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Novel arsine ligands for selective hydroformylation of alk-1-enes employing platinum/tin catalysts†

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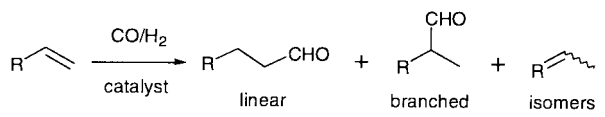
The synthesis and application of new wide bite angle arsine based ligands in the platinum/tin-catalysed hydroformylation of oct-1-ene is reported; an unprecedented high activity and selectivity is obtained employing a mixed phosphine/arsine ligand.

Hydroformylation of alkenes is one of the world's largest homogeneously catalysed reactions in industry (Scheme 1), producing more than six million tons of aldehydes and alcohols annually.[1] The commercial hydroformylation processes are run exclusively on cobalt or rhodium complexes as catalysts. Platinum complexes also give active hydroformylation catalysts, but are mainly of academic interest. Both terminal and internal alkenes can be hydroformylated selectively employing platinum–diphosphine complexes activated by tin chloride as the co-catalyst.[2] Tin-free catalyst systems have been reported as well.[3] Despite the very high linear over branched (l:b) aldehyde ratios induced by the platinum/tin–diphosphine catalysts, these systems have mainly been applied to asymmetric hydroformylation so far.[1,4] The major drawbacks of these catalysts are extensive isomerisation and hydrogenation of the substrate alkenes.

Both in the rhodium- and in the platinum/tin-catalysed hydroformylation of alk-1-enes, widening of the natural bite angle of the diphosphine ligands has proven to be favourable for the catalytic performance.[2a,5] Recently, it was also demonstrated that in the selective hydroformylation of internal alkenes toward linear aldehydes wide bite angle diphosphine ligands can be very efficient.[6] Based on these results we wondered whether wide natural bite angles could also improve the catalytic performance of ligands having donor atoms other than phosphorus. Since the xanthene backbone is an excellent scaffold for the construction of ligands with wide natural bite angles, we set out to synthesise the (mixed) group 15 derivatives of the xantphos ligand **1** (Fig. 1). Here, we report the synthesis of the arsine analogues of xantphos **1** and their excellent performance in the platinum/tin-catalysed hydroformylation reaction. To our knowledge, xantarsine and xantphosarsine ligands **2** and **3** constitute the first efficient arsine modified platinum/tin catalysts for selective hydroformylation of terminal alkenes.

The xantarsine and xantphosarsine ligands **2** and **3** were synthesised *via* procedures similar to the synthesis of xantphos **1** (Scheme 2).[6a] Dilithiation of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene **5** with *n*-butyllithium in THF at −65 °C, followed by reaction with chlorodiphenylarsine gave xantarsine



Scheme 1 The hydroformylation reaction.

† Electronic supplementary information (ESI) available: full characterisation data for the new compounds. See http://www.rsc.org/suppdata/cc/a9/a906903h/

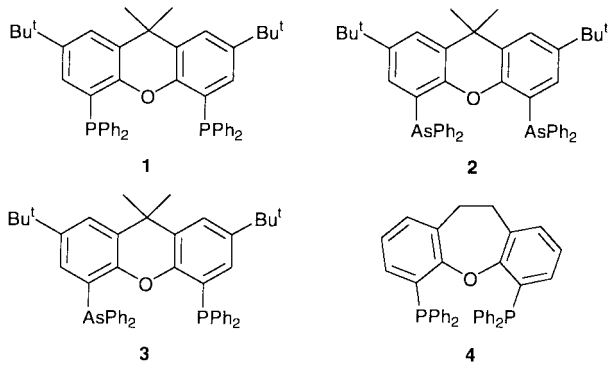
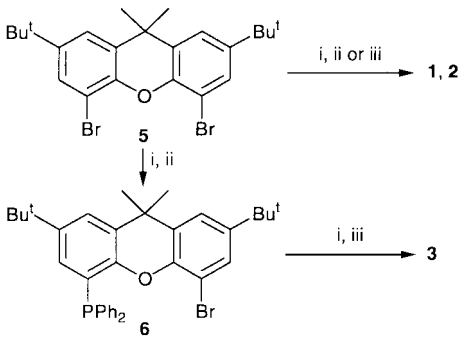


