Ionic diamine rhodium(I) complexes—highly active catalysts for the hydroformylation of olefins†

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Rhodium(I) complexes composed of an anionic rhodium centre containing chloride ligands, and a cationic rhodium centre coordinated by a diamine ligand, were synthesized and characterized. These complexes are able to catalyze the hydroformylation reaction under mild reaction conditions in excellent activity and regioselectivity, and in the absence of a phosphorus ligand.

The metal-catalyzed hydroformylation reaction is one of the most useful chemical processes for the production of linear or branched aldehydes by the reaction of alkenes, carbon monoxide, and hydrogen. Commercially, more than seven million tons of aldehydes and alcohols are produced by homogeneous hydroformylation per year.[1]

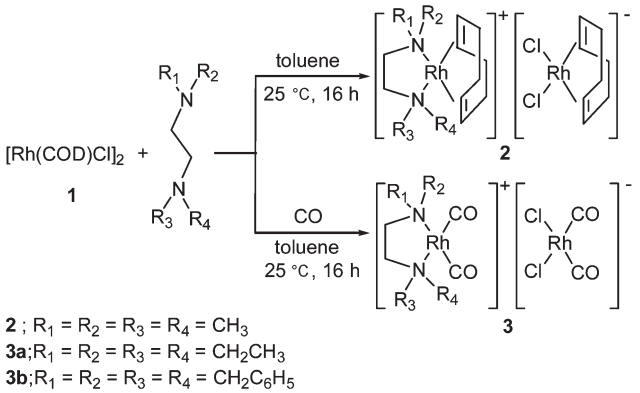
The most frequently used catalyst system for hydroformylation is a rhodium complex with phosphorus compounds as added ligands.[2] Many kinds of phosphorus ligands have been synthesized, and applied as auxiliary ligands for rhodium-catalyzed hydroformylation reactions to improve activity, regioselectivity, and stereoselectivity.[3] The drawbacks of using most phosphorus ligands are that larger than stoichiometric amounts are often required to achieve good selectivity, and reaction conditions can be harsh in some cases. These problems tend to limit the application of hydroformylation for the preparation of functionalized organic molecules. However, relatively few results have been published concerning cooperative effects involving several metal centers for the rhodium catalyzed hydroformylation,[4] as well as the use of rhodium without ancillary ligands.[5]

We now describe the first application of ionic rhodium(I) diamine complexes for the hydroformylation reaction. These rhodium complexes are composed of an anionic rhodium center containing chloride ligands, and a cationic rhodium center coordinated by a diamine ligand. These complexes are able to catalyze the hydroformylation reaction under mild reaction conditions in excellent activity and regioselectivity, and in the absence of a phosphorus ligand. It should be noted that ruthenium carbonyl carboxylates with nitrogen containing ligands have been used for hydroformylation but the yields are rather modest.[6]

The reaction of the rhodium complex $[Rh(COD)Cl]_2$, **1** (COD: 1,5-cyclooctadiene) with the bidentate N-donor ligand, *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) in toluene at 25 °C for 16 hours, afforded the ionic complex $[Rh(TMEDA)(COD)]^+[Rh(COD)Cl_2]^-$, **2** in 90% yield (Scheme 1).[7] Fig. 1 shows the crystal structure of complex **2**.‡ The chlorine ligands of **2** reside in the anion, and the cationic rhodium center is coordinated by both the olefin and diamine ligands. The bond angles of N–Rh–N′ and Cl–Rh–Cl′ are 83.11° and 89.63°, respectively. This indicates that the core structure has a distorted square planar configuration.

In contrast, no reaction occurred when **1** was treated with *N*,*N*,*N*′*N*′-tetraethylethylenediamine (TEEDA) or *N*,*N*,*N*′*N*′-tetrabenzylethylenediamine (TBzEDA) even under reflux conditions.

The ionic rhodium carbonyl complexes, **3a** and **3b** were formed by the reaction of **1** with TEEDA or TBzEDA respectively, under CO pressure at room temperature (See ESI†). These complexes have structures similar to those of complex **2** with the chlorine atoms localized in the anion, and diamine coordinated cationic rhodium centers.



Scheme 1 Synthesis of diamine–rhodium complexes.

