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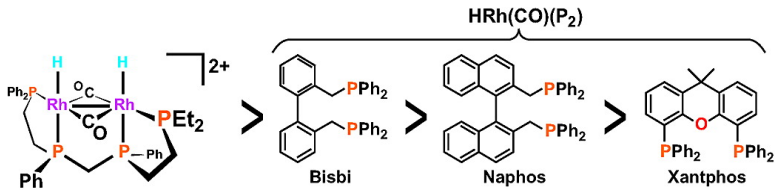

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Polar Phase Hydroformylation: The Dramatic Effect of Water on Mono- and Dirhodium Catalysts

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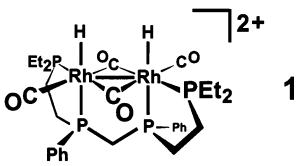
Hydroformylation (also called oxo) is the catalytic reaction of alkenes, H_2, and CO to produce linear (normal) or branched (iso) aldehyde products.[1] One of the major problems with most homogeneous catalytic processes involves the separation of product from catalyst. This has led to considerable research on novel solvents and modified catalysts that allow the facile separation of catalyst and product: aqueous phase hydroformylation using water-soluble sulfonated triphenylphosphine (TPPTS),[2] supported aqueous-phase variants,[3] fluorocarbon solvents and soluble rhodium catalysts,[4] catalysis in liquid or supercritical CO_2,[5] and most recently supported ionic liquid systems.[6] We report here that the addition of 30% water by volume to acetone creates a simple polar-phase solvent system that produces 30−115% rate enhancements for the hydroformylation of 1-hexene with a variety of monometallic rhodium phosphine catalysts, and a 265% rate increase for a dirhodium tetraphosphine catalyst along with considerably improved chemoselectivity to aldehyde products.

[*rac*-Rh_2(nbd)$_2$(et,ph-P4)](BF_4)$_2$ (nbd = Norbornadiene, et,ph-P4 = ($Et_2CH_2CH_2$)(Ph)PCH_2P(Ph)($CH_2CH_2PEt_2$)) reacts with H_2/CO to generate an active and regioselective dirhodium catalyst proposed to be [*rac*-$Rh_2H_2(\mu$-CO$)_2$(CO)$_4$(et,ph-P4)]$^{2+}$, **1**, that operates via highly effective homobimetallic cooperativity.[7] This dicationic catalyst works best in a polar solvent such as acetone.



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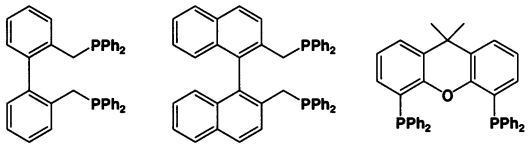
The hydroformylation of 1-hexene using **1** and some of the best monometallic Rh−ligand combinations are presented in Table 1. The phosphine ligands used include PPh_3, Bisbi,[8] Naphos,[9] and Xantphos.[10] The very effective bulky bisphosphite ligand developed



by Billig at Union Carbide was not included due to its sensitivity to fragmentation by water.[11] Hirsch has reported an extensive comparison of these and other Rh catalysts in toluene under somewhat different conditions.[12]

1 with 30% water in acetone (volume basis) gave the fastest initial turnover frequency (TOF) of 73 min^{-1} with a 33:1 linear: branched (L:B) aldehyde ratio (constant throughout the catalytic run) with virtually no alkene isomerization and hydrogenation side reactions (less than 0.2%). This is in marked contrast to **1** in pure acetone that gives an initial TOF of 20 min^{-1}, 25:1 L:B aldehyde regioselectivity, and 2.5% alkene isomerization and 3.4% hydrogenation. The initial TOF in pure acetone is almost twice as fast as originally reported.[7a,13]

Table 1. Hydroformylation Data Comparing Various Rh Catalysts (1 mM) Using 1-Hexene (1 M) at 90 °C and 6.2 bar 1:1 H_2/CO in Acetone with and without Added Water[a]

catalyst	% H_2O	Initial TOF (min^{-1})	aldehyde L:B	% iso
1	0	20(1)	25:1	2.5
1	30	73(1)	33:1	< 0.5
Rh/PPh_3[b]	0	13(1)	9.1:1	< 0.5
Rh/PPh_3[b]	30	17(1)	14:1	1.0
Rh/Bisbi[c]	0	25(2)	70:1	< 0.5
Rh/Bisbi[c]	30	37(1)	80:1	2.0
Rh/Naphos[c]	0	27(1)	120:1	1.5
Rh/Naphos[c]	30	35(1)	100:1	2.2
Rh/Xantphos[c]	0	13(2)	80:1	5.0
Rh/Xantphos[c]	30	28(1)	60:1	< 0.5

[a] **1** generated from [*rac*-Rh_2(nbd)$_2$(et,ph-P4)](BF_4)$_2$, constant pressure conditions, 1000 rpm, numbers in parentheses for the initial TOF are standard deviations derived from at least four consistent runs, % iso = alkene isomerization, hydrogenation side reactions all less than 0.5%, except for **1** in acetone where it is 3.4%. All reactions convert 98% or more of the starting alkene. [b] 0.4 M PPh_3 (400 equiv), 1 mM Rh(CO)$_2$(acac). [c] 5 equiv of ligand.

There is a dramatic drop-off in rate for **1** as the water content is increased past 30% (Supporting Information). This is likely due to the insolubility of the alkenes in the increasingly polar solvent. 1-Hexene, for example, is barely soluble in water, making it a very poor solvent for hydroformylation and a major limitation of the current water-soluble Rh-TPPTS industrial process where only smaller chain alkenes such as propylene can be used.

