derived from petrochemical sources. However, unsaturated fatty acid derivatives derived from vegetables oils as soybean, linseed, safflower, and olive oil have also attracted increasing attention with respect to sustainable chemistry.[2] The aldehydes that are formed can be used as intermediates in several applications.[3] Most common is the subsequent reduction of the formyl and/or ester group, which gives rise to primary alcohols. The latter are particularly valuable as components in biobased plasticizers for polyvinyl chloride (PVC),[4] in novel polyurethane elastomers,[5] or in hyperbranched polyols.[6] Another application is the use as biodegradable lubricants.[7]

Due to the presence of sometimes multiple double bonds in different geometries and positions as well as the presence of functional groups (mainly carboxylic groups), know-how accumulated in the hydroformylation of unfunctionalized olefins cannot be simply applied to the conversion of fatty acid compounds.[3] Migration of double bonds, isomerization of *Z*/*E*-isomers, and hydrogenation of olefins and products may affect or even block the hydroformylation.[8] Another side reaction which may complicate the hydroformylation of fatty acids is decarbonylation catalyzed by modified Rh complexes.[9] Moreover, several impurities are usually present in a biotechnically generated feed stock like water, fatty alcohols, wax esters, hydrocarbons, tocopherols, phenols, pigments, phospholipids, and triterpenic acids.[10] During storage, the composition can be changed due to oxidation. These compounds can poison or decompose sensitive hydroformylation catalysts, in particular when the latter are used only in small concentrations.

Pioneering work in the hydroformylation of fatty acids was completed about 50 years ago by Lai, Naudet, and Ucciani.[11,12] These first investigations were carried out with methyl oleate (MO) as substrate using an unmodified cobalt catalyst [$Co_2(CO)_8$] at high synthesis gas pressure (240–310 bar) and a temperature of 175–190 °C. Under these conditions, formed aldehydes were immediately reduced to the corresponding alcohols. More detailed investigations by Pryde showed that at least eight isomeric alcohols were formed.[13] In contrast, the groups of Frankel and Friedrich obtained exclusively aldehydes under milder conditions (<70 bar, 100–120 °C) and by using a PPh_3-modified rhodium catalysts supported on heterogeneous surfaces ($CaCO_3$, Al_2O_3, or C).[14] Mainly C_9- and C_{10}-formylstearates were formed in an almost quantitative yield. Under these conditions, hydrogenation of the

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yielded aldehyde was not observed even when syngas was replaced by pure hydrogen. Also, a rhodium catalyst modified with $P(OPh)_3$ was quite efficient under similar conditions.[15]

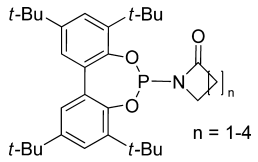
Later, van Leeuwen and co-workers applied a homogeneous rhodium catalyst based on the sterically hindered ligand tris-(2-*tert*-butyl-4-methylphenyl)phosphite in the same transformation under 20 bar syngas pressure and 100 °C (Rh/L = 1/25).[16] A fast isomerization of MO into the *trans*-configurated fatty acid ester methyl elaidate (ME) was noted prior to the hydroformylation. Within 1.2 h, when a 50% conversion of MO and ME was achieved, regioisomeric methyl formylstearates (MFS) were obtained with 49% yield. It was concluded that ME is hydroformylated much slower than MO. The use of a technical-grade substrate containing also methyl linoleate resulted in a complex mixture of products.

