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Hydroformylation

In Situ FTIR and NMR Spectroscopic Investigations on Ruthenium-Based Catalysts for Alkene Hydroformylation

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Abstract: Homogeneous ruthenium complexes modified by imidazole-substituted monophosphines as catalysts for various highly efficient hydroformylation reactions were characterized by in situ IR spectroscopy under reaction conditions and NMR spectroscopy. A proper protocol for the preformation reaction from $[Ru_3(CO)_{12}]$ is decisive to prevent the formation of inactive ligand-modified polynuclear complexes. During catalysis, ligand-modified mononuclear ruthenium(0) carbonyls were detected as resting states. Changes in the ligand structure have a crucial impact on the coordination behavior of the ligand and consequently on the catalytic performance. The substitution of CO by a nitrogen atom of the imidazolyl moiety in the ligand is not a general feature, but it takes place when structural prerequisites of the ligand are fulfilled.

Introduction

Homogenously catalyzed hydroformylation is used for the synthesis of aldehydes from alkenes, carbon monoxide, and hydrogen. Large-scale processes have been established for different feedstocks with catalysts based on rhodium and cobalt to product a range of aldehydes and alcohols, which are utilized as intermediates or final products in plasticizers, detergents, surfactants, pharmaceuticals, aroma compounds, and as solvents.[1–4] Due to its industrial importance hydroformylation belongs to the most studied homogeneously catalyzed reactions. Extensive research has been performed for the development of new catalysts and the study of kinetic and mechanistic aspects. Irrespective of these attempts, clear correlations between catalyst structure and catalytic performance are scarce.

In research on alkene hydroformylation and related reactions there is an increasing interest in studies on catalysts based on metals other than rhodium and cobalt.[5–28] For example, regioselective and asymmetric hydroformylation systems with Pt or modified Pt/Sn catalysts have been studied intensively since the 1970s.[29] Compared to chiral rhodium complexes, sometimes higher enantioselectivities could be achieved.[30] Palladium phosphine complexes in the presence of acids provided high regioselectivities in isomerizing hydroformylation.[7,8,31] Catalyst systems based on Pd were also successfully used in the hydroformylation of alkynes.[32] Another application is the alkoxycarbonylation of nonfunctionalized alkenes, unsaturated fatty acid derivatives, and alkynes for the synthesis of corresponding esters.[33] Complexes based on iridium have been frequently used as model systems in mechanistic studies related to hydroformylation reactions.[34] Other investigations gave evidence that ligand-modified neutral and cationic iridium catalysts can develop considerable activity for the production of aldehydes under optimized and mild conditions.[9–12,27,35] The relevance of ruthenium catalysts for alkene hydroformylation and related catalytic reactions are discussed in more detail below.

Detailed structural and quantitative information about the catalyst system, which often is a mixture of several components, is the basis of any kinetic and mechanistic study.[36] In carbonylation reactions homogeneously catalyzed by transition metals, in situ high-pressure (HP) FTIR and NMR techniques are applied as diagnostic tools that allow for comprehensive characterization of catalyst complexes and intermediates under relevant reaction conditions.[37–39] Isotopic labeling experiments in combination with in situ spectroscopy afford the elucidation of

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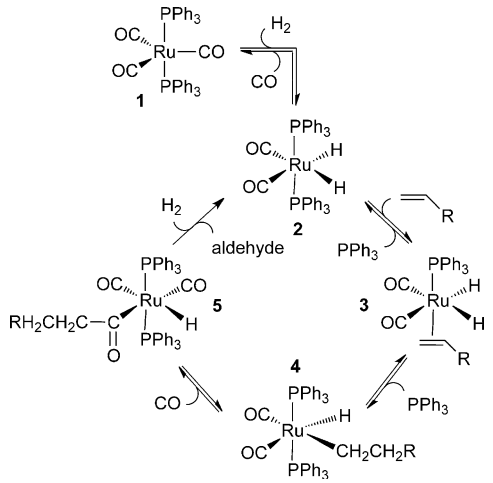
specific structural and mechanistic aspects. Correlation between the composition of catalytic species determined by in situ spectroscopy and the kinetics of organic starting materials and products, often analyzed by chromatographic methods, deliver valuable information about the kinetics and mechanism of the reaction.[40]

Chemometric treatment of the data obtained from in situ spectroscopic measurements (especially FTIR spectroscopy) is increasingly performed to extract the maximum information from these experiments.[38,41] The interpretation of experimental IR spectra of catalytic intermediates, which are in most cases non-isolable and sometimes present only in low concentrations, can be supported beneficially by considering vibrational spectra calculated by DFT methods.[11,12,38,40b,42]

Wilkinson et al. studied triphenylphosphine-modified ruthenium-catalyzed hydroformylation and proposed a dissociative reaction mechanism involving 18- and 16-electron complexes, which has been confirmed in many aspects by others (Scheme 1, unsaturated 16-electron species are not



Scheme 1. Proposed simplified catalytic cycle of PPh_3-modified ruthenium-catalyzed hydroformylation.[45] Unsaturated 16-electron complexes have been omitted.

shown).[43–47] Starting from the ruthenium(0) complex $[Ru(CO)_3(PPh_3)_2]$ (**1**), dissociation of a carbonyl ligand first occurs, followed by oxidative addition of molecular hydrogen yielding the ruthenium(II) dihydride complex **2**. After dissociation of PPh_3, alkene activation takes place giving the π complex **3**. Insertion of the alkene into the Ru–H bond and coordination of PPh_3 provides complex **4**. Migratory insertion of CO followed by coordination of another carbonyl ligand yields the acyl complex **5**. In the last step molecular hydrogen is activated followed by aldehyde elimination and regeneration of complex **2**. Formation of the dihydride complex has been proposed to be rate-determining.[44]

The development of new catalysts based on ruthenium for alkene hydroformylation has been a challenge since the investigations by Wilkinson and co-workers. The activity of ruthenium complexes is generally lower than that of rhodium congeners.[5] Therefore, appropriate organic ligands such as phosphines or amines are applied as co-catalysts.[5,13,24,48] Unmodified and modified ruthenium complexes have been applied in the hydroformylation of alkenes with carbon dioxide.[49]

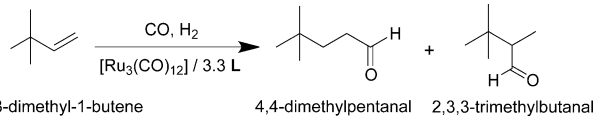
In recent studies with carbon monoxide and hydrogen as co-substrates Nozaki et al. utilized $[\{Cp^*Ru^{II}(acac)\}_2]/\widehat{PP}$ (acac = acetylacetonate, $\widehat{PP}$ = bidentate ligand) to form a catalyst complex of the type $[Cp^*Ru^{II}(\widehat{PP})H]$ for *n*-selective hydroformylation of propene and 1-decene.[14] In further studies Ru complexes combined with rhodium catalysts or as single-component catalyst were applied in cascade hydroformylation/hydrogenation and isomerization/hydroformylation/hydrogenation reactions.[15–17]

Recently, a breakthrough was reported by Beller and co-workers, who discovered that ruthenium(0) complexes formed from $[Ru_3(CO)_{12}]$ and modified with imidazole-substituted monophosphines are unusually active towards the formation of the desired aldehyde products.[18–22] Noteworthily, the new catalyst system operates under mild reaction conditions and allows the conversion of a broad scope of substrates. Moreover, these complexes have been successfully applied in cascade reactions such as hydroformylation/reduction[18,21] and hydroaminomethylation.[19,22] With respect to the optimal reaction conditions it was found that the best catalytic performance was obtained by running the reactions in polar organic solvents such as propylene carbonate. Since an excess of ligand led to a decrease of the activity, a low ratio of [**L**]/[Ru] = 1.1 was employed.

