Zwitterionic Metal Complexes of the New Triphosphine $NaO_{3}S(C_{6}H_{4})CH_{2}C(CH_{2}PPh_{2})_{3}$ in Liquid Biphasic Catalysis: An Alternative to Teflon "Ponytails" for Facile **Catalyst Separation without Water**

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Summary: The new ligand $NaO_3S(C_6H_4)CH_2C(CH_2 PPh_{2}$ (sulphos) has been synthesized. The application of the zwitterionic Rh(I) complexes (sulphos)Rh(cod) and $(sulphos)Rh(CO)_2$ in liquid biphasic catalysis has been demonstrated for the hydrogenation of styrene and the hydroformylation of 1-hexene, respectively. The latter reaction gives C_7 alcohols in an alcohol/hydrocarbon system and C₇ aldehydes in an alcohol-water/hydrocarbon system. All rhodium is recovered in the polar phase at the end of the catalytic reactions.

In the field of liquid biphase catalysis, increasingly endeavors are being directed toward the elaboration of new techniques and new concepts in order to achieve selective chemical transformations and easy and efficient catalyst/product recovery.

An exciting approach to biphasic reactions has recently been developed by Horváth and Rabái.² The method is based on the limited miscibility of fluorinated solvents in hydrocarbons and the immobilization of the metal catalyst in the fluorocarbon phase by means of perfluoroalkylated phosphines (Teflon ponytails).

In this communication, we describe an alternative to fluorous biphasic systems for facile catalyst separation without water. Our strategy has involved the modification of a phosphine ligand, the tripodal triphosphine $MeC(CH_2PPh_2)_3$ (triphos) which has seen wide use in catalysis,³ so as to make its metal complexes exclusively soluble in light alcohols (e.g. methanol) which have low miscibility in hydrocarbons at room temperature.

The new ligand NaO₃S(C₆H₄)CH₂C(CH₂PPh₂)₃ (sulphos) is basically a triphos ligand with a hydrophilic tail attached to the bridgehead carbon atom. The synthesis of sulphos is outlined in Scheme 1. The procedure involves the treatment of benzyltris(chloromethyl)methane⁴ with concentrated H_2SO_4 (96%) at 100 °C, which results in the regioselective para sulfonation of the phenyl ring. Reaction of $NaO_3S(C_6H_4)CH_2C(CH_2-$



 $Cl)_3$ with KPPh₂ in DMSO at 100 °C gives sulphos, which is recovered as colorless needles after recrystallization from hot ethanol (65% yield based on the trichloride).5

The complexes $(sulphos)Rh(cod)^6$ (1; cod = 1,5-cyclooctadiene) and $(sulphos)Rh(CO)_2^7(2)$ have been prepared by following the procedures used for the synthesis of the analogous triphos complexes (Scheme 1). Because of the distance of the negative charge from the phosphorus donors, the coordination properties of sulphos do not significantly differ from those of triphos. However, the complexes which are cationic with triphos^{3a} are zwitterionic with sulphos, as this ligand can act as an internal counteranion itself. As a matter of fact, the main spectroscopic characteristics (NMR, IR) of the sulphos complexes are identical with those of the triphos

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⁽⁵⁾ Anal. Calcd for $C_{47}H_{42}NaO_3P_3S$ ($M_r = 802.82$): C, 70.32; H, 5.27; (b) Anal. Catch for $C_47142(\text{Ad}_3\text{F}_3\text{S}(M_1^- = 602.82))$. C, 70.327, H, 5.27, P, 51.27, C, 15.27, ppm, d, 7 Hz, 2H (m-H of NaO₃SPh)

ppm, d, 7 H2, 2H (*m*-H of Na0₃SPh). (6) Anal. Calcd for $C_{55}H_{54}O_3P_3RhS$ ($M_r = 990.21$): C, 66.65; H, 5.50; P, 9.38. Found: C, 67.08; H, 5.40; P, 9.51. ³¹P{¹H} NMR (20 °C, CD₂-Cl₂, 81.01 MHz): 5.80 ppm, d, $J_{RhP} = 104.5$ Hz. ¹H NMR (20 °C, CD₂-Cl₂, 200.13 MHz): 2.41 ppm, m, br, 4H (CH₂ of cod); 2.62 ppm, s, br, 6H (CH₂P); 2.78 ppm, m, br, 4H (CH₂ of cod); 3.12 ppm, s, br, 2H (PhCH₂C); 4.05 ppm, s, br, 4H (CH of cod); 6.92 ppm, br, 12H (o-H of PPh); 7.17 ppm, t, 5 Hz, 12H (*m*-H of PPh); 7.30 ppm, d, 8 Hz, 2H (o-H of $-O_3$ SPh); 7.34 ppm, t, 5 Hz, 6H (*p*-H of PPh); 7.94 ppm, d, 8 Hz, 2H (*m*-H of $-O_3$ SPh) (m-H of -O₃SPh)

⁽m-H of O_3SPh). (7) Anal. Calcd for $C_{49}H_{42}O_5P_3RhS$ ($M_r = 938.76$): C, 62.69; H, 4.51; P, 9.90. Found: C, 62.50; H, 4.43; P, 9.70. ³¹P[¹H] NMR (20 °C, CD₂-Cl₂, 81.01 MHz): 6.60 ppm, d, $J_{RhP} = 98$ Hz. ¹H NMR (20 °C, CD₂Cl₂, 200.13 MHz): 2.65 ppm, d, 8 Hz, br, 6H (CH₂P); 3.27 ppm, s, br, 2H (PhCH₂C); 7.04 ppm, br, 12H (o-H of PPh); 7.15 ppm, t, 6 Hz, (m-H of PPh); 7.27 ppm, t, 6 Hz, 6H (p-H of PPh); 7.35 ppm, d, 8 Hz, 12H (o-H of $-O_3SPh$); 8.01 ppm, d, 8 Hz, 2H (m-H of $-O_3SPh$). IR: ν_{CO} 1971 (sst) cm⁻¹.

