[D$_6$]DMSO, 25 °C): $\delta = 2.34$ (s, 3H; CH$_3$), 5.67–5.69 (m, 2H; CH), 5.96 (t, ^3J(H,H) = 6.3 Hz, 1H; CH), 6.67 (d, ^3J(H,H) = 6.8 Hz, 1H; CH), 7.55 (d, ^3J(H,H) = 15.0 Hz, 1H; CH), 7.57 (dd, ^3J(H,H) = 7.3, 7.4 Hz, 2H; CH), 7.67 (t, ^3J(H,H) = 7.3 Hz, 1H; CH), 7.87 (d, ^3J(H,H) = 15.3 Hz, 1H; CH), 8.13 (d, ^3J(H,H) = 7.5 Hz, 2H; CH); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): $\delta = 18.76$ (CH$_3$), 91.77 (CH), 94.53 (CH), 95.39 (CH), 96.86 (CH), 100.11 (C$_{quat}$), 124.05 (CH), 128.75 (CH), 129.02 (CH), 133.64 (CH), 137.31 (C$_{quat}$), 138.32 (CH), 188.59 (C$_{quat}$), 233.65 (C$_{quat}$); MS (70 eV, EI): *m*/*z* (%): 358 (14) [M^+], 302 (5) [$M^+ - 2$CO], 274 (100) [$M^+ - 3$CO]; IR (KBr): $\tilde{\nu} = 1959$ cm^{-1} (CO), 1876 (CO), 1661 (C=O), 1588 (C=C). **4d**: M.p. 68 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): $\delta = 5.64$–5.84 (m, 5H, CH), 6.21 (d, ^3J(H,H) = 16.0 Hz, 1H; CH), 6.30 (d, ^3J(H,H) = 16.0 Hz, 1H; CH), 7.21 (d, ^3J(H,H) = 16.1 Hz, 1H; CH), 7.31 (d, ^3J(H,H) = 15.9 Hz, 1H; CH), 7.33–7.83 (m, 5H; CH); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): $\delta = 94.19$ (CH), 95.46 (CH), 95.75 (CH), 101.76 (C$_{quat}$), 125.70 (CH), 126.49 (CH), 128.74 (CH), 129.18 (CH), 130.86 (CH), 134.72 (C$_{quat}$), 140.30 (CH), 143.65 (CH), 188.06 (C$_{quat}$), 233.45 (C$_{quat}$); MS (70 eV, EI): *m*/*z* (%): 370 (19) [M^+], 314 (15) [$M^+ - 2$CO], 286 (100) [$M^+ - 3$CO]; IR (KBr): $\tilde{\nu} = 1965$ cm^{-1}(CO), 1886 (CO), 1651 (C=O), 1618 (C=C).

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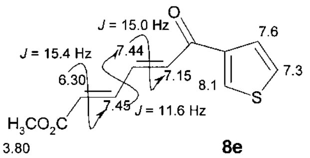

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Novel Water-Soluble Calix[4]arene Ligands with Phosphane-Containing Groups for Dual Functional Metal-Complex Catalysts: The Biphasic Hydroformylation of Water-Insoluble Olefins[**]

Shoichi Shimizu,* Seiji Shirakawa, Yasuyuki Sasaki, and Choichiro Hirai

The design and development of environmentally benign chemical processes has been the subject of growing attention, given the growing international consensus on green chemistry.[1] The Ruhrchemie–Rhône-Poulenc process[2] for the hydroformylation of propene, catalyzed by a water-soluble rhodium complex with triphenylphosphane trisulfonate (TPPTS, see Scheme 1) as a ligand, has been repeatedly discussed in the literature[3] because it allows the catalyst in the aqueous phase to be recycled by simple decantation, and the exclusive use of water as the reaction medium. However, its application is limited to olefins which have appreciable water solubility. To circumvent this problem, a variety of alternate strategies have been reported primarily for the hydroformylation of oct-1-ene. These include the addition of co-solvents,[4] promoter ligands,[5] or partially methylated β-cyclodextrins (β-CDs),[6] and the use of surface-active phosphanes,[7] thermoregulated phase-transfer catalysts,[8] or β-CD-modified diphosphanes[9] in place of TPPTS. None of these approaches have proved ideal, since all inevitably increase the difficulty of product separation[10] and, in addition for certain cases, a substantial decrease in activity takes place over consecutive catalytic cycles.