The aim of this work was to rationalize the outstanding catalytic performance of the highly versatile system[18–22] reported by Beller et al by application of in situ IR and NMR spectroscopy. Our special concern was to characterize resting states spectroscopically under hydroformylation conditions.[20] The interpretation of IR spectra is supported by vibrational analysis through DFT calculations. Catalysts with different ligands were selected in order to correlate their catalytic performance with spectroscopic features.

Results and Discussion

For the IR spectroscopic study we chose the hydroformylation of 3,3-dimethyl-1-butene with $[Ru_3(CO)_{12}]$/**L** (Scheme 2). Experiments were performed at 100 °C, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa with a ruthenium concentration of 4 mmol L^{-1} and a ratio of [**L**]/[Ru] = 1.1. The alkene concentration was 900 mmol L^{-1}. Toluene was used as solvent for IR and NMR experiments. The substrate 3,3-dimethyl-1-butene, which is incapable of double-bond isomerization, was selected with the intention to keep the kinetics as simple as possible.[41f,50] For the sake of comparison with the work of Beller et al., who used a polar solvent, we performed selected reactions also in pro-



Scheme 2. Hydroformylation of 3,3-dimethyl-1-butene.

pylene carbonate (PC) and analyzed the solutions by NMR spectroscopy. Due to the strong absorption of PC in the frequency region of transition metal carbonyl complexes, it was not possible to apply IR spectroscopy to reactions performed in this solvent.

To acquire more detailed knowledge of possible ruthenium complexes, we started our investigations with the unmodified Ru system (without ligand) and then turned to the PPh_3-modified system, for which IR data are available in the literature.

Unmodified system

For the unmodified system, $[Ru(CO)_5]$ ($\tilde{\nu}(CO) = 1998$, 2034 cm^{-1}) and $[Ru_3(CO)_{12}]$ ($\tilde{\nu}(CO) = 2009$, 2029, 2060 cm^{-1}) are the dominant species under the reaction conditions without added alkene (see first spectrum in Figure 1).[51,52] In a preformation step, in which the precursor $[Ru_3(CO)_{12}]$ was subjected to 2.0 MPa of carbon monoxide and 4.0 MPa of hydrogen at 100 °C, the mixture of the two complexes changed slowly to a new equilibrium composition. The corresponding mononuclear dihydride complex $[Ru(CO)_4H_2]$, which has been identified and characterized under high hydrogen pressures by Whyman,[53] was not detected under our reaction conditions. A more detailed description of spectroscopic results is given in the Supporting Information (SI-A).

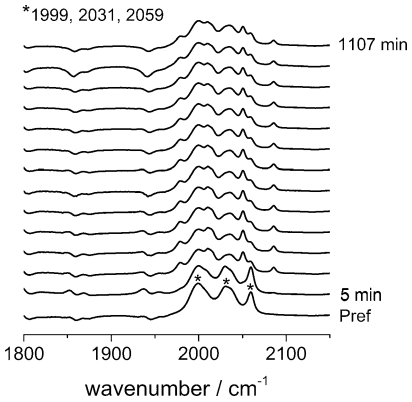


Figure 1. IR spectra collected during the hydroformylation of 3,3-dimethyl-1-butene with the unmodified Ru catalyst. The first spectrum (Pref) was collected after a preformation period of 230 min. Bands can be assigned to $[Ru(CO)_5]$ ($\tilde{\nu}(CO) = 1998$, 2034 cm^{-1}) and $[Ru_3(CO)_{12}]$ ($\tilde{\nu}(CO) = 2009$, 2029, 2060 cm^{-1}). Reaction conditions: $[Ru] = 4 \times 10^{-3}$ mol L^{-1}, [alkene] = 0.9 mol L^{-1}, $T = 100$ °C, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, solvent = toluene.

After the addition of the alkene, slow regioselective formation of the *n*-aldehyde occurred with a yield of 4.4% after 4 h, with about 0.6% formation of the alkane. For results from GC analysis of samples taken during the investigated reaction time, see the Supporting Information (SI-A). In the in situ IR spectra, a change in the ratio of $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$ was observed. The intensity of the band of $[Ru_3(CO)_{12}]$ at 2059 cm^{-1} decreased significantly. Throughout the reaction, additional bands were detected with $\tilde{\nu}(CO) = 1978$, 2017, 2051, and 2086 cm^{-1}, which probably belong to a single species.[54] Despite further experimental attempts by FTIR and NMR spectroscopy, including ^{13}CO enrichment and deuteration, these bands could not yet be assigned (details are given in Supporting Information SI-A).

PPh_3-modified system

On applying 1.1 equivalents of triphenylphosphine with respect to the ruthenium concentration, the dominant complex after the preformation step is $[Ru(CO)_4(PPh_3)]$ ($\tilde{\nu}(CO) = 1951$, 1985, 2059 cm^{-1}).[53,55] In this complex with trigonal-bipyramidal structure and C_{3v} symmetry, the phosphine is coordinated in the axial position. Only a weak contribution from $[Ru(CO)_3(PPh_3)_2]$ with *trans* trigonal-bipyramidal structure (D_{3h}, $\tilde{\nu}(CO) = 1900$ cm^{-1})[55] was observed. Peaks for the phosphine-free complexes were not detected. The IR spectra are given in Figure 2 (further details are presented in Supporting Information SI-B). The composition of these complexes did not change after addition of the alkene and remained constant during the entire time investigated.

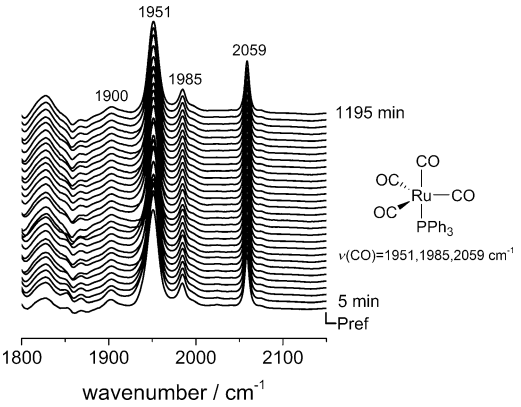


Figure 2. IR spectra collected during the hydroformylation of 3,3-dimethyl-1-butene with $[Ru_3(CO)_{12}]/PPh_3$. The first spectrum (Pref) was collected after the preformation period. Reaction conditions: $[Ru] = 4 \times 10^{-3}$ mol L^{-1}, $[PPh_3] = 4.4 \times 10^{-3}$ mol L^{-1}, [alkene] = 0.9 mol L^{-1}, $T = 100$ °C, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, solvent = toluene.