Da Rosa and co-workers used $RhH(CO)(PPh_3)_3$ as a precatalyst for the hydroformylation of MO.[17] They achieved quantitative conversion along with a high selectivity toward the formation of aldehydes (80−91%) when an excess of PPh_3 (PPh_3/Rh = 10) was applied under 40 bar of syngas pressure (CO/H_2 = 2:1) at 100 °C. The same authors reported that $RhH(CO)(PPh_3)_3$ gives rise to a similar catalytic performance.[18] Notably, catalysts generated from $RhCl_3{\cdot}3H_2O$, $[Rh(OMe)(cod)]_2$ or $Rh(CO)_2(acac)$ were inferior. Recently, Monflier and co-workers gave evidence that the hydroformylation of MO can be advantageously carried out in aqueous media with Rh-TPPTS [trisodium salt of 3,3′,3″-phosphinidynetris(benzenesulfonic acid] as catalyst and activated carbon as an additive.[19] The reaction proceeded under 50 bar of syngas pressure at 80 °C and resulted in a high conversion (93−95%) and regioselectivity (97%) for both pure and technical grade MO. The group of Suarez investigated $RhH(CO)(PPh_3)_3$ as a catalyst in an ionic liquid for the biphasic hydroformylation (CO/H_2 = 2:1, 40 bar, 100 °C) of technical-grade biodiesel and noted consecutive reactions like hydrogenation and decarbonylation particularly with an excess of PPh_3.[20]

Behr and co-workers observed in the hydroformylation of MO (10 bar, 115 °C) the formation of methyl ω-formylstearate in a yield of 26% yield using a rhodium catalyst based on the bidentate ligand BIPHEPHOS.[21] The formation of the linear product can be forced by using a ternary Rh/Ru/Ru-catalyst system as shown by Nozaki's group.[22] At a syngas pressure of 2.5 bar and a temperature of 120 °C, 19-hydroxynonadecanoic acid methyl ester was isolated in a yield of 53%.

The above evidence indicates that in strong contrast to the hydroformylation of petro-based olefins, up to now only a few phosphorus ligands have been tested in the reaction with fatty acid derivatives. Moreover, most results were obtained under different reaction conditions. Therefore, it is not possible to make a meaningful comparison between ligand structure and reactivity or chemo/regioselectivity. In addition the stability of modifying ligands was not addressed at all, although several studies emphasize the importance of this issue with respect to industrial hydroformylation processes.[23]

Therefore, we initiated a study on the synthesis of a new class of phosphorus ligands covering a set of strongly related individuals with the aim to test them in the hydroformylation of MO. As a basic structure, monophosphoramidites **1** bearing lactam units of different ring size were chosen.



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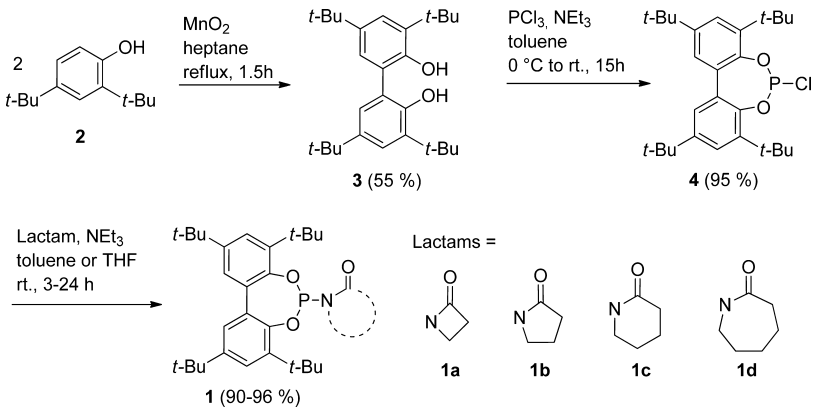
Usually phosphoramidites are employed as a phosphitylation reagent on the way to phosphite ligands. Their benefits also as monodentate ligands for hydroformylation catalysts have been recognized for only a couple of years.[24,25] The nitrogen substituent can be used for the tuning of steric and electronic properties. Especially electron-withdrawing amide groups should be advantageous, because ligands with strong π-accepting properties enhance the activity of rhodium-based hydroformylation catalysts.[26] Interestingly, such structures have never been tested in this reaction, probably due to the assumed high hydrolysis sensitivity.[27−29] A few examples concern chiral binaphthol phosphoramidites with a *N*-sulfonamide moiety suggested by Reek et al. for rhodium-catalyzed asymmetric hydrogenation.[30] *N*-Acyl-phosphoramidites, which are part of five-membered heterocycles, were tested by Takeuchi et al. in the iridium asymmetric alkylation, where an additional metal−ligand interaction via the carboxylic amide group was assumed.[31]

In this study, we will report on the synthesis of these new monodentate phosphoramidites and their evaluation as ligands in the rhodium-catalyzed hydroformylation of MO. The assessment of their stability toward water by hydrolysis experiments and modeling will complete this study.

