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Communications

Rhodium Carbene Complexes: Highly Selective Catalysts for the Hydroformylation of Styrene Derivatives

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Summary: Two new carbene−rhodium complexes are reported that are active hydroformylation catalysts, giving very high selectivities for the branched isomer (>95:5) when vinyl arenes are used as substrates. The carbene analogue of Wilkinson's catalyst, [RhIMes-(PPh$_3$)$_2$Cl] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene), and the related carbonyl complex [RhIMes(PPh$_3$)(CO)Cl] were both prepared, and the latter was fully characterized using spectroscopic and crystallographic means.

The hydroformylation reaction is one of the most important catalytic reactions in industry that employs homogeneous metal complexes.[1] Its main use is the conversion of propylene into butanal, which is then used to prepare several other products, including paint solvents and plasticizers.[2] The hydroformylation reaction also has applications in the synthesis of pharmaceuticals and fine chemicals. With styrene derivatives as substrates, hydroformylation followed by oxidation of the aldehyde provides a useful method for the synthesis of 2-arylpropanoic acids such as ibuprofen.[3,4] Directed hydroformylation reactions have also been reported that are extremely useful for the preparation of a variety of aldehydes with high levels of stereocontrol.[5,6]

In all of these examples, achieving high selectivities

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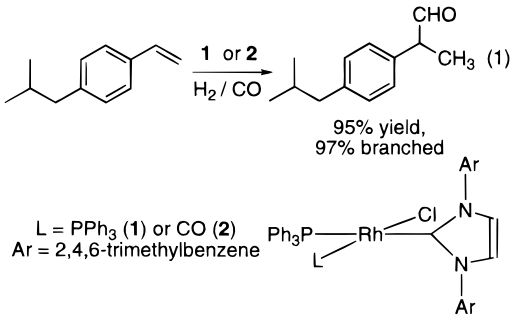
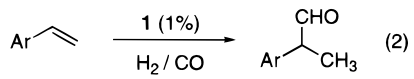
for either the branched or the linear isomer (depending on the application) is critical. Optimizing the branched/linear ratio is generally accomplished by altering the nature and the number of ligands on rhodium, which are usually phosphorus-based.[7] We report herein the first example of carbene rhodium complexes **1** and **2** as catalysts for the hydroformylation reaction.[8] These complexes are highly selective for the hydroformylation of styrene derivatives, giving up to 50:1 selectivity for the branched isomer (eq 1).



Rhodium complex **1** was prepared by treatment of IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)[9] with freshly recrystallized Wilkinson's complex ([RhCl(PPh$_3$)$_3$]). The resulting yellow solid was characterized by ^{1}H and ^{31}P NMR. In the ^{1}H NMR spectrum, the two ortho methyl residues on the IMes ligand are inequivalent. Saturation transfer experiments revealed that these two methyl groups are undergoing slow exchange on the NMR time scale.[10] In the ^{31}P NMR spectrum, two resonances with distinct ^{31}P−^{103}Rh coupling constants were observed at 48.7 and 35.4 ppm, attributable to triphenylphosphine ligands that are trans and cis to IMes. It is likely that the large bulk of the IMes ligand overrides the usual preference of [LRhCl(PPh$_3$)$_2$]-type derivatives of Wilkinson's complex to have the two phosphine ligands in a trans arrangement.[11] Complex **1** proved to be relatively sensitive to oxygen in solution, decomposing to give a green solution that contained uncomplexed PPh$_3$ along with triphenylphosphine oxide.

As phosphine lability is often beneficial to catalytic activity, we decided to assess the catalytic behavior of the IMes catalyst **1** in the hydroformylation reaction.

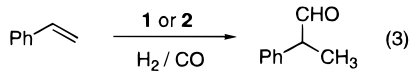
Table 1. Hydroformylation of Aromatic Olefins with Carbene Catalyst 1[a]



entry	Ar	loading (%)	yield[b] (%)	B:L[c]
1	Ph	1.0	85	96:4
2	*p*-MePh	1.0	88	94:6
3	*p*-ClPh	0.8	94	98:2
4	*p*-MeOPh	1.0	91	95:5
5	*p*-*i*-BuPh	1.1	95	97:3

[a] Reaction conditions: substrate (0.8 mmol), catalyst (ca. 1%), and solvent (5 mL, dry, deoxidized benzene) were treated with 500 psi of CO and 500 psi of H_2 at 60 °C for 20−22 h, except for entry 5 (16 h). [b] Isolated yield of chromatographically and spectroscopically homogeneous material. [c] B:L = branched:linear ratio.

Table 2. Hydroformylation of Styrene with Various Catalysts[a]



entry	cat.	additive	conversn[b] (%)	TOF[c]	B:L[d]
1	**1**	none	78	7	95:5
2	**2**	none	38	4	94:6
3	**2**	1 PPh$_3$	74	8	96:4
4	**2**	2 PPh$_3$	79	8	96:4
5	**2**	10 PPh$_3$	80	8	96:4
6	**3**[e]	2 PPh$_3$	27	3	88:12

[a] Reaction conditions: see Table 1 footnote, 0.5% catalyst loading employed for 19 h, except entry 1, which was run for 20 h. [b] conversn = conversion. [c] TOF = turnover frequency per hour. [d] B:L = branched:linear ratio. [e] Catalyst **3** = Rh(CO)Cl(PPh$_3$)$_2$.

As can be seen in Table 1, aromatic olefins are hydroformylated with extremely high branched to linear selectivities. The selectivities range from 94:6 for *p*-methylstyrene to 98:2 for *p*-chlorostyrene.[12] Although **1** displays good selectivity, its reactivity is marginal. As shown in Table 2, under the conditions studied, approximately 7 turnovers/h are obtained.