Under these conditions the *n*-aldehyde was formed as the only product with a yield of about 0.2% after 4 h. Regarding the effect of the preformation protocol discussed below, we did not find such an influence on the resting state for the Ru/PPh_3 system. The mononuclear complexes were formed irrespective of whether the solution was first heated to 100 °C under argon followed by pressurization, or the heating process was initiated in the presence of the gases. No decomposition of PPh_3 due to P–C cleavage was observed. After pressure release, singlets in the ^{31}P NMR spectrum were detected at 47.6 ppm for $[Ru(CO)_4(PPh_3)]$ and 56.6 ppm for $[Ru(CO)_3(PPh_3)_2]$. These complexes were stable under ambient conditions. In the $^{13}C\{^1H\}$ NMR spectra the two complexes could be distinguished by the splitting of the carbonyl signals with $\delta(^{13}C, [Ru(CO)_4(PPh_3)]) = 204.7$ ppm (d, $^2J_{CP} = 3.9$ Hz) and $\delta(^{13}C, [Ru(CO)_3(PPh_3)_2]) = 208.7$ ppm (t, $^2J_{CP} = 16.1$ Hz).[56] These ^{13}C NMR data are consistent with values reported in the literature.[46]

Systems modified by imidazole-substituted monophosphines

For this study three ligands, of which **L1** and **L2** were screened by Beller et al., were selected from the class of imidazole-substituted monophosphines (Figure 3).

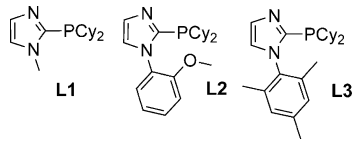


Figure 3. Imidazole-substituted monophosphines selected for this study.[18,20]

Catalytically inactive polynuclear complexes

On performing the preformation reaction in such a way that the solution of the precursor and the ligand were heated to 100 °C under argon before adding carbon monoxide and hydrogen, we found that a fairly stable and inactive ligand-modified polynuclear complex was formed with each of the ligands. The IR spectra showed similar band patterns for all three ligands (Figure 4). These complexes remained stable even at 6.0 MPa synthesis gas (p(CO) = 2.0 MPa, p(H_2) = 4.0 MPa) in the presence of the alkene during the investigated time of about 16 h. After the addition of 3,3-dimethyl-1-butene, no substantial change in complex composition occurred. Very low yields of aldehydes were detected: about 0.1 % (**L1**), about 0.7 % (**L2**), and about 1.0 % (**L3**) after 4 h (GC data for different time intervals are given in Supporting Information SI-C).

The solutions after pressure release showed signals in the ^{31}P NMR spectra at 197.4 ppm for Ru/**L1**, 195.8 ppm for Ru/**L2**, and 192.7 ppm for Ru/**L3**. These complexes were stable under ambient conditions. Repetition experiments performed in glass Schlenk tubes under argon with **L3**, which gave practically only one product, revealed that the polynuclear complex contains one equivalent of ligand. The band pattern of the IR spectrum registered at atmospheric pressure was identical to that measured under reaction conditions. Consequently, the obvious stability of such a complex allowed further spectroscopic characterization under ambient conditions.

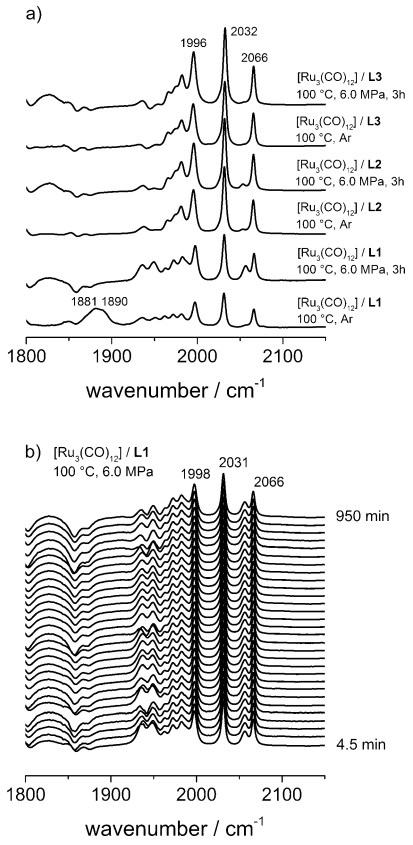


Figure 4. a) IR spectra for [$Ru_3(CO)_{12}$]/**L** (**L** = **L1**, **L2**, **L3**) after heating to 100 °C under argon and further treatment with 6.0 MPa synthesis gas (p(CO) = 2.0 MPa and p(H_2) = 4.0 MPa). b) Series of spectra after the addition of 3,3-dimethyl-1-butene for Ru/**L1**. Further experimental conditions: [Ru] = 4×10^{-3} mol L^{-1}, [**L**] = 4.4×10^{-3} mol L^{-1}, [alkene] = 0.9 mol L^{-1}, solvent = toluene. The full sets of IR spectra collected for the systems including [$Ru_3(CO)_{12}$]/**L** (**L** = **L2**, **L3**) are given in the Supporting Information SI-C.

Molecular structure of polynuclear complexes

^{31}P NMR spectroscopy indicated a polynuclear complex in which the P atom of the ligand is involved in multiple bonds. The chemical shift $\delta(^{31}P) \approx 190$–200 ppm is indicative of a phosphido ligand, which can be formed by P–C bond cleavage.[57–65] Additionally, ^{1}H,^{15}N HMBC NMR spectroscopy provided further details of the coordination behavior of the imine nitrogen atom. The chemical shifts of the imine nitrogen atoms in the free ligand and the complex clearly differ, which is evidence that coordination took place (see Figure 5, $\delta(^{15}N) = -187$ and -216 ppm). A further characteristic feature is the loss of symmetry in this complex; the two cyclohexyl groups appear to no longer be symmetry-equivalent, as is observed in the mononuclear complexes described below. A detailed discussion of the NMR observations is given in the Supporting Information (SI-C).

To clarify the coordination modes of the ligand in the complex, we attempted to obtain suitable crystals for X-ray structure analysis from concentrated solutions with [Ru] = 40×10^{-3} mol L^{-1}. We were successful when performing the stoi-

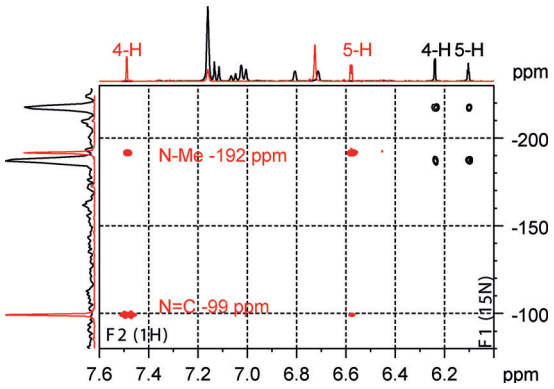


Figure 5. ^{1}H,^{15}N HMBC NMR spectra (benzene solution) of the free ligand **L3** (red) and the Ru/**L3** carbonyl complex obtained after preformation without syngas (black).