The approach described herein involves the use of novel water-soluble calix[4]arenes with phosphane-containing groups, named phosphacalix[4]arenes,[11] as ligands for dual functional metal-complex catalysts. Our hypothesis was that water-soluble phosphacalix[*n*]arene–metal complexes would function not only as homogeneous metal catalysts but also as inverse phase-transfer catalysts,[12, 13] which facilitate reactions

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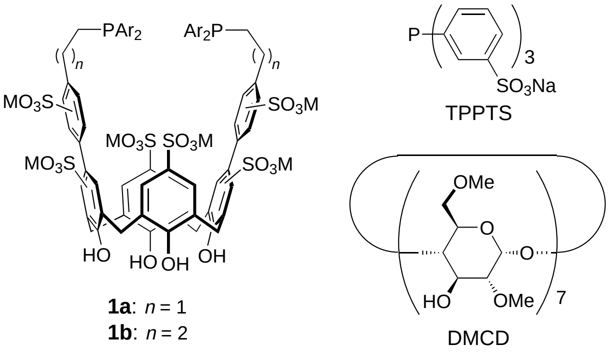
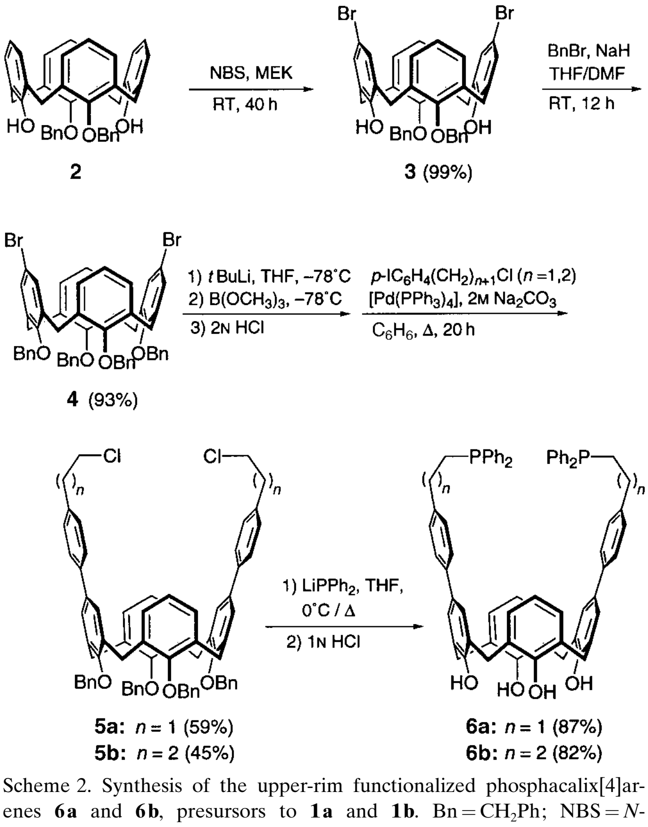
through transporting an organic substrate into an aqueous phase. We report here on the catalytic behavior of complexes with ligands **1a** and **1b** (Scheme 1) in the aqueous biphasic hydroformylation of oct-1-ene and dec-1-ene. These phosphacalix[4]arene–rhodium complexes perform dual functional catalysis without the need for additives, thereby leading to enhanced catalytic activity.



Scheme 1. The structures of TPPTS and DMCD, and of the water-soluble phosphacalix[4]arenes **1a** and **1b** (Ar = *m*-$MOSO_2C_6H_4$). For **1a** and **1b**, the ten M are nine Na^+ and one H^+, or ten Na^+, respectively.