RESULTS AND DISCUSSION

Synthesis of Phosphoramidites. Phosphoramidites **1** were prepared in a three-step sequence in overall yields of 47−50% starting from 2,4-di-*tert*-butylphenol (**2**, Scheme 1).

Scheme 1. Synthesis of Phosphoramidites



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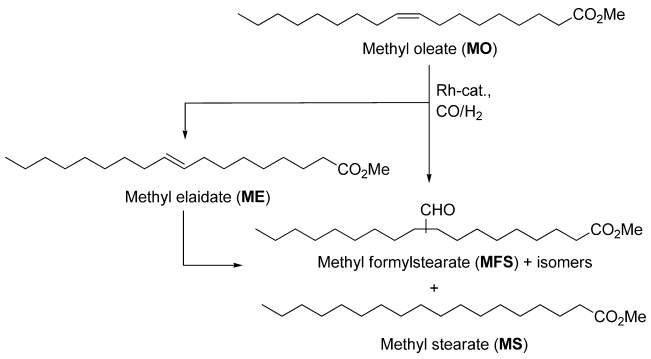
Scheme 2. Intermediates and Products in the Hydroformylation of Methyl Oleate



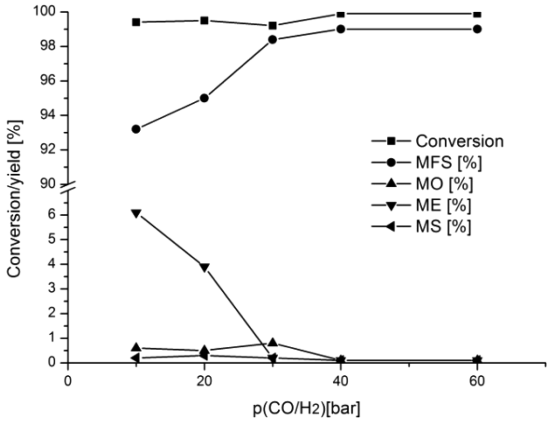


Figure 1. Variation of syngas pressure in the hydroformylation of methyl oleate. Conditions: 0.11 mol % $Rh(acac)(CO)_2$, **1a**/Rh = 25, 1.0 mmol methyl oleate, 10 mL of toluene, 80 °C, 6 h; MFS = methyl formylstearate, MO = methyl oleate, ME = methyl elaidate, MS = methyl stearate.

In the first step, the phenol was coupled with MnO_2 in refluxing heptane to give 2,2′-biphenol **3**.[32] This compound was treated with 1 equivalent of phosphorus trichloride and an excess of triethylamine in toluene to afford phosphorchloridite **4**.[33] The latter was finally condensed with the corresponding lactam in the presence of triethylamine as HCl-scavenger.

Hydroformylations. Phosphoramidites **1a–d** were used as ligands in the rhodium-catalyzed hydroformylation of methyl oleate (MO) (Scheme 2). In this reaction, besides the desired methyl formylstearate (MFS) isomers, the isomerized olefin, methyl elaidate (ME), as well as the hydrogenation product, methyl stearate (MS), can be formed.

The investigations were started performing a parameter screening using **1a** as ligand. For characterization, the precatalyst was generated by reaction of $Rh(acac)(CO)_2$ with an equimolar amount of ligand in toluene. After stirring for 4 h,