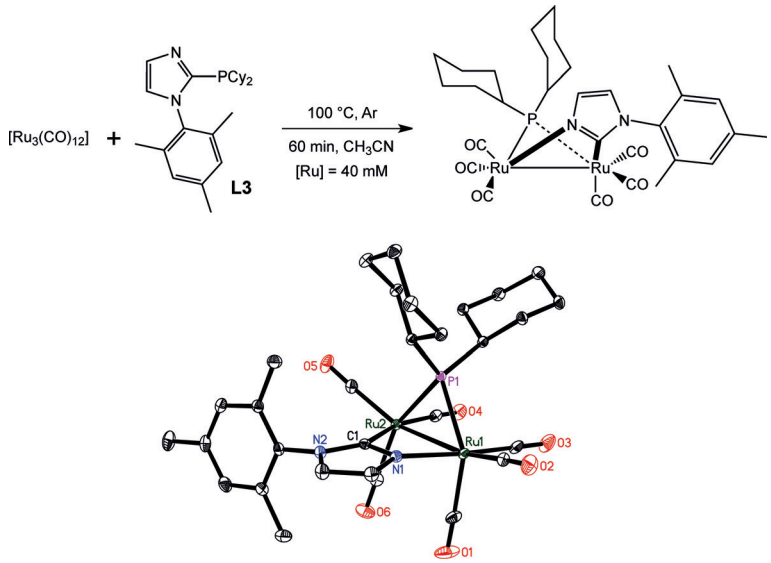


Figure 6. Formation and X-ray molecular structure of a diruthenium complex obtained from the thermal reaction of $[Ru_3(CO)_{12}]$ with ligand **L3**. Thermal ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity.

chiometric reaction of $[Ru_3(CO)_{12}]$ with **L3** in CH_3CN at 100 °C. For that solution a signal in the ^{31}P NMR spectrum at $\delta(^{31}P) = 194.0$ ppm was observed. Figure 6 shows the X-ray molecular structure. Surprisingly, a dinuclear complex was obtained. The monophosphine **L3** underwent P–C cleavage affording a phosphido ligand μ_2-P(Cy)$_2$ bridging the two ruthenium atoms.[57c] Consequently, through a formal oxidative addition, a bond between the involved carbon atom and one ruthenium atom is formed. In accordance with the results from ^{15}N NMR spectroscopy the imine nitrogen atom coordinates to a ruthenium center. In a recently published work in which $[Os_3(CO)_{12}]$ was used with two equivalents of **L2**, formation of a similar complex was reported, with the difference that the trinuclear structure was retained.[66]

Catalytically active mononuclear complexes

When the preformation reaction was carried out by heating the solution in the presence of the gaseous components carbon monoxide and hydrogen, mononuclear complexes were obtained. IR spectra for the three systems prior to alkene addition are shown in Figure 7a. Interestingly, a mixture of the ligand-modified complex and $[Ru(CO)_5]$ ($\tilde{\nu}(CO) = 1998$, 2034 cm^{-1}) was formed with **L2** and **L3**. This indicates an influence of the ligand properties on the coordination behavior, which is discussed further below. The complex composition did not change after addition of 3,3-dimethyl-1-butene and remained constant during the investigated time. Figure 7b shows the series of IR spectra for the reaction with Ru/**L1**. Spectra for the other catalytic systems are presented in Supporting Information SI-D. The performances of the catalysts in the hydroformylation differ (Table 1). The system Ru/**L2** shows the highest activity, followed by Ru/**L3** and then Ru/**L1**. The high *n* regioselectivity (>99%) probably originates from the steric hindrance of the 3,3-dimethyl-1-butene substrate.[67] With

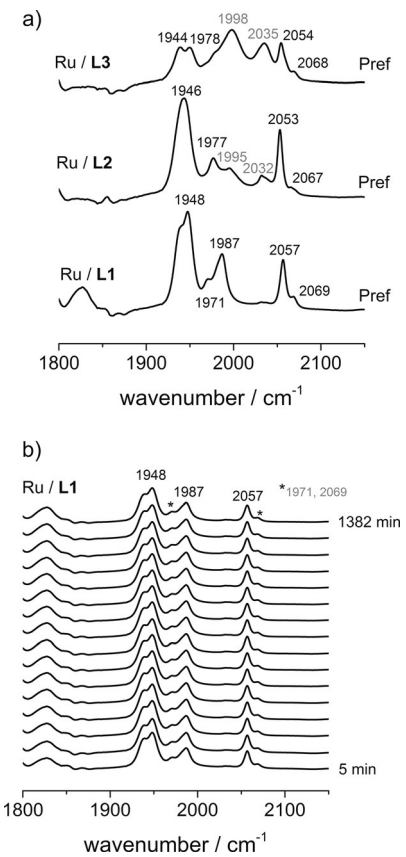


Figure 7. a) IR spectra for $[Ru_3(CO)_{12}]$/**L1**, **L2**, **L3** after heating to 100 °C in the presence of 6.0 MPa synthesis gas ($p(CO) = 2.0$ MPa and $p(H_2) = 4.0$ MPa). b) IR spectra for $[Ru_3(CO)_{12}]$/**L1** during the hydroformylation of 3,3-dimethyl-1-butene. Experimental conditions: $T = 100$ °C, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, $[Ru] = 4 \times 10^{-3}$ mol L^{-1}, $[L] = 4.4 \times 10^{-3}$ mol L^{-1}, [alkene] = 0.9 mol L^{-1}, solvent = toluene. The band splitting at 1948 cm^{-1} may be caused by difficulties with the background subtraction, because toluene has an intensive band at 1940 cm^{-1}. Splitting of the band at 1948 cm^{-1} (E representation) can occur also due to the C_1 symmetry of the ligand.

Table 1. Results from catalytic experiments by GC analysis. Reaction conditions: [Ru] = 4×10^{-3} mol L^{-1}, [**L**] = 4.4×10^{-3} mol L^{-1}, [alkene] = 0.9 mol L^{-1}, T = 100 °C, p(CO) = 2.0 MPa, $p(H_2)$ = 4.0 MPa, solvent = toluene.