A number of phosphacalix[*n*]arenes have already been prepared,[14–16] but relatively few are known which contain phosphane moieties on the upper rim.[16] We were interested in using the water-soluble phosphacalix[4]arenes **1a** and **1b**, which were synthesized starting from the known dibenzyloxycalix[4]arene **2**[17] (Scheme 2). We believed that the structure of **1a** and **1b** would enable an olefin to be included in the hydrophobic cavity and to simultaneously interact with a catalytic transition-metal center coordinated to the phosphane moieties.



Scheme 2. Synthesis of the upper-rim functionalized phosphacalix[4]arenes **6a** and **6b**, presursors to **1a** and **1b**. Bn = CH_2Ph; NBS = *N*-Bromosuccinimide; MEK = methyl ethyl ketone; RT = room temperature.

Controlled sulfonations of the precursors **6a** and **6b** were conducted according to literature methods,[18] that avoid phosphane oxidation and complex product mixtures. As a result, both **1a** and **1b** were obtained as precisely decasulfonated derivatives. Furthermore, the ^{31}P NMR spectra of both products showed only two peaks. The most plausible structures are shown in Scheme 1, as deduced from the structures of analogous products obtained by sulfonations of triphenylphosphane[18] and calix[4]arene.[19]

The activity and selectivity of complexes with ligands **1a** and **1b**[20] were tested using [Rh(acac)$(CO)_2$] (acac = acetylacetonate) as the metal complex for the biphasic hydroformylation of oct-1-ene and dec-1-ene. That, in all cases, high catalytic activities were observed was gratifying. For comparison purposes, a TPPTS ligand and the combination of TPPTS and 2,6-di-*O*-methyl-*β*-cyclodextrin (DMCD) as inverse phase-transfer catalysts were also examined under the same reaction conditions. These results are summarized in Table 1.

Table 1. The rhodium-catalyzed biphasic hydroformylation of water-insoluble olefins.[a]

Entry	Ligand/Additive	Olefin	Conversion [%][b]	Yield [%][b,c]	1:b[d]
1	TPPTS[e]	oct-1-ene	trace	trace	–
2	TPPTS[e]/DMCD[f]	oct-1-ene	26	21	2.4
3	**1a**	oct-1-ene	55	40	3.0
4[g]	**1a**	oct-1-ene	96	75	2.6
5	**1b** (1st use)	oct-1-ene	95	73	1.7
6	**1b** (2nd use)[h]	oct-1-ene	97	84	1.7
7	**1b** (3rd use)[i]	oct-1-ene	98	86	1.9
8	**1b**[j]	oct-1-ene	96	76	2.0
9	**1b** + TPPTS[k]	oct-1-ene	66	51	3.5
10	**1b**	dec-1-ene	94	52	2.3

[a] Reaction conditions: olefin (4.0 mmol), ligand (0.032 mmol), [Rh(acac)$(CO)_2$] (0.016 mmol), mole ration olefin:P:Rh = 250:4:1, H_2O (3 mL), undecane (GC internal standard; 0.40 mmol), CO:H_2 = 1:1, p = 4.0 MPa, T = 100 °C, t = 12 h. [b] Determined by GC. [c] Yield of aldehydes. [d] Linear:branched ratio includes all branched aldehydes. [e] Triphenylphosphane trisulfonate (0.064 mmol). [f] 2,6-Di-*O*-methyl-*β*-cyclodextrin (0.032 mmol). [g] t = 24 h. [h] Aqueous layer used in Entry 5. [i] Aqueous layer used in Entry 6. [j] Ligand (0.064 mmol). [k] **1b** (0.032 mmol), TPPTS (0.016 mmol).