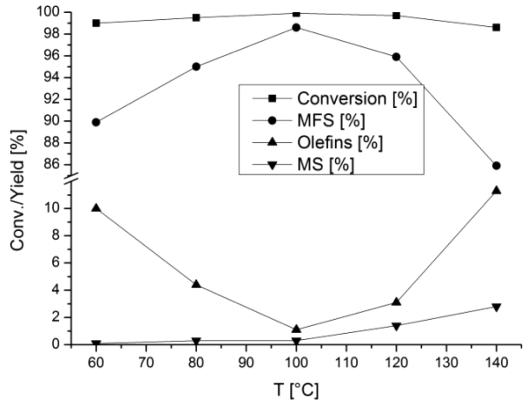


Figure 2. Variation of the temperature in the hydroformylation of methyl oleate. Conditions: 20 bar, 0.11 mol % $Rh(acac)(CO)_2$, **1a**/Rh = 25, 1 mmol methyl oleate, 10 mL of toluene, t = 6 h. Olefin = MO% + ME%; for abbreviations, compare Figure 1

the yielded complex [Rh(acac)(CO)(**1a**)] was characterized in the ^{31}P NMR spectrum by a doublet at δ 131.3 (J_{PRh} = 276 Hz ppm). The hydroformylation was carried out with a Rh/L ratio of 1/25. The distribution of regioisomeric aldehydes in the hydroformylation product was analyzed following an established procedure of Frankel et al.[34] Due to this procedure, formyl products were subjected to air-oxidation in the presence of the remaining catalyst in order to obtain the corresponding carboxylic acids. Esterification with BF_3-methanol gave a mixture of methyl esters, which were finally analyzed by GC/MS.

Variation of Syngas Pressure. The influence of the syngas pressure on the hydroformylation was investigated by increasing the pressure stepwise from 10 to 60 bar at a constant ratio of CO/H_2 = 1:1 at 80 °C in toluene. In all trials, full conversion (>99%) was noted (Figure 1/Table 1). Already at 10 bar, high yields of isomeric aldehydes can be found. Under the same pressure the *trans*-isomerization product ME was detected to an extent of 6%. It also underwent hydroformylation but more slowly than the *cis*-isomer (Run 1), which confirms observations of van Leeuwen with a Rh-monophosphite catalyst.[16]

With increasing syngas pressure, the chemoselectivity toward the hydroformylation was also improved affording finally the desired aldehydes in 99% yield (entry 4 and 5).[35] The product was identified as a mixture of 9- and 10-MFS. Careful analysis by GC/MS showed traces of minor isomers 8-, 11-, 12-, and 13-MFS (see Supporting Information).

Variation of Reaction Temperature. In turn, the hydroformylation of MO was conducted at different reactions temperatures (60 to 140 °C) using a constant syngas pressure of 20 bar in toluene (Figure 2/Table 2). Also in these experiments, the conversions were good or excellent (up to >99%). The yield of MFS increased gradually from 89.9% up to 98.6%. But by enhancing the temperature to 120 and 140 °C,

Table 1. Hydroformylation of MO at Different Syngas Pressures with 1a as Ligand[a]

entry	p [bar]	conversion [%][b]	MO [%][c]	MFS [%][c]	ME [%][c]	MS [%][c]	regioselectivity[d]
1	10	99.4	0.6	93.2	6.1	0.2	C5–C17
2	20	99.8	0.2	97.7	1.9	0.2	C8–C13
3	30	99.2	0.8	98.4	0.2	0.2	C8–C13
4	40	99.9		99.0			C8–C13
5	60	99.9		99.0			C8–C12

[a]Reaction conditions: see Figure 1. [b]Conversions were determined by GC (100 − % GC yield of MO). [c]Determined by GC. [d]C_n, n = carbon atom where the formyl group is linked.

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Table 2. Hydroformylation of MO at Several Reaction Temperatures with 1a as Ligand[a]

entry	T [°C]	conversion [%][b]	olefin (MO + ME)[%][c]	MFS [%][c]	MS [%][c]	regioselectivity[d]
1	60	99.0	10.0	89.9	0.1	C9−C12
2	80	99.8	2.1	97.7	0.2	C8−C13
3	100	99.9	1.1	98.6	0.3	C3−C18
4	120	99.7	3.1	95.9	1.4	C3−C18
5	140	98.6	11.3	85.9	2.8	C3−C18

[a]Reaction conditions: CO/H_2 = 1:1, 20 bar; for other conditions, see Figure 1. [b]Conversions were determined by GC (100 − % GC yield of MO). [c]Determined by GC. [d]C_n, n = carbon atom where the hydroformylation took place.