Fig. 1

2 in 83% yield. Xantphosarsine ligand **3** was obtained in 49% yield by monolithiation of bromoxantphos **6** and subsequent reaction with chlorodiphenylarsine. Bromoxantphos **6** was synthesised by monolithiation of compound **5**, followed by reaction with chorodiphenylphosphine. The calculated natural bite angles of ligands **1**, **2**, **3** and **4** are 110, 113, 111 and 102°, respectively.[7]

Ligands **1**–**4** were tested in the platinum/tin-catalysed hydroformylation of oct-1-ene (Table 1). In the hydro-



Scheme 2 Synthesis of ligands **1**–**3** and **6**: (i) Bu^{n}Li, THF, −65 °C; (ii) Ph_2PCl, THF, −65 to 25 °C, 81% (**1**), 48% (**6**); (iii) Ph_2AsCl, THF, −65 to 25 °C, 83% (**2**), 49% (**3**).

Table 1 Platinum/tin-catalysed hydroformylation of oct-1-ene at 60 °C[a]

Ligand	l:b Ratio[b]	% *n*-Nonanal[b]	% Isomerization[b]	TOF[bc]
1	230	95	4.5	18
2	> 250	92	8.0	210
3	200	96	3.1	350
4	> 250	88	12	720

[a] Reactions were carried out in a 180 mL stainless steel autoclave in dichloromethane at 60 °C under 40 bar of $CO–H_2$ (1:1), catalyst precursor $[Pt(cod)Cl_2]$, [Pt] = 2.5 mM, $Pt:SnCl_2:P$:1-octene = 1:2:4:255. [b] Determined by GC with decane as the internal standard. [c] Averaged turnover frequencies (TOF) were calculated as (mol of aldehyde) (mol Pt)$^{-1}$ h^{-1} at 20–30% conversion.

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formylation of oct-1-ene the arsine based ligands **2** and **3** proved to give more efficient catalysts than the parent xantphos ligand **1**. The xantarsine ligand **2** is only slightly less selective than xantphos **1**, but more than 10 times as active. The xantphosarsine ligand **3** is even 20 times as active as xantphos **1**, while displaying the same excellent selectivity for linear aldehyde formation. This is remarkable, since up to now, without exception, arsine ligands have performed worse than phosphine ligands in platinum/tin-catalysed hydroformylation.[2c,3a,8] To our knowledge the high activity and selectivity displayed by the mixed xantphosarsine ligand **3** under these mild conditions is unprecedented.

Comparison of the activities of the xantphos ligands **1** and **4** reveals a dramatic effect of the natural bite angle. Narrowing of the natural bite angle from 110 to 102°, results in a 40 fold higher hydroformylation rate. This is accompanied, however, by a considerable increase in isomerization activity. As a result, the selectivity for linear aldehyde obtained for xantphos **4** is lower than that for xantphos **1**. It is striking that the selectivities of the xantphos ligands **1** and **4** observed in the platinum/tin-catalysed hydroformylation are virtually identical to those obtained before for rhodium.[5c,6a]

The high selectivities of ligands **1**, **2** and **3** compared to xantphos **4** can be ascribed to the wider natural bite angles of the former ligands.‡ Widening of the bite angle of the ligand will increase the steric congestion around the platinum centre resulting in more selective formation of the sterically less hindered linear aldehydes. An explanation for the higher activities of ligands **2**, **3** and **4** compared to xantphos **1** is still lacking, but we speculate that it is caused by the coordination behaviour of the ligands in the platinum/tin complexes. Increasing the natural bite angle of bidentate ligands favours the formation of *trans* complexes. Compared to xantphos **1**, xantphos **4** and the arsine ligands **2** and **3** probably give more or easier formation of the *cis*-platinum complexes, a prerequisite for efficient hydroformylation.[10]

In conclusion, wide bite angle arsine based ligands can give very efficient catalysts for selective hydroformylation of terminal alkenes. The catalytic performances of the arsine modified platinum/tin systems can compete with the best results obtained using rhodium catalysts.[1,5c,11] Especially in applications where very high l:b ratios are a necessity these systems could be interesting alternatives for rhodium–diphosphine catalysts.

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Notes and references

‡ When comparing the activities and selectivities of ligands **1**, **2**, and **3**, it should be noted that in general the σ-donor ability and the steric effects of substituents on the donor atom decrease in the order of P > As.[9]

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