System	*n*-Aldehyde [%] (linearity)	Alkane [%]	Alcohol [%]	Reaction time [min]
Ru/**L1**	0.9 | 3.8 (> 99)	0 | 0.1	0 | < 0.1	240 | 1382
Ru/**L2**	11.3 | 43.2 (> 99)	0.2 | 0.9	0 | 0.2	240 | 1378
Ru/**L3**	3.3 | 14.1 (> 99)	0.2 | 0.7	0 | 0.2	240 | 1381

1-octene as a linear alkene and PC as a solvent, a regioselectivity of *n*:*b* = 95:5 was reported for Ru/**L2**.[20] No significant change in linearity was observed for a series of ligands with different substituents on the imidazolyl moiety. Notably, no pronounced variation in activity was observed. It has been reported that the steric properties of this olefin are responsible for lower reaction rates in hydroformylation with rhodium catalysts in comparison with linear 1-alkenes.[67a]

After pressure release at room temperature the IR spectra showed only minor changes. The mononuclear complexes stored under argon were stable even for longer time. This permitted us to again perform further spectroscopic characterizations under ambient conditions. The ^{31}P NMR spectra are characterized by singlets at δ(Ru/**L1**) = 32.1, δ(Ru/**L2**) = 43.8, and δ(Ru/**L3**) = 41.6 ppm. The signals in the ^{13}C NMR spectra[68] for the carbonyl groups [$\delta(^{13}$C,Ru/**L1**) = 207.3 ppm (d, $^2J_{CP}$ = 2.1 Hz), $\delta(^{13}$C,Ru/**L2**) = 205.7 ppm (d, $^2J_{CP} \approx$ 3-4 Hz), and $\delta(^{13}$C,Ru/**L3**) = 206.5 ppm (d, $^2J_{CP} \approx$ 3–4 Hz)] showed a doublet splitting, which is in accordance with monophosphine complexes (further details are given in Supporting Information SI-D).

Molecular structures of mononuclear complexes

In the following we give evidence that the IR spectra can actually be assigned to ligand-modified ruthenium(0) complexes of the type [Ru(CO)$_4$**L**]. Comparing the spectrum of Ru/**L1** with [Ru(CO)$_4$(PPh$_3$)] shows a good agreement with respect to the band positions, see Figure 8a. Interestingly, the intensity pattern of Ru/**L1** is notably modified. This can be caused possibly by the lower symmetry: C_1 symmetry of **L1** versus C_3 of PPh$_3$. However, as DFT calculations showed, the band pattern should not differ so strongly (see Figure 8b). Perhaps the lone pair of the imine nitrogen atom of **L1** interacts in some way with the metal center. Bidentate coordination of such heteroaryl phosphines (imidazole or pyridine) with a second bonding interaction between nitrogen and ruthenium has been reported.[69–72] Nevertheless, we found that it does not substitute one carbonyl ligand. Relative band positions in the vibrational spectra obtained from DFT calculations on [Ru(CO)$_4$(PPh$_3$)] point to a tetracarbonyl complex (Figure 8a,b). The corresponding mass for the [Ru(CO)$_4$**L1**] structure was detected by ESI-MS. In this regard we observed a strong dependence of the extent of fragmentation on temperature and cone voltage during ESI-MS measurements. At higher values the complex is prone to CO dissociation. An optimum was found between 90 and 180 V. ^{1}H,^{15}N HMBC NMR spectroscopy was performed, and no significant shift was observed for the corresponding frequency of the imine nitrogen atom ($\delta(^{15}$N, free **L1**) = −99 ppm versus $\delta(^{15}$N, Ru/**L1**) = −97 ppm), which would otherwise implicate the coordination of nitrogen (for details, see Supporting Information SI-D).

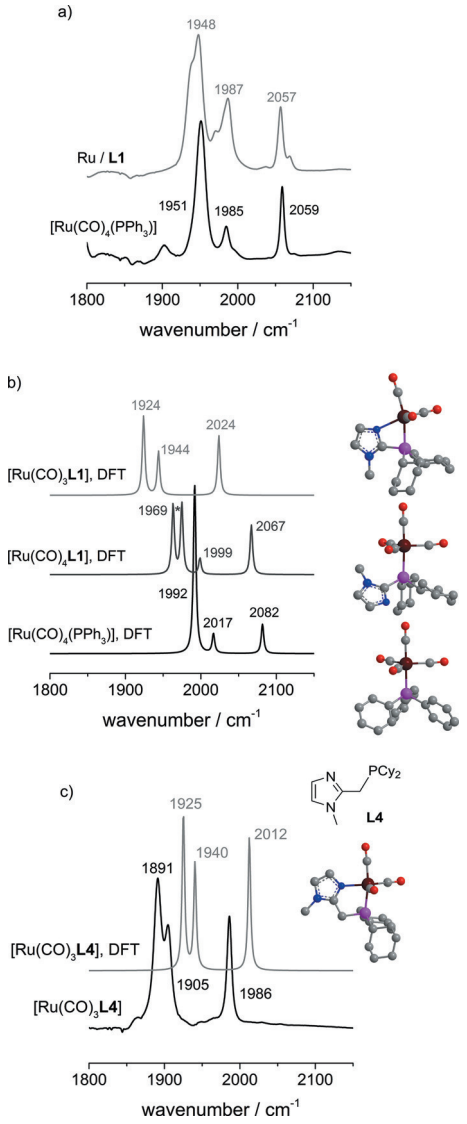


Figure 8. a) Comparison between experimental IR spectra for [Ru(CO)$_4$(PPh$_3$)] and Ru/**L1**. b) Calculated vibrational spectra for [Ru(CO)$_4$(PPh$_3$)], [Ru(CO)$_4$(**L1**)], and [Ru(CO)$_3$(**L1**)]. c) Experimental and calculated spectra for [Ru(CO)$_3$(**L4**)].

The following experimental results confirm the aforementioned assignment indirectly. We found that a monophosphine **L4**, which is similar to **L1** but has an additional methylene group between the phosphorus atom and the imidazolyl moiety, gives rise to a complex of the type [Ru(CO)$_3$**L**] in which the imine nitrogen atom substitutes one carbonyl ligand so that **L** coordinates in a bidentate fashion (see Figure 8c).[71] The molecular structure was verified by X-ray crystal structure analysis. In concert with this structure, an obvious shift in frequency for the imine nitrogen atom was found by ^{1}H,^{15}N HMBC NMR spectroscopy ($\delta(^{15}$N, free **L4**) = −117 ppm versus

$\delta(^{15}N, [Ru(CO)_3\mathbf{L4}]) = -194$ ppm). The corresponding IR spectrum is in accordance with the spectrum calculated by DFT methods. The band pattern of the experimental IR spectrum for Ru/**L4** deviates significantly from the pattern for Ru/**L1**, whereas a nearly identical spectrum would be expected considering the spectra of $[Ru(CO)_3\mathbf{L1}]$ and $[Ru(CO)_3\mathbf{L4}]$ calculated by DFT. From these results it can be concluded that in this case formation of the five-membered ring in $[Ru(CO)_3\mathbf{L4}]$ stabilizes the bidentate coordination.

Spectroscopic investigation of catalyst systems that showed poor catalytic performance

We performed in situ IR spectroscopic measurements on catalyst systems tested by Beller et al. that were characterized by poor hydroformylation activities compared to Ru/**L2**. Thus, in Ref. [20] inferior results were noted when the cyclohexyl groups of ligands were substituted by *tert*-butyl or adamantyl groups. The yields of aldehydes collapsed almost completely. Furthermore, when a 2-pyrrolyl group was incorporated instead of the 2-imidazolyl unit, a significant loss in activity was observed. Therefore, the ligands depicted in Figure 9 were selected for our IR spectroscopic experiments.