Treatment of oct-1-ene with a 1:1 mixture of carbon monoxide and hydrogen in water using the TPPTS/[Rh(acac)$(CO)_2$] complex for 12 h at 100 °C and 4.0 MPa pressure afforded only trace amounts of nonanals (Entry 1). The addition of DMCD to the reaction mixture increased the yield of nonanals to 21 % (Entry 2).[21] However, when the same reaction was carried out using the **1b**/[Rh(acac)$(CO)_2$] catalyst (Entry 5), the yield of aldehydes increased to 73 % though the proportion of linear to branched aldehydes was somewhat smaller than that of TPPTS/DMCD. For the case of **1a** (Entries 3 and 4), the catalytic activity was inferior to that of **1b** and resulted in a l:b ratio comparable to that of the TPPTS/DMCD system. The beneficial effect of water-soluble phosphacalix[4]arenes **1a** and **1b** on the yield of aldehydes can be attributed to an improvement in the mass transfer of the substrate and products between the phases, since it is generally accepted that the biphasic hydroformylation of water-insoluble olefins is limited by the rate of mass transfer.[3, 6, 9] Thus the (**1a**, **1b**)/[Rh(acac)(CO)$_2$] complexes function, not only as homogeneous metal catalysts but also as inverse phase-transfer catalysts, that is, they perform a dual functional catalysis.

It is indeed remarkable that the activity and selectivity of the **1b**/[Rh(acac)(CO)$_2$] catalyst could be retained after being consecutively recycled in the second and third reactions and that the yields are practically identical to that observed with fresh catalyst, as shown in Entries 6 and 7 (Table 1). When a phosphorus to rhodium ratio of 8:1 is employed, no change in the activity is apparent, even though a slight improvement in the linear to branched ratio is observed (Entry 8). On the other hand, addition of TPPTS to the **1b**/[Rh(acac)(CO)$_2$] catalyst results in a significant enhancement in selectivity but the yield is relatively low (Entry 9). In addition, for the hydroformylation of dec-1-ene, the ligand **1b** was effective and satisfactory, although the formation of isomerization products slightly depressed the measured aldehyde yields (Entry 10).

The novel water-soluble phosphacalix[4]arene–rhodium complexes have acceptable levels of activity, stability, and reusability. This water-soluble catalytic system provides additional options in the field of aqueous organometallic catalysis for synthetic chemistry and process engineering.

Experimental Section

Sulfonation of **6a** and **6b**: Orthoboric acid (0.927 g, 15.0 mmol) was dissolved in concentrated H_2SO_4 (97%, 18 mL) and the resulting solution was cooled to 0°C. **6a** or **6b** (1.0 g, 1.0 mmol) was added. The mixture was stirred at room temperature under argon until all solids had dissolved. A solution of oleum (60 wt%, 10 mL) at 0°C was added dropwise to the solution over a 1 h period, followed by stirring for 24 h at 30°C. All organic solvents and water employed in the workup of products were degassed by bubbling with argon. After cooling and hydrolysis (water 80 mL), the products were isolated by extraction into toluene/triisooctylamine (70 mL/15 mL) under argon. Further workup was performed according to previously described methods,[18] and **1a** or **1b** was obtained as a cream-colored powder (yield: 83% (**1a**), 88% (**1b**)). **1a**$\cdot 3\,CH_3OH \cdot 6\,H_2O$: $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD, external 85% H_3PO_4): $\delta = -14.1$ (s, 72%), -14.8 (s, 28%), 35.3 (vw s, P=O); elemental analyses for $C_{68}H_{49}Na_9O_{34}P_2S_{10} \cdot 3\,CH_3OH \cdot 6\,H_2O$ (2203.80): calcd: C 38.70, H 3.34, Na 9.39, P 2.81, S 14.55; found: C 38.26, H 3.43, Na 9.44, P 2.89, S 14.82. **1b**$\cdot 3\,CH_3OH \cdot 6\,H_2O$: $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD, external 85% H_3PO_4): $\delta = -14.3$ (s, 41%), -15.0 (s, 59%), 36.4 and 37.2 (vw s, P=O); elemental analyses for $C_{70}H_{52}Na_{10}O_{34}P_2S_{10} \cdot 3\,CH_3OH \cdot 6\,H_2O$ (2253.84): calcd: C 38.90, H 3.40, Na 10.20, P 2.75, S 14.22; found: C 39.23, H 3.41, Na 10.50, P 2.74, S 14.30.