Table 3. Hydroformylation of MO with Different Ligands[a]

ligand	conversion [%][b]	MO [%][c]	MFS [%][c]	ME [%][c]	MS [%][c]	regioselectivity[d]
1a	99.8	0.2	97.7	1.9	0.2	C8−C13
1b	91.5	8.5	32.9	58.1	0.5	C7−C14
1c	88.7	11.3	32.2	56.2	0.3	C7−C13
1d	98.7	1.3	89.1	9.3	0.3	C8−C13
PPh_3	59.0	41.0	51.8	7.1	0.1	C9−C12
Alkanox 240[e]	99.6	0.4	96.0	3.4	0.2	C8−C13

[a]Reaction conditions: CO/H_2 = 1:1, 20 bar; for other conditions, see Figure 1. See also ref 36. [b]Conversions were determined by GC (100 − % GC yield of MO). [c]Determined by GC. [d]C_n, n = carbon atom where the hydroformylation took place. [e]Tris[2,4-di(*tert*-butyl)phenyl]phosphite.

respectively, the yield of MFS decreased to 95.9% and 85.9%, respectively. Remarkably, an increase in the formation of olefins and MS was noted (entries 4 and 5). Apparently, at high temperatures, hydroformylation is accompanied by decarbonylation and olefin hydrogenation. At 60 or 80 °C, isomerization of the double bond is small; however, at higher temperatures, this reaction is forced, and consequently, several regioisomeric aldehydes are formed finally (entries 3−5).

Variation of Solvent. By changing the solvent to methanol, the conversion, along with the yield of MFS, dropped drastically to 39.1% and 25.7%, respectively. Nevertheless with this solvent the best regioselectivity, exclusively a mixture of C9- and C10-formyl compound, was observed. The formation of dimethylacetals by tandem reaction of the aldehyde formed with the solvent did not take place.

Screening of Ligands. The hydroformylation experiments under variation of the ligands were carried out at 80 °C where best reactivity and regioselectivity were found in proceeding experiments (Table 3). Although a syngas pressure above of 30 bar lead to superior chemo- and regioselectivity with ligand **1a**, we conducted the reactions at 20 bar in order to identify more pronounced differences between ligands.

There is no clear trend between activity and ring size of the lactam ligands. Thus, the best reactivity was found with the four-membered ring lactam ligand **1a** with 99.8% conversion and 97.7% yield of MFS. In the case of the five- and six-membered ring lactam ligands, **1b** and **1c**, the conversion decreased to 91.5% and 88.7%, respectively. Only around 32% of MFS was formed. This could be due to the high *cis/trans*-isomerization tendency of catalysts of **1b** and **1c**, which gives ME in 58.1% and 56.2% yield. Obviously, the lowered hydroformylation activity with this isomeric substrate decreases the final yield of MFS. Unexpectedly, the seven-ring lactam **1d** led to the production of 89.1% yield of MFS along with a high conversion of 98.7%. In all trials, the formation of MS was at a minimum (<0.5%). With regard to the regioselectivity of the reaction with all ligands **1a−d**, mainly a mixture of 9- and 10-MFS was formed; only traces of other isomers were detected.

In order to compare these results with PPh_3, which present a standard ligand in technical nonisomerizing hydroformylation, we tested it under identical reaction conditions. All new phosphoramidite ligands **1** induced superior reactivities and chemoselectivities. PPh_3 formed a very sluggish catalyst (59.0% conversion) and yielded only 51.8% of MFS. It should be noted that only 7.1% ME is formed, which corresponds to a low isomerization activity. The regioselectivity was slightly improved.