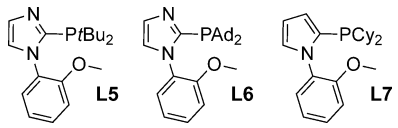


Figure 9. Selected monophosphines for which comparatively low activities in hydroformylation were found in Ref. [20].

In the preformation routine we heated the solution to 100 °C in the presence of carbon monoxide and hydrogen. The experiments with Ru/**L5** and Ru/**L6** gave a plausible rationalization for the observed poor catalytic performance. In the IR spectra, $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$ were observed as the dominant detectable ruthenium species (Figure 10). In the ^{31}P NMR spectra of the reaction solutions only the signals of the free ligands at $\delta(^{31}P) = 5.5$ ppm (Ru/**L5**) and $\delta(^{31}P) = 5.6$ ppm (Ru/**L6**) were found. Consequently, no ligand coordination took place at all with both ligands, and catalysis with unmodified catalysts occurred. By GC analysis[73] we determined yields for the *n*-aldehyde as the only product of about 2.7% (**L5**) with about 0.4% alkane formation and about 2.6% (**L6**) with about 0.4% alkane after 4 h. FTIR spectroscopic results are virtually identical to the findings for the phosphine-free system discussed above.

For the system with the pyrrole-substituted phosphine **L7** the *n*-aldehyde was formed regioselectively with a yield of 0.8% after 4 h with less than 0.1% of side products. The IR spectra clearly identified a mononuclear ruthenium(0) complex of the type $[Ru(CO)_4(\mathbf{L7})]$ (Figure 11). Thus, the lower catalytic activity in comparison to $[Ru(CO)_4(\mathbf{L2})]$ can probably be ascribed to the absence of the imine nitrogen atom. In the ^{31}P NMR spectrum of the depressurized solution, we observed

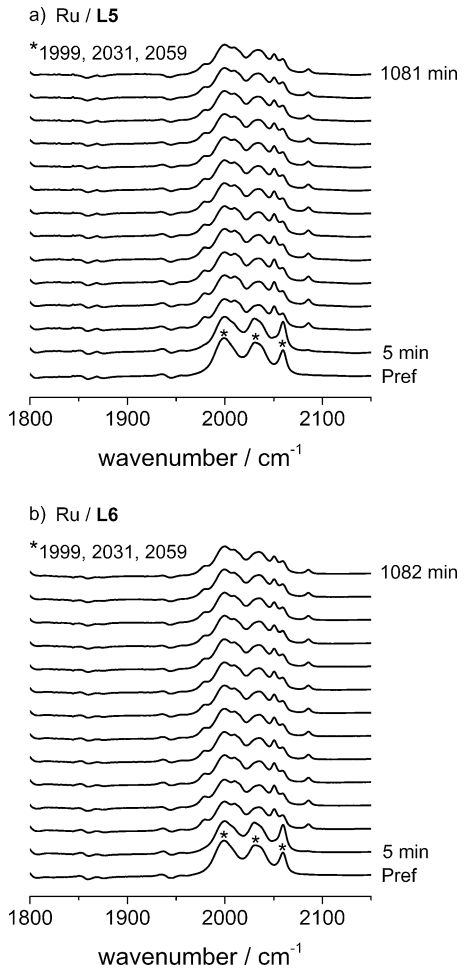


Figure 10. a) IR spectra for $[Ru_3(CO)_{12}]$/**L5** after a preformation phase of 60 min and during the hydroformylation of 3,3-dimethyl-1-butene. b) Same sequence of IR spectra for $[Ru_3(CO)_{12}]$/**L6**. Experimental conditions: $T = 100$ °C, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, $[Ru] = 4 \times 10^{-3}$ mol L^{-1}, $[\mathbf{L}] = 4.4 \times 10^{-3}$ mol L^{-1}, [alkene] = 0.9 mol L^{-1}, solvent = toluene.

a singlet signal at $\delta(^{31}P) = 48.9$ ppm ($\delta(^{31}P$, free ligand) $= -27.0$ ppm). From the ^{13}C NMR spectroscopic data of the carbonyl region, the assignment to the monophosphine complex is supported by the doublet splitting at $\delta(^{13}C$, Ru/**L7**) = 206.2 ppm (d, $^2J_{CP} = 3.4$ Hz).[74]

Characterization of ligand properties

From the spectroscopic data it is clear that ligand properties have a significant influence on the complexes formed and consequently on the catalytic performance. To characterize the ligands in more detail, we attempted 1) to determine the donor character of the phosphorus center by measuring the $^1J_{PSe}$ coupling constants of respective selenides and 2) to characterize the steric bulk by determining cone angles of the ligands from molecular structures obtained by DFT calculations.

The Lewis basicity of phosphines correlates with the magnitude of the $^1J_{PSe}$ coupling constants of the corresponding selenides.[75–78] Less-donating phosphines exhibit larger values of $^1J_{PSe}$ than electron-rich ones. Reaction of **L1**–**L3**, **L5**–**L7**, and

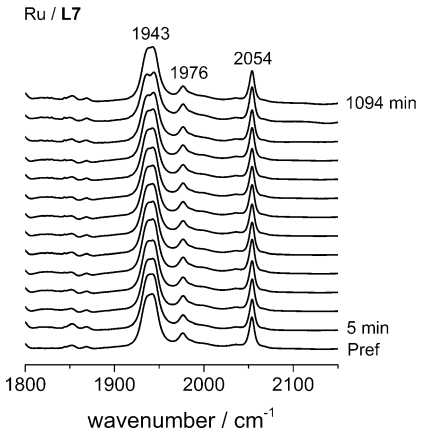


Figure 11. IR-spectra for [Ru(CO)$_4$(**L7**)] after preformation from [Ru$_3$(CO)$_{12}$]/**L7** and during the hydroformylation of 3,3-dimethyl-1-butene. Experimental conditions: $T = 100\,^{\circ}C$, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, [Ru] = 4×10^{-3} mol L^{-1}, [**L**] = 4.4×10^{-3} mol L^{-1}, [alkene] = 0.9 mol L^{-1}, solvent = toluene. The splitting of the band at 1943 cm^{-1} is probably caused by difficulties with the background substraction, because toluene has an intensive band at 1940 cm^{-1}. Additionally, band splitting can occur due to the C_1 symmetry of the ligand, because the vibrational mode at 1943 cm^{-1} is classified as E.

PPh_3 with three equivalents of selenium in toluene at 80 °C gave quantitative conversion to **L**-Se in 4.5 h. The $^{31}P,^{77}Se$ coupling constants obtained by ^{31}P NMR spectroscopy varied within a rather small range of 24 Hz (Table 2). Thus, comparable donor abilities of the phosphorus atoms can be assumed. Additionally, we calculated the energy for the HOMO (phosphine lone pair) of the ligands and nuclear NBO charges of the phosphorus atom by DFT calculations, which also are correlated with the basicity of the phosphines.[79–82] The HOMO energies and nuclear charges of the phosphorus atom exhibit comparable values with minor variations. Thus, the ligands under consideration represent a rather homogeneous series with respect to selected electronic properties. Compared to PPh_3, which was selected as a reference for which data are available in the literature,[79] they behave as better sigma donors.