The results demonstrate that **1** in 30% water−acetone has the highest initial turnover frequency and the fewest side reactions, making it one of the fastest and most selective hydroformylation catalysts known. Although Rh−Naphos has a better aldehyde L:B ratio, there is also higher alkene isomerization that lowers the overall conversion. Note that the L:B aldehyde ratio tends to exaggerate the higher selectivities: 80:1 corresponds to 98.8% linear, while 33:1 is 97.1% linear aldehyde.

Interestingly, added water has a generally beneficial effect on the monometallic catalysts. There are 31, 48, and 30% rate increases for the PPh_3, Bisbi, and Naphos-based catalysts, respectively, upon addition of 30% water to the acetone solvent. The L:B aldehyde regioselectivity increases moderately for PPh_3 and slightly for Bisbi, but decreases a bit for Naphos. Somewhat higher alkene isomerization is seen for all three of these systems on addition of water. Because the catalytic rate is first order in alkene for each of these systems, a local increase in the nonpolar alkene concentration around the nonpolar catalyst enhanced by the polar solvent could explain the modest rate increases seen for these systems. Water is definitely causing this effect as the monometallic catalysts have the same activity and selectivity in either acetone or toluene.

Added water, however, causes a relatively dramatic 115% rate increase for the Rh−Xantphos system and a considerable decrease

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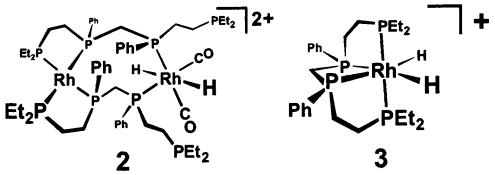
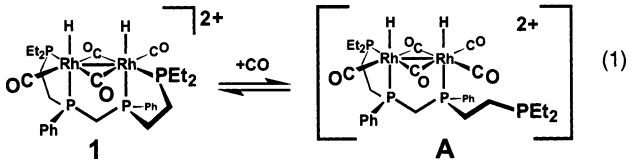
in the alkene isomerization side reaction. Van Leeuwen and co-workers have characterized cationic rhodium complexes where the central oxygen atom of the Xantphos ligand is coordinated to the metal and have shown that these are very poor hydroformylation catalysts.[14] We believe that the oxygen atom of the Xantphos ligand is also weakly coordinating to the neutral HRh(CO)(Xantphos) catalyst, leading to partial inhibition via the formation of a saturated five-coordinate complex (Supporting Information). The addition of water should engage in hydrogen bonding to the oxygen atom of the coordinated Xantphos ligand, inhibiting the internal Rh−O interaction and generating more of the active unsaturated HRh(CO)(η^2-Xantphos) catalyst that can react with alkene to start hydroformylation.

A key question is why does the added water have such a huge effect on the dirhodium catalyst **1**? This is proposed to be mainly due to effective inhibition of the fragmentation of bimetallic **1** into inactive complexes. *In situ* NMR spectroscopic studies have indicated that when **1** sits under H_2/CO, complexes **2** and **3** are formed, both of which are very poor hydroformylation catalysts.



2 **3**

These can both be generated via dissociation of one of the external phosphine chelate arms in **1** (eq 1) to form **A**, which leads to loss of the nonchelated rhodium atom. Either the resulting monometallic complex can dimerize to form the double-ligand dirhodium complex **2**, or the et,ph-P4 ligand can wrap around a single rhodium, forming the η^4-coordinated complex **3**. The closely related complexes [*rac*,*rac*-Rh_2(et,ph-P4)$_2$]$^{2+}$ and [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$ have been characterized.[15]



1 **A** (1)

The dramatically enhanced activity and reduced side reactions in the presence of water is consistent with inhibition of the initial phosphine dissociation from **1** that leads to catalyst fragmentation. HRh(CO)(TPPTS)$_3$, for example, has considerably slower phosphine dissociation equilibria in water relative to HRh(CO)(PPh$_3$)$_3$ in organic solvents.[16] A similar effect inhibiting the dissociation of the "nonpolar" PEt_3-like chelate arm into the highly polar water−acetone solvent is proposed here. Preliminary ^{31}P NMR *in situ* studies indicate dramatically reduced formation of fragmentation products **2** or **3** in 30% water−acetone.

Allowing the bimetallic catalyst solution to sit in pure acetone at 90 °C under 5.4−6.1 bar of H_2/CO, prior to alkene addition, leads to steadily decreasing catalyst activity. After 50 min **1** has only about 20% the activity of the 20-min system, and after 80 min there is essentially no hydroformylation activity. However, with 30% water in acetone, the catalyst can sit under H_2/CO at 90 °C for 2 h with only a small 10% loss in activity. In fact, during the initial ∼15−20 min of heating of the autoclave to the operating temperature of 90 °C, the catalyst is steadily fragmenting and deactivating in acetone. Thus, different initial heating times can lead to considerable fluctuations in the initial TOF for **1** when using acetone. The improved stability of the catalyst in 30% water−acetone is further indicated by the fact that one can easily perform 10 000 turnovers using 0.1 mM catalyst and 1.0 M 1-hexene (initial TOF = 60(3) min^{-1}, L:B = 29:1, 2% alkene isomerization, > 0.1% alkene hydrogenation).

Phase separation of the product heptaldehyde does occur for the catalytic runs using water at or in excess of 20% of the acetone volume, which was an important aspect of why a polar-phase solvent system was initially studied. Unfortunately, the dirhodium catalyst is more soluble in the heptaldehyde organic layer than in the water−acetone solvent. New tetraphosphine ligand systems that impose a considerably stronger chelate effect combined with higher polar (or ionic) solvent compatibility are being prepared to generate even more active and robust dirhodium catalysts for hydroformylation and related reactions.

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Supporting Information Available: Experimental details and additional schemes, table, and figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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