Hydroformylation: In a typical experiment, **1a** or **1b** (0.032 mmol) and [Rh(acac)(CO)$_2$] (0.016 mmol) were dissolved in degassed water (3 mL) under argon. The resulting aqueous solution was filtered through a 0.45 μm PTFE membrane filter and the filtrate was transferred into an autoclave (80 mL), equipped with a glass liner and a magnetic stirring bar. Internal standard (undecane; 0.40 mmol) and oct-1-ene (4.0 mmol) were added. After purging with CO, the autoclave was pressurized to 4.0 MPa with a mixture of CO:H_2 (1:1) and heated to 100°C with stirring at 800 rpm for 12 h. The autoclave cooled to room temperature and the reaction mixture was extracted with chloroform (5 mL × 3). The combined extracts were dried (Na_2SO_4) and subjected to GC analysis. For recycling experiments, after a reaction time of 12 h per cycle, the autoclave was depressurized and the contents transferred to a Schlenk flask under argon. After extraction with chloroform, the aqueous catalyst solution was reinjected in the autoclave for the next cycle.

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[20] **1a** and **1b** were treated with [Rh(acac)(CO)$_2$] in CD$_3$OD, giving rhodium complexes with the phosphacalix[4]arenes acting as ligands. Complexation was indicated by the ^{31}P NMR spectrum, for example, the **1b**/[Rh(acac)(CO)$_2$] complex showed two doublets at $\delta = 45.2$ (J(P,Rh) = 173 Hz) and 45.7 (J(P,Rh) = 174 Hz).

[21] DMCD may form inclusion complexes with TPPTS, which are capable of transferring into the organic phase. An analogous formation of inclusion complexes between unmodified β- and γ-CDs and TPPTS has been proved: E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *New J. Chem.* **1999**, *23*, 469–472. Consequently, it is possible to leach out rhodium from the aqueous phase.

[Mo(CH$_3$)$_6$] and [Mo(CH$_3$)$_7$]$^-$**

Beatrice Roessler and Konrad Seppelt*

More than two decades ago Wilkinson prepared [W(CH$_3$)$_6$] and [Re(CH$_3$)$_6$], which at the time were the only neutral hexamethyl transition neutral compounds.[1, 2] Later these compounds gained importance because they are classical examples for d^0 and d^1 complexes containing only σ-binding ligands, and therefore they should be not be octahedral, as predicted by several corresponding theoretical papers.[3–7] In the meantime the structures of [Zr(CH$_3$)$_6$]$^{2-}$,[8] [W(CH$_3$)$_6$],[9] [Re(CH$_3$)$_6$],[9] [Nb(CH$_3$)$_6$]$^-$,[10] [Ta(CH$_3$)$_6$]$^-$,[10] [Ta(C$_6$H$_5$)$_6$]$^-$,[11] and [Ta(4-CH$_3$C$_6$H$_4$)$_6$]$^-$[11] have been determined experimentally, and agree fully with the theoretical predictions: The structures are based on a trigonal prism, either regular as in [Re(CH$_3$)$_6$], [Ta(CH$_3$)$_6$]$^-$, and [Zr(CH$_3$)$_6$]$^{2-}$, or more or less distorted trigonal prismatic as in [W(CH$_3$)$_6$] and [Nb(CH$_3$)$_6$]$^-$ with retention of the C_{3v} symmetry.

The structure of [W(CH$_3$)$_6$] has been of special interest because it is strongly C_{3v}-distorted trigonal prismatic, having nonequivalent W–C bonds; that is, three longer ones which have a very narrow angle to each other, and three shorter ones with a larger angle to each other. According to the latest theoretical calculation,[4] that has also predicted the experimental structure in detail, the C_{3v} distortions should be especially large in the case of [Mo(CH$_3$)$_6$], [Re(CH$_3$)$_6$]$^+$, and [Tc(CH$_3$)$_6$]$^+$. All three molecules or cations, respectively, are presently unknown.