Table 2. Electronic and steric properties of imidazole-substituted monophosphines.

L	$^1J_{PSe}$[a] [Hz]	HOMO energy[b]	NBO charge[c]	$\tilde{\nu}$(CO) [cm−1][d] ([Ni(CO)$_3$**L**], A_1)	Steric properties ECA [°]	G [%]
L1	723	−5.74 eV	+0.73	2074.9	137.3	31.8
L2	747	−5.79 eV	+0.75	2074.6	138.7	32.4
L3	747	−5.82 eV	+0.74	2071.1	154.6	39.0
L5	742	−5.75 eV	+0.73	2067.5	161.4	41.9
L6	735	−5.72 eV	+0.73	2067.5	161.0	41.7
L7	738	−5.48 eV	+0.77	2071.0	143.0	34.1
PPh_3	761	−5.94 eV	+0.79	2080.7	125.9	27.2

a) For selenides $R_2R'P{=}Se$. b) Energy of electron lone pair at phosphorus. c) NBO charge on P^{III} center. d) Uncorrected values.

The ligand structures might have different effects on the thermodynamic and kinetic stability of the respective ruthenium complexes. For the complexes Ru/**L5** and Ru/**L6** notably larger effective cone angles and G values in comparison to Ru/**L2** were calculated, which is in agreement with the experimental finding that no complexation with **L5** and **L6** occurred during the experiments (see Figure 10a, b). With regard to the steric properties of the ligands and the applied low ratio of [**L**]/[Ru] = 1.1 it would be interesting how an increase in phosphine concentration would affect the composition of complexes and the catalytic activity. Respective studies are underway.

We also calculated the A_1 frequencies of [Ni(CO)$_3$**L**] complexes, which are a measure of the net electronic effect including σ-donating and π-accepting properties.[83] Among the complexes with **L1**–**L3**, the electron density on the metal center for [Ni(CO)$_3$**L3**] is slightly higher. For the complexes with ligands **L5** and **L6**, somewhat lower frequencies were found in comparison with [Ni(CO)$_3$**L2**], so that in consequence the metal centers in Ni/**L5** and Ni/**L6** are more electron rich. The slightly lower frequency for [Ni(CO)$_3$**L7**] compared to [Ni(CO)$_3$**L2**] provides no direct explanation for the differences in the cocatalytic effect observed for Ru/**L7** and Ru/**L2**.

Because electronic differentiation between the ligands was not possible in a straightforward manner, steric effects and the interaction of the imine nitrogen atom with the ruthenium center may play a decisive role. Bidentate ligand coordination has not been proven here, but subtle interactions will affect the reactivity of respective 16-electron complexes, which are of importance for the catalysis. Such hemilabile behavior was reported for heteroaryl phosphines structurally similar to **L1**–**L3**.[69,84]

For the characterization of steric properties we used the program Solid-G for the determination of solid angles and the sphere shielded by the ligand in the ruthenium complexes (G value in percent).[85,86,82] For this we used optimized molecular structures of the complexes [Ru(CO)$_4$**L**] obtained from DFT calculations. The equivalent cone angles (ECA), which are calculated in Solid-G from solid angles, are normalized for an M–P distance of 2.28 Å. They are usually smaller than Tolman cone angles because the program Solid-G does not assume free rotation around the M–L axis. On comparing the ECA and G values of the ligands (**L1**, **L2**, **L3**), it is notable that **L3** shows significantly larger values (Table 2). This is in accord with the fact that, with respect to complexation under reaction conditions, the fraction of [Ru(CO)$_5$] is clearly higher than for Ru/**L1** and Ru/**L2** (Figure 7a). Direct clarification of the lower catalytic activity for the Ru/**L1** system relative to Ru/**L2** and Ru/**L3** could not be achieved here.

Comparison of NMR data for complexes formed in toluene and PC

Since we could not apply IR spectroscopy to characterize the ruthenium carbonyl complexes formed under hydroformylation conditions in PC, we used NMR spectroscopy in order to compare the results with those obtained with toluene as a solvent. The reaction of [Ru$_3$(CO)$_{12}$] with **L1**, **L2**, and **L3** under argon at 100 °C for 60 min led most probably to the same type of phosphido-bridged complexes, because we observed signals at $\delta(^{31}P) = 198.2$ (Ru/**L1**), $\delta(^{31}P) = 195.8$ (Ru/**L2**), and $\delta(^{31}P) =$

194.4 ppm (Ru/**L3**). The chemical shifts of the mononuclear complexes in PC with $\delta(^{31}P) = 33.2$ ([$Ru(CO)_4$**L1**]), $\delta(^{31}P) = 48.0$ ([$Ru(CO)_4$**L2**]), and $\delta(^{31}P) = 47.4$ ppm ([$Ru(CO)_4$**L3**]) are comparable to those measured in toluene. In addition, for specifically prepared samples, we observed signals in the ^{13}C NMR spectra in the carbonyl region with $\delta(^{13}C$,Ru/**L1**$) = 207.4$ (d, $^2J_{CP} = 1.7$ Hz), $\delta(^{13}C$,Ru/**L2**$) = 206.0$ (d, $^2J_{CP} = 3.0$ Hz), and $\delta(^{13}C$,Ru/**L3**$) = 206.4$ ppm (d, $^2J_{CP} = 2.9$ Hz) that showed the expected doublet splitting. Likewise, ^{15}N NMR chemical shifts are in accordance with a mononuclear complex of the type [$Ru(CO)_4$**L**]. Respective NMR data are given in the Supporting Information SI-D. The catalytic activity in PC as solvent (Table 3) was significantly higher than that obtained in toluene.[20] Reaction rates are lower for 3,3-dimethyl-1-butene compared with 1-octene, which was used as substrate in the aforementioned study.[20,67] The same relative trend in activity was found as observed for toluene as solvent: the system Ru/**L2** showed the highest activity followed by Ru/**L3** and then Ru/**L1** (cf. Table 1).

Table 3. Results from catalytic experiments by GC analysis. Reaction conditions: [Ru] = 4×10^{-3} mol L^{-1}, [**L**] = 4.4×10^{-3} mol L^{-1}, [alkene] = 0.9 mol L^{-1}, $T = 100\,^{\circ}C$, $p(CO) = 2.0$ MPa, $p(H_2) = 4.0$ MPa, solvent = PC.