Moreover, we were pleased to see that the four-ring lactam **1a** even successfully competed with tris[(di(2-*tert*-butyl)phenyl]-phosphite (Alkanox 240), one of the most prominent monophosphites used in rhodium-catalyzed hydroformylation.[37]

Hydrolysis. In a subsequent investigation, the stability of phosphoramidites **1a−d** toward water was tested. For this purpose, a 0.0175 M solution of phosphoramidite in 1,4-dioxane was treated with water at 85 °C in a sealed NMR tube. The degree of decomposition was analyzed by ^{31}P NMR spectroscopy using tri(*n*-octyl)phosphine oxide as an internal standard. Notably, huge differences were observed (Figure 3).[38]

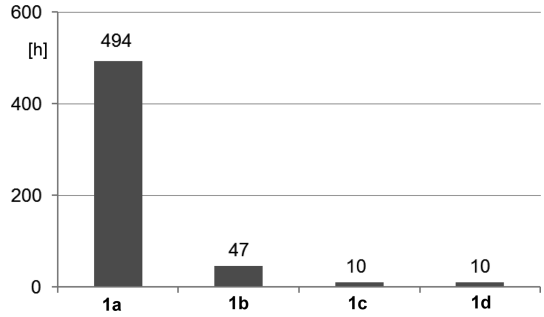

Figure 3. Resistance of lactam-based phosphoramidites **1a−d** toward hydrolysis. Results for the reaction of a 0.0175 M solution in dioxane-1,4 with 100 mol equivalents of water at 85 °C. The time (h) required for full decomposition is given.

Poor hydrolysis resistance was observed for phosphoramidites with large lactam rings **1c** and **1d**, which decomposed within a few hours. Phosphoramidite **1b**, bearing a five-membered lactam ring, proved to be more stable. Surprisingly, azetidinone-phosphoramidite **1a**, which performed best as ligand in the

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hydroformylation of MO, was most stable. The compound was fully hydrolyzed only after about 20 days.[39]

Computational Calculations. In order to understand the relative stability of phosphoramidites **1a**–**d**, we have carried out B3LYP/TZVP DFT calculations (the computational details are given in the Supporting Information). At first, we computed the relative stability caused by the rings of different sizes on the basis of the exchange reaction (Scheme 3/Table 4, ΔE_x). For

Scheme 3. Exchange Reaction for the Calculation of the Gibbs Free Energy

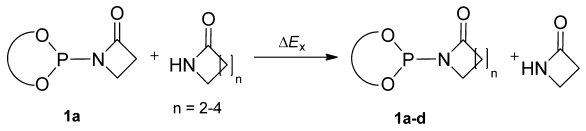


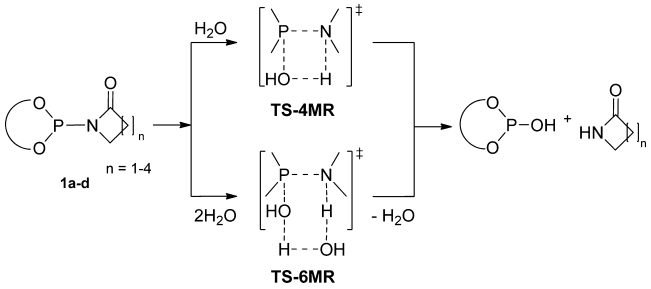
Table 4. B3LYP/TZVP Computed Exchange Energies (ΔE_x, kcal/mol), Reaction Free Energy (ΔG, kcal/mol), and Activation Free Energy (ΔG_a, kcal/mol) of Hydrolysis

	ΔE_x	ΔG	ΔG_a (TS-4MR)	ΔG_a (TS-6MR)
1a	0.00	−11.88	49.71	48.96
1b	3.36	−12.54	49.34	51.06
1c	6.26	−18.14	48.99	51.53
1d	6.09	−17.97	46.36	51.50

n = 2–4, the calculated Gibbs free energy for the exchange reaction is endergonic by 3.36, 6.26, and 6.09 kcal/mol, respectively. This energetic order indicates clearly that **1a** is most stable, followed by **1b**, whereas **1c** and **1d** are the least stable.

In addition, we also calculated the thermodynamic (ΔG) and kinetic data (ΔG_a) of the hydrolysis (Scheme 4/Table 4).