We report here on the preparation of [Mo(CH$_3$)$_6$] from MoF$_6$ and Zn(CH$_3$)$_2$, as well as on its structure. This reaction pathway is so far the only one with reasonable yields. Oxidic (MoOCl$_4$) or starting materials with nonhexavalent Mo centers (MoCl$_5$) should be avoided. Common methylating agents other than Zn(CH$_3$)$_2$, such as LiCH$_3$, reduce MoF$_6$. [Mo(CH$_3$)$_6$], prepared in this way, is an orange-brown crystalline compound at low temperatures, which is volatile in high vacuum, and thermally stable up to about 10 °C. It is very sensitive towards oxygen. Proof of its existence and structure stems mainly from a single-crystal X-ray structure determination (Figure 1). Single crystals were obtained by recrystallization from acetone at −80 °C. The crystal structure is notable for the existence of three crystallographically different, but otherwise essentially similar [Mo(CH$_3$)$_6$] molecules. As in [W(CH$_3$)$_6$] and [Re(CH$_3$)$_6$], the intermolecular interactions can be considered as weak; the shortest Mo–Mo distances are 580 pm.[9] We concluded from the fact that the three crystallographically different molecules have essentially the same molecular structure that the latter is not influenced by packing effects but rather represents the structure of the free molecule (Table 1). Crystallographically it may be of interest that molecules I and III can be interconverted by a pseudo-inversion center, not however, molecule II with itself. This led to the choice of a noncentrosymmetric space group. Of the 54 different hydrogen atom positions all except one were located in difference Fourier maps and refined. None of

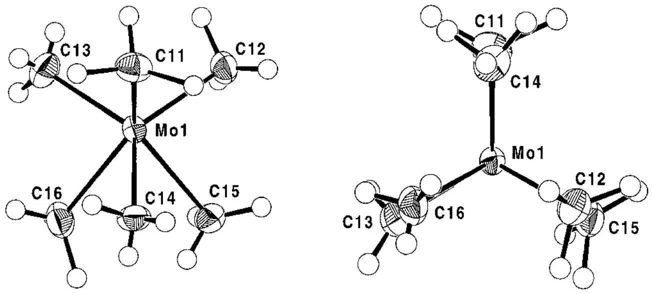

Figure 1. ORTEP representation of [Mo(CH$_3$)$_6$], molecule I, 50% probability ellipsoids, view perpendicular and along the threefold molecular axis. Because of the smaller angle to the molecular axis of the longer bonded methyl groups these appear closer to the molybdenum atom in the projection on the right-hand side. Distances [pm] and angles [°] (the corresponding values of [Mo(CH$_3$)$_6$] II and [Mo(CH$_3$)$_6$] III are given in parentheses): Mo1-C11 212.6(8) (208.8(6), 213.8(8)), Mo1-C12 210.3(7) (209.6(7), 211.3(5)), Mo1-C13 210.7(6) (211.8(6), 209.5(5)), Mo1-C14 220.0(7) (220.0(6), 216.7(8)), Mo1-C15 217.5(9) (218.8(6), 220.7(5)), Mo1-C16 219.5(6) (220.5(7), 219.7(6)); C11-Mo1-C12 93.6(3) (97.0(3), 96.1(3)), C11-Mo1-C13 93.8(4) (98.9(3), 96.6(3)), C12-Mo1-C13 97.5(3) (96.0(3), 98.2(2)), C14-Mo1-C15 75.2(3) (75.8(2), 75.7(2)), C14-Mo1-C16 76.9(3) (74.7(3), 74.7(3)), C15-Mo1-C16 75.1(3) (75.7(3), 74.2(2)).

Table 1. Structure of [Mo(CH$_3$)$_6$] in the crystal, mean (angles are given only between C_{3v}-symmetry equivalent bonds) and calculated values.[4]

	[Mo(CH$_3$)$_6$]-I	[Mo(CH$_3$)$_6$]-II	[Mo(CH$_3$)$_6$]-III	calcd
Mo–C [pm]	211.2	210.1	211.5	213.6
	219.0	219.7	219.0	220.6
C-Mo-C [°]	94.9	97.3	96.9	97.3
	75.7	75.4	74.5	74.7

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