Ta	ble	1.	Hyo	droforn	nylation	of 1	-Hexene	Catalyzed	by 2^a
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		product composition ^b				
entry	solvent	hexane, % ^c	aldehyde (amt, %)	alcohol (amt, %)		
1	methanol/isooctane (1:1, v:v)	24	heptanal (5) 2-methylhexanal (9) 2-ethylpentanal (3)	1-heptanol (43) 2-methylhexanol (14) 2-ethylpentanol (2)		
2	H_2O -methanol/isooctane (1:1:1, v:v:v)	46	heptanal (37) 2-methylhexanal (17)	1-heptanol (traces)		

^a Conditions: 80 °C, 5 h, 15 bar of CO, 15 bar of H₂, [cat] = 2.5×10^{-4} mol⁻¹, 1:100 catalyst to substrate ratio. ^b Analyzed as a unique phase obtained by addition of THF. ^c Mixture of hexenes: entry 1, hexane (2%), 1-hexene (10%), *trans*-2-hexene (49%), *cis*-2-hexene (24%), *trans*-3-hexene (14%), *cis*-3-hexene (1%); entry 2, hexane (2%), 1-hexene (24%), *trans*-2-hexene (52%), *cis*-2-hexene (19%), *trans*-3-hexene (3%), *cis*-3-hexene (1%).

complexes apart from the differences intrinsically due to the $^{-}O_{3}S(C_{6}H_{4})CH_{2}$ tail.^{3a}

The sulphos Rh complexes are not soluble in water, hydrocarbons, or diethyl ether, whereas they dissolve in light alcohols (MeOH, EtOH) or in 1:1 (v:v) alcoholwater mixtures. Most importantly, an alcohol phase containing either 1 or 2 (yellow color) is well-separated from a hydrocarbon phase (e.g. n-heptane) at room temperature, whereas a single homogeneous phase is observed as the temperature of the biphasic system is increased above 60 °C. Cooling the homogeneous solution back to room temperature gives phase separation again.⁸ This characteristic of sulphos complexes allows the quantitative recovery of the metal in the polar phase after 1 and 2 have been used as catalyst precursors in liquid biphasic systems.

A preliminary investigation of the potential of 1 and 2 in liquid biphasic catalysis has been carried out. Styrene is hydrogenated to ethylbenzene in the presence of 1 in a 1:1 (v:v) mixture of methanol and n-heptane (30 atm of H₂, 65 °C, 1:500 catalyst to substrate ratio, 3 h, conversion >90%). Complete disappearance of styrene occurs after a further 2 h of reaction. After cooling to room temperature, the separation of the two phases does not give complete organic product separation, whereas all the rhodium in the form of a soluble species, as yet unidentified,⁹ remains in the alcoholic phase.¹⁰ However, the simple addition of water leads to the complete elimination of ethylbenzene (as well as residual styrene, if any) from the alcoholic phase. Interestingly, the same catalytic activity for the hydrogenation of styrene is shown by 1 in pure methanol, which confirms that truly a homogeneous phase forms at the reaction temperature.

Table 1 summarizes the results obtained for the hydroformylation of 1-hexene catalyzed by 2 in either methanol/isooctane or methanol-water/isooctane. In the absence of water, the reaction (15 atm of H_2 , 15 atm of CO, 80 °C, 5 h) gives alcohols (1-heptanol, 2-methylhexanol, and 2-ethylpentanol) and aldehydes (heptanal, 2-methylhexanal, and 2-ethylpentanal) in an overall ratio of 78:22. For longer reaction times only alcohols are produced. The formation of alcohols is quite surprising, since rhodium catalysts typically only produce aldehydes (e.g. the triphos/Rh system).^{3a} The typical chemoselectivity is found in the presence of water, as only aldehydes are formed (heptanal and 2-methylhexanal in a 69:31 ratio), although with a lower turnover frequency. Most importantly, in this latter case, it is not necessary to add water for product separation as only traces of aldehydes (as well as all the rhodium)¹⁰ remain in the water/methanol phase after cooling to room temperature.

To the best of our knowledge, the overall characteristics of the present sulphos complexes have no precedent in the literature.

Current investigations center on the use of 1 and 2in other liquid biphasic catalytic processes (e.g. the hydrogenation of carbonylic componds in light of the capability of 1 to catalyze the reduction of aldehydes) as well as the design of other tail-sulfonated polydentate ligands, possibly bearing stereocenters for use in asymmetric liquid biphase catalysis.

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Supporting Information Available: Text giving experimental details of the synthesis and characterization of the ligand $NaO_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$ (sulphos) and of the new complexes described in this paper (4 pages). Ordering information is given on any current masthead page.

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⁽⁸⁾ In the absence of either 1 or 2, the methanol/n-heptane mixture does not form a homogeneous phase at a temperature as high as 65 °C.

⁽⁹⁾ Studies aimed at identifying the catalytically active species are currently in progress.

⁽¹⁰⁾ After the hydrocarbon layer was separated, the solvent was removed in vacuo and the residue was analyzed by ³¹P NMR spectroscopy and atomic absorption spectrometry. No appreciable amount of either phosphorus compounds or rhodium was detected.