System	*n*-Aldehyde [%] (linearity)	Alkane [%]	Alcohol [%]	Reaction time [min]
Ru/**L1**	42.6 (>99)	0.5	<0.1	240
Ru/**L2**	93.3 (>99)	0.8	0.7	240
Ru/**L3**	69.1 (>99)	1.1	0.2	240
Ru/–	3.9 (>99)	0.5	<0.1	240

Conclusion

To find a rationalization for the outstanding catalytic performance of monodentate phosphine ligands in various types of ruthenium-catalyzed hydroformylation reactions discovered by Beller et al., we conducted a spectroscopic/DFT study. We found that mononuclear ruthenium(0) carbonyl complexes of the type [$Ru(CO)_4$**L**] (**L** = imidazole-substituted monophosphines: **L1**, **L2**, **L3**) are the dominant species during the hydroformylation of 3,3-dimethyl-1-butene. Additional ligand-modified complexes were not detected. At a ligand/ruthenium ratio of nearly one, a mixture of [$Ru(CO)_4$**L**] and [$Ru(CO)_5$] was formed in dependence on the steric properties of the ligand. For preformation of the mononuclear complexes it is decisive to start the heating process in the presence of carbon monoxide. Heating under argon leads to P–C cleavage of the phosphine and to the formation of inactive and fairly stable phosphido-bridged complexes! For catalytically active mononuclear complexes data from ^{15}N NMR, ESI-MS, and IR spectroscopy proved that the unsubstituted nitrogen atom of the imidazolyl moiety does not replace a carbonyl ligand. Remarkably, on using ligands with *tert*-butyl and adamantyl groups instead of cyclohexyl, no coordination of the ligands occurred. On utilization of a pyrrole derivative a complex of the type [$Ru(CO)_4$**L7**] was also formed, but the catalytic performance was deteriorated. Since we did not find strong differences in the donor behavior and steric properties compared to **L2**, the disparate hydroformylation activity found by Beller and co-workers induced by different ligands may be attributable to a subtle interaction between the imine nitrogen atom of the imidazolyl unit and the ruthenium center. From NMR measurements with selected systems evidence could be derived that in PC as solvent the same ruthenium complexes are dominant. Noteworthily, compared to the reactions in toluene a significant increase in catalytic activity was found in PC, which remains to be clarified. However, for a further study on the correlation between the kinetics and the detectable metal carbonyl complexes, as well as for the design of new ligands, our results are an important basis.

Experimental Section

Materials

Dried toluene (>99%) was taken from the dispensing system PureSolv MD7 from Innovative Technologies. Propylene carbonate (>99%) from Sigma-Aldrich was flushed with argon and dried over molecular sieves. 3,3-Dimethyl-1-butene (>99%, GC) was purchased from Sigma-Aldrich and distilled in an argon atmosphere over sodium. The internal GC standard dodecane (>99%, Sigma Aldrich) was stored over Sicapent (Merck) and distilled under vacuum. The catalyst precursor [$Ru_3(CO)_{12}$] (99%, Strem) was stored under argon. Imidazolyl monophosphines were obtained from Beller et al. at LIKAT and stored under argon.[18–22] The internal IR standard diphenyl carbonate (99%, Aldrich) and triphenylphosphine (99%, Aldrich) were used as received. The following gases were used in this study: synthesis gas (CO/H_2 1/1, from 99.997% carbon monoxide and 99.999% hydrogen, Linde), carbon monoxide (99.997%, Linde), hydrogen (99.9993%, Linde), and argon (99.999%, Linde).

Devices and procedures

All preparations of solutions and transfers were carried out under argon atmosphere by using standard Schlenk techniques. In situ IR experiments for the study of homogeneously catalyzed hydroformylation were performed in a semibatch reactor system equipped with a pressurizable and heatable transmission flow-through IR cell (Dr. Bastian Feinwerktechnik GmbH, Wuppertal, Germany) and an automated sampling device collecting GC samples (amplius GmbH, Rostock-Warnemünde, Germany). The reactor consisted of a 200 mL stainless steel autoclave with a gas-entrainment impeller and an oil-bath thermostat (Premex Reactor AG, Leimen, Germany). A high-pressure syringe pump (PHD Ultra 4400, Harvard Apparatus GmbH, March-Hugstetten, Germany) with a 20 mL syringe made of stainless steel was used for injection of the alkene. Circulation of the liquid reaction solution through the IR cell was realized by a micro gear pump (mzr-7255, HNP Mikrosysteme GmbH, Parchim, Germany). A Bruker Tensor 27 FTIR spectrometer with a MCT-A detector was used for the IR spectroscopic measurements. For the IR cell we used CaF_2 as window material and a 0.1 mm spacer. A scheme of the HP FTIR apparatus can be found elsewhere.[40] The micro gear pump was set to 2333 rpm (displacement volume: 48 μL).

Hydroformylation experiments

Toluene (or PC) solutions of $[Ru_3(CO)_{12}]$, phosphine ligand, diphenyl carbonate as internal IR standard, and dodecane as internal GC standard were transferred into the autoclave. Because of the lower solubility of $[Ru_3(CO)_{12}]$ at room temperature, the solutions were heated and handled at 50 °C. Preformation routine 1: the solution was heated to 100 °C prior to the addition of the gases. Then the argon atmosphere was substituted with carbon monoxide and a partial pressure of $p(CO) = 2.0$ MPa was set. Hydrogen with $p(H_2) = 4.0$ MPa was added. Preformation routine 2: at 50 °C the argon atmosphere was replaced by carbon monoxide. The partial pressure of the gas components was set to $p(CO) = 2.0$ MPa and $p(H_2) = 4.0$ MPa. After the preformation reaction was accomplished, the pressure was released to 2.4 MPa ($p(CO) = 0.8$ MPa, $p(H_2) = 1.6$ MPa). The alkene was then injected through the syringe pump and the partial pressures were again set to $p(CO) = 2.0$ MPa and $p(H_2) = 4.0$ MPa. Olefin injection was taken as the reaction start.

FTIR spectra were recorded between 3950 and 700 cm^{-1} with a spectral resolution of 2 cm^{-1}. Ten scans were collected per FTIR spectrum (double-sided, forward–backward). The mirror speed was set to 40 kHz.

GC analyses were performed with a 7890A GC System from Agilent Technologies with a Petrocol DH 150 column (Supelco, Inc.).

NMR experiments

$^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were collected with a Bruker ARX-300 or ARX-400 spectrometer and referenced internally to the deuterated solvents. For $^{31}P\{^1H\}$ NMR chemical shifts, 85% H_3PO_4 was used as an external standard. Further details of $^1H,^{15}N$ HMBC NMR measurements are given in the Supporting Information.

ESI mass spectrometry

The ESI-MS spectra were recorded with a 6210 Time-of-Flight LC/MS system from Agilent. Acetonitrile and methanol were used as eluents for polynuclear and mononuclear complexes, respectively. Complexes were prepared in the same solvents. Further details are given in the Supporting Information.

X-ray crystal structure analysis

Diffraction data were collected with a Bruker Kappa APEX II Duo diffractometer by using $Mo_{K\alpha}$ radiation. Further details are given in the Supporting Information (SI-C). CCDC 1419829 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Computational details

Geometry optimizations and frequency calculations were performed with the Turbomole V6.3.1 program package.[87] For the calculation of vibrational spectra, DFT calculations were carried out with the BP86[88] functional and def-SV(P)[89] basis set on all atoms. For the determination of orbital energies the B3LYP[90] functional and def-TZVP[89] basis set on all atoms were used. No scaling factor was used for the correction of the calculated wavenumbers. Natural Bond Orbital (NBO)[91] analysis was performed for the calculation of NBO charges, as implemented in Turbomole V6.3.1.

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Keywords: homogeneous catalysis · hydroformylation · IR spectroscopy · P ligands · ruthenium

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