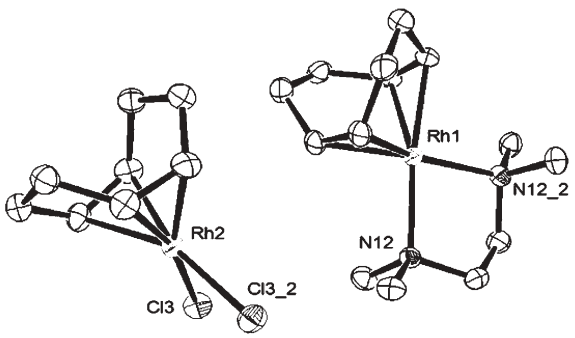


Fig. 1 Thermal ellipsoid representation of [(TMEDA)Rh(COD)][(COD)$RhCl_2$], **2**. Selected bond angles [°]; N(12)–Rh(1)–N(12_2) = 83.11(18), Cl(3)–Rh(2)–Cl(3_2) = 89.63(6).

† Electronic Supplementary Information (ESI) available: Experimental details—general procedure for the hydroformylation reaction and synthesis of catalysts. See http://www.rsc.org/suppdata/cc/b5/b502435h/

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Table 1 Hydroformylation of styrene and vinyl acetate catalyzed by diamine–rhodium complexes[a]

Entry	Catalyst	Olefins	Olefin/cat. ratio	Temp./°C	Conv.[b] (%)	B/L ratio[c]
1	**1**	Styrene	500	25	<5	—
2	**1**	Styrene	1000	45	14	21
3[d]	**1** + Et_3N	Styrene	500	25	30	30
4	**2**	Styrene	500	25	99>	39
5	**2**	Styrene	1000	25	60	28
6	**3a**	Styrene	1000	25	55	30
7	**3b**	Styrene	1000	25	42	28
8	**2**	Styrene	1000	45	99>	14
9	**2**	Styrene	2000	45	99>	14
10	**2**	Styrene	3000	45	85	16
11	**3a**	Styrene	1000	45	99>	13
12	**3b**	Styrene	1000	45	99>	13
13	**1**	Vinyl acetate	500	25	<5	—
14	**1**	Vinyl acetate	1000	70	45	16
15[e]	**2**	Vinyl acetate	500	25	73	21
16	**2**	Vinyl acetate	1000	45	91	18
17	**2**	Vinyl acetate	1000	70	99>	19
18[e]	**3a**	Vinyl acetate	500	25	49	24
19	**3a**	Vinyl acetate	1000	70	60	18
20[e]	**3b**	Vinyl acetate	500	25	21	41
21[f]	**3b**	Vinyl acetate	500	25	37	40
22	**3b**	Vinyl acetate	1000	70	99>	23

[a] Reaction conditions: catalyst (10 mg), toluene (10 mL), CO/H_2 (500/500 psi g), 16 h. See ESI for the general procedure. [b] Determined by GC and ^{1}H NMR. [c] Branched/linear ratio; determined by ^{1}H NMR. [d] 0.02 mmol of **1** and 0.02 mmol of Et_3N were used for reaction. [e] 22 h reaction time. [f] 48 h reaction time.

The catalytic activity of these rhodium complexes was evaluated for the hydroformylation of various olefins. Table 1 shows the hydroformylation results for styrene and vinyl acetate. Rhodium complexes **2**, **3a**, and **3b** exhibit excellent catalytic activity and selectivity for the hydroformylation of styrene even at room temperature (entries 4–7), while complex **1** shows poor activity (entries 1, 2). The high activity and selectivity showed by the ionic rhodium complexes under mild reaction conditions is a competitive advantage of the ionic complexes as hydroformylation catalysts.

$$L_3RhCl + H_2 + CO + R_3N \rightleftharpoons L_3Rh(CO)H + (R_3NH)^+Cl^- \quad (1)$$

The addition of a base such as a tertiary amine has been known to induce a strong promotion effect on the formation of rhodium hydride species (eqn. 1).[8]

The activity of the catalyst system with **1** and Et_3N was tested to elucidate the role of the diamine ligand, but it showed poor activity (30% conversion) compared to the use of ionic rhodium complexes reacted under the same conditions (entry 3). This result supports the observation that the diamine ligand does not act as a Lewis base and the catalytic function of the ionic complex is different from that of the **1** and Et_3N catalyst system.