During hydroformylation, the originally bright yellow suspension of **1** in benzene was converted into a homogeneous, pale yellow solution that underwent no appreciable color change with time, provided that an inert argon atmosphere was maintained. This prompted us to prepare and isolate the corresponding carbonyl complex. Indeed, rhodium complex **2**, a pale lime yellow powder, could be readily prepared by passing a stream of CO through a THF solution of **1**. The resulting complex (**2**) is highly stable, and no special precautions were required in its manipulation. In the ^{1}H NMR spectrum of complex **2**, the two ortho methyl substituents on IMes are equivalent. The ^{31}P NMR spectrum of **2** contained, as expected, only one phosphine doublet at 31.7 ppm, with a ^{31}P−^{103}Rh coupling constant of 115 Hz, consistent with a phosphine ligand trans to the IMes.[13] X-ray-quality crystals were grown by layering

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(12) Hydroformylation of aliphatic olefins was also performed with limited success. For example, with 1-octene as substrate, a linear to branched ratio of 2.7:1 was obtained. Conversion was quantitative after 16 h; the yield of the aldehyde was determined to be 97% (NMR yield, with hexamethylbenzene as internal standard) and was not accompanied by isomerization.

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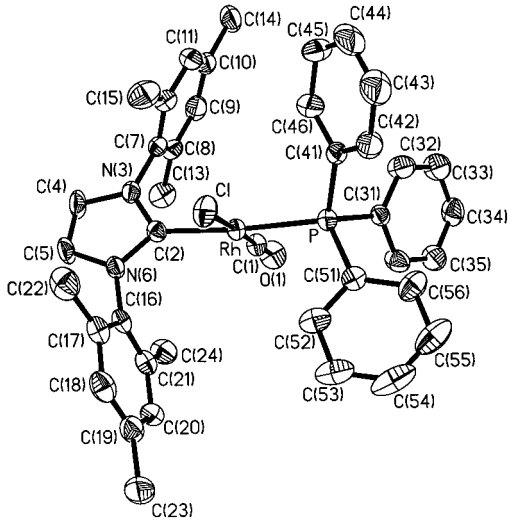


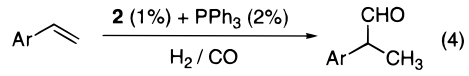
Figure 1. Thermal ellipsoids and numbering scheme for **2**. Ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−C(2), 2.032(4); Rh−C(1), 1.704(15); Rh−P, 2.3016(12); Rh−Cl, 2.396(6); C(1)−Rh−C(2), 91.5(7); C(1)−Rh−P, 92.6(7); C(2)−Rh−P, 174.46(12); C(1A)−Rh−ClA, 176.8(7); C(2)−Rh−Cl, 89.3(2); P−Rh−Cl, 86.9(2).[14]

a dichloromethane solution of **2** with pentane at −25 °C (Figure 1).

The X-ray crystal structure reveals a distorted-square-planar Rh center (sum of bond angles around Rh 360.19°) and a trans relationship between the IMes and PPh_3 ligands. The C(2)−Rh−P tensor is 174.46(12)° and deviates slightly from linearity. The Cl and CO positions are disordered and were refined with site occupancies of 0.55 and 0.45, respectively. The Rh−C(2) distance of 2.032(4) Å and the Rh−P distance of 2.3016(12) Å is in accord with expected values.[9,15] The bulky mesityl substituents adopt a propeller-like arrangement, forming dihedral angles of 81.3 and 75.5° with respect to the central imidazole ring.

In the hydroformylation reaction, complex **2** is approximately half as active as **1**, but the selectivity is essentially retained (compare entries 1 and 2 in Table 2). Gratifyingly, activity could be recovered by the addition of triphenylphosphine. In comparison with the corresponding Rh−phosphine complex $Rh(CO)Cl(PPh_3)_2$ (**3**), carbene catalyst **2** is approximately twice as active and gives higher selectivity for the branched isomer (compare entries 4 and 6 in Table 2). Under optimized conditions, a variety of vinyl arenes could be hydroformylated to give the corresponding aldehydes as shown in Table 3.

Table 3. Hydroformylation of Vinyl Arenes with Carbene Catalyst 2[a]



entry	Ar	yield[b] (%)	B:L[c]
1[d]	Ph		96:4
2	*p*-MePh	96	96:4
3	*p*-ClPh	94	97:3
4	*p*-MeOPh	98	95:5
5[e]	*p*-*i*-BuPh	93	96:4

[a] Reaction conditions: see Table 1 footnote, reaction time 22 h. [b] Isolated yield of chromatographically and spectroscopically homogeneous material. [c] B:L = branched:linear. [d] 0.5% catalyst used. [e] 2% catalyst used.

In conclusion, we have successfully prepared two new rhodium carbene catalysts capable of hydroformylating vinylarenes with high selectivity for the branched isomer. The preparation of an asymmetric version is currently underway.

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Supporting Information Available: Tables giving data and details of the crystal structure determination for **2** and text giving spectral data for **1** and **2** and experimental procedures for the synthesis of **1** and **2**, as well as for the hydroformylation reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal data for **2**: $C_{40}H_{39}ClN_2OPRh$, crystal size 0.04 × 0.20 × 0.27 mm, monoclinic, $P2_1/c$, a = 17.7743(14) Å, b = 13.7175(11) Å, c = 15.0069(12) Å, β = 92.818(2)°, V = 3654.5(5) Å^3, Z = 4, 2θ(max) = 52.8°, ω scans, 17 895 reflections scanned, 7485 unique reflections (R(int) = 0.0954), T = 293(2) K, full-matrix least squares on F^2, wR2 = 0.0712, R1 = 0.0436. Full details for the crystallographic analysis of **2** are described in the Supporting Information.

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