Scheme 4. Reaction of Phosphoramidites with Water



As detailed in Table 4, hydrolyses of **1a**–**d** are exergonic in each case. However, the computed free energies (ΔG) clearly show that the hydrolysis of **1a** is least exergonic (−11.88 kcal/mol), followed by that of **1b** (−12.54 kcal/mol). The reaction of **1c** and **1d** with water is more exergonic (−18.14 and −17.97 kcal/mol). This gives evidence that **1a** is most inert toward the attack of water. These energetic data are in line with the computed relative stability based on the exchange reaction discussed above.

In addition, the computed activation free energies (ΔG_a) for the hydrolysis also reveal that the reaction of **1a** with one water molecule via the four-membered transition state (TS) has the highest activation barrier (49.71 kcal/mol), tightly followed by **1b** (49.34 kcal/mol), whereas the barriers of **1c** and **1d** are somewhat lower (48.99 and 46.36 kcal/mol, respectively). It is also shown that the activation free energy for **1a** with two water molecules involving a six-membered transition-state structure is approximately the same as found for the four-membered transition-state structure with only one water molecule. In contrast, activation free energies for **1b**–**1d** with the six-membered transition-state structures are very close, and they are higher than those for the four-membered transition-state structures. In conclusion, both kinetic and thermodynamic parameters evidence the extremely enhanced hydrolysis stability of **1a**, which is in full agreement with the experimental results.

Indeed, such energetic performances correlate with the electronic properties of the P–N bond as listed in Table 5. For example, the P–N bond length increases from **1a** to **1d** continually, and the same is also found for the Wiberg bond indexes; however, the orbital occupancy decreases accordingly. The atomic hybrid contributions from NLMO analysis on both P and N atoms show clearly that the shorter P–N distance in **1a** originates from the stronger s character of the hybrid orbitals, whereas the longer P–N bond in **1d** is due to the stronger p character of the hybrid orbitals. The highest thermodynamic stability of **1a** has its electronic origin. In contrast, the computed natural charge of both P and N atoms, which reflects their total bonding effects, does not show a clear trend.

SUMMARY AND CONCLUSIONS

A set of new phosphoramidites bearing lactam rings was synthesized and evaluated as ligands in the rhodium-catalyzed hydroformylation of methyl oleate under mild conditions (syngas pressure: 20 bar, 80 °C). The size of the lactam ring has a significant influence on all reaction parameters, like degree of *E*/*Z*-isomerization, conversion, yield of methyl formylstearate, and regioselectivity. Superior results were obtained with a ligand based on a four-membered lactam ring. Remarkably, the ligand which performs best in the catalytic reaction is also by far the most stable toward water. Preliminary experiments in the hydroformylation of *n*-octenes showed a similar trend.[40] Up to now, it is not clear whether such a correlation between hydroformylation activity and hydrolysis stability exist or whether we witnessed only a random coincidence.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of phosphoramidites **1a**–**d**, hydroformylation procedures, characterization of products, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org

Table 5. Computed P–N Distance (r, Å), Wiberg Bond Index (WBI), and Orbital Occupancy, As Well As Natural Charge (δ), Percentage Contribution (%), and the Atomic Hybrid Contribution (sp^x) of P and N Atoms from Natural Localized Molecular Orbital (NLMO) Analysis

	r_{P-N}	WBI	occupancy	δ_P	δ_N	P%	N%	P(sp^x)	N(sp^x)
1a	1.737	0.785	98.9%	1.499	−0.747	23.34	74.80	4.89	1.77
1b	1.752	0.766	98.5%	1.514	−0.736	24.26	74.47	5.07	2.16
1c	1.780	0.744	98.1%	1.508	−0.715	24.85	73.62	5.30	2.80
1d	1.782	0.745	98.1%	1.513	−0.727	24.26	74.19	5.39	2.38

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Notes

The authors declare no competing financial interest.

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(40) Thus, in the Rh-catalyzed hydroformylation of *n*-octenes (mixture of 3.3% 1-octene, 29.2% *E/Z*-2-octene, 29.2% *E/Z*-3-octene, 16.4% *E/Z*-4-octene, 2.1% structural isomers, 0.6% octane) with ligands **1a−d** the yields of aldehydes were in the following order: **1a** (96%), **1b** (98%), **1c** (32%), **1d** (20%).