When the reaction temperature was increased to 45 °C, the activity increased with moderate loss of selectivity (more than 90% branched aldehyde, entries 8–12). When the substrate/catalyst ratio was increased to 3000, the catalytic activity and selectivity were retained (*e.g.* conversion is 85% and selectivity for the branched aldehyde is 94%, entry 10).

In the case of vinyl acetate, complex **2** and **3a** show good activity and selectivity. However complex **3b**, containing the sterically hindered rhodium cation, is much less active as a catalyst but the selectivity is excellent at 25 °C (entries 20, 21). This result indicates that the diamine ligand is retained in the original coordination position, and this affects the access of the substrate to the rhodium center. When the reaction temperature was increased to 70 °C, the activity increased with a slight loss of selectivity (more than 95% branched aldehyde) and there is no activity difference between complexes **2**, **3a**, and **3b** (entries 17, 19, 22). These results suggest that the reaction pathways may be different depending on the reaction temperature.

In order to determine the scope of the hydroformylation reaction catalyzed by ionic rhodium complexes, a variety of olefins were reacted at room temperature for 22 h, and the results are summarized in Table 2.

For all substrates, less than 1% of hydrogenated product is formed. All aryl olefins (styrenes and naphthalenes) are efficiently hydroformylated, with high selectivity for the branched aldehyde. The regioselectivity is similar for all styrenes irrespective of whether they contain electron withdrawing or donating groups. 4-Isobutylstyrene and 2-vinyl-6-methoxynaphthalene are also converted to branched aldehydes in high yield, both of which are important precursors to the nonsteroidal anti-inflammatory agents, ibuprofen and naproxen, respectively (entries 5, 7).[9]

Table 2 Hydroformylation of various olefins catalyzed by **2a**[a]

Entry	Substrate	Conversion[b] (%)	Selectivity[c] B/L ratio
1	1-Octene	99>	1
2	2,4-Dimethylstyrene	99>	27
3	4-Chlorostyrene	99>	21
4	4-Bromostyrene	99>	21
5	4-Isobutylstyrene	99>	26
6	2-Vinylstyrene	99>	28
7	2-Vinyl-6-methoxynaphthalene	99>	26
8	Vinyl benzoate	75	29
9	Isopropyl vinyl ether	37	3.5
10	2,2-Dimethyl-4-vinyl-1,3-dioxolane	46	2.5

[a] Reaction conditions: substrate (8.2 mmol), catalyst (0.016 mmol), toluene (10 mL), CO/H_2 (1000 psi g), temperature (25 °C), 22 h. [b] Determined by GC and ^{1}H NMR. [c] Determined by ^{1}H NMR.

While vinyl acetate and vinyl benzoate also show good conversions and selectivities, 1-octene reacts well but with no selectivity. Several functionalized olefins did not react under these conditions (for example phenyl vinyl sulfone, *N*-methylvinylacetamide), while isopropyl vinyl ether and 2,2-dimethyl-4- vinyl-1,3-dioxolane gave aldehydes in moderate yield but in quite low selectivity.

In conclusion, ionic diamine–rhodium complexes, which have a chloride localized anionic rhodium and a chlorine free cationic rhodium center, were synthesized and used as catalysts for the hydroformylation reaction. These complexes show excellent activity and regioselectivity without any phosphorus ligand, under very mild reaction conditions.

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Notes and references

‡ Crystal data. For complex **2**: $C_{11}H_{20}ClNRh$, M = 304.6, monoclinic, a = 10.9386(18), b = 9.6760(16), c = 11.3108(19), Å, U = 1181.0(3) Å^3, T = 205(2) K, space group $P2/n$, Z = 4, β cell angle = 99.428(3)°, absorption coefficient = 1.635 mm^{-1}, reflections collected = 7324, independent reflections = 2804 [$R_{(int)}$ = 0.0435], The final wR_2 was 0.0849 (all data). CCDC 264125. See http://www.rsc.org/suppdata/cc/b5/b502435h/ for crystallographic data in CIF or other electronic format.

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