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Wide bite angle amine, arsine and phosphine ligands in rhodium- and platinum/tin-catalysed hydroformylation †

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New wide bite angle amine, arsine and mixed phosphineamine and phosphinearsine ligands based on xanthene backbones were synthesized. The co-ordination chemistry and the catalytic performance of these ligands were compared to those of the parent phosphine ligands. The amine based xanthene ligands do not form rhodium–hydride complexes and therefore give very poor rhodium hydroformylation catalysts. The catalytic performance of the xantarsine and the mixed xantphosarsine ligands is comparable with that of the xantphos ligands and they form similar (ligand)-$Rh(CO)_2H$ and $[(ligand)Rh(CO)_2]_2$ complexes. In the platinum/tin-catalysed hydroformylation the xantarsine and the mixed xantphosarsine ligands proved to be superior to the xantphos ligands. The remarkably high selectivity and activity that is displayed by the mixed xantphosarsine ligand is explained by its wide natural bite angle and the formation of *cis* co-ordinated platinum complexes.

Introduction

Hydroformylation of alkenes is one of the world's largest homogeneously catalysed reactions in industry, producing more than six million tons of aldehydes and alcohols annually.[1–3] The commercial hydroformylation processes are run exclusively on cobalt or rhodium complexes as catalysts. Platinum complexes can also give active hydroformylation catalysts, but are mainly of academic interest. Extensive research has been devoted to improve the selectivity of these catalyst systems toward the formation of the industrially more important linear aldehydes. High selectivities in the hydroformylation of terminal alkenes have been reported for both diphosphine and diphosphite modified rhodium catalysts.[4–10] Novel rhodium catalysts for the selective hydroformylation of internal alkenes to linear aldehydes, which is of great interest in both industry and synthetic organic chemistry, were developed recently.[11,12]

Both terminal and internal alkenes can be hydroformylated selectively also by employing platinum–diphosphine complexes activated by tin chloride as the co-catalyst.[13–19] Tin free catalyst systems, however, have been reported as well.[20–23] 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. Major drawbacks of these catalyst systems are extensive isomerisation and hydrogenation of the substrate alkenes.[3,24] In the asymmetric platinum/tin-catalysed hydroformylation very high enantioselectivity has been obtained for a variety of prochiral alkenes applying diphosphine ligands derived from 4-hydroxy-L-proline.[25]

The role of the tin chloride in the platinum/tin-catalysed hydroformylation is not yet fully understood, since it can act as a Lewis acid, as a ligand directly bonded to platinum, and as $SnCl_3^-$ counter ion.[26,27] According to the ionic mechanism for platinum/tin–diphosphine catalysed hydroformylation postulated by Tóth and co-workers, the effect of the $SnCl_3^-$ ligand is an increase of the cationic character of platinum.[28] A recent theoretical study on the alkene insertion in the $Pt(H)(PH_3)_2(SnCl_3)(C_2H_4)$ complex shows that the major role of the $SnCl_3^-$ ligand is to stabilise the five-co-ordinated intermediates of this complex and to weaken the platinum–hydride bond *trans* to it, thus favouring alkene insertion.[29]

Both in the rhodium- and the platinum/tin-catalysed hydroformylation phosphines have proven to be superior to other donor ligands, such as nitrogen- or arsine-containing compounds.[15,20,30,31] Owing to their extensive use in catalysis, the influence of phosphine structure on catalytic performance has been studied in great detail.[2] Tolman introduced the concept of the cone angle θ and the electronic parameter χ to classify phosphorus ligands with respect to their steric bulk and phosphine basicity.[32,33] Casey and Whiteker developed the concept of the natural bite angle as an additional characteristic of diphosphine ligands.[34] The pronounced influence of the natural bite angle of diphosphine ligands on the activity and selectivity of several catalytic reactions has been reviewed recently.[35,36] In a number of these reactions, including the rhodium- and platinum/tin-catalysed hydroformylation, diphosphines having wide natural bite angles proved to be favourable to the catalytic performance. Unfortunately, ligands having relatively wide natural bite angles are scarce. A family of diphosphine ligands having wide natural bite angles was developed in our group by computer-assisted design.[6,7,12] These ligands, based on the readily available heterocyclic xanthene-type backbones, give very efficient catalysts for several reactions.[6,7,12,37–39]

Based on these results we wondered whether wide natural bite angles would 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 synthesize the (mixed) Group 15 derivatives of the xantphos ligands. Here we report the synthesis of the amine and arsine analogues of the xantphos ligands **1a** and **2a** (Table 1), and their performance in the rhodium-, and platinum/tin-catalysed hydroformylation reaction. The amine based xanthene ligands give very poor rhodium hydroformylation catalysts, since they do not co-ordinate to rhodium at all. The catalytic performance of the xantarsine and the mixed xantphosarsine ligands, on the other hand is comparable with that of the xantphos ligands and they form the same $(ligand)Rh(CO)_2H$ and $[(ligand)Rh(CO)_2]_2$ complexes. In the platinum/tin-catalysed hydroformylation the

† Electronic supplementary information (ESI) available: details of syntheses and characterisations. See http://www.rsc.org/suppdata/dt/b0/b002126l/

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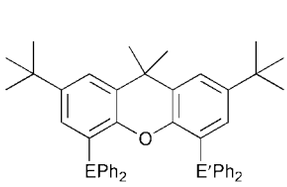
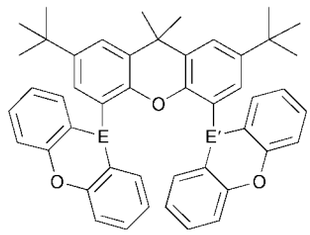
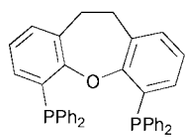


1a E,E′ = P,P
1b E,E′ = N,N
1c E,E′ = As,As
1d E,E′ = N,P
1e E,E′ = As,P



2a E,E′ = P,P
2b E,E′ = N,N
2c E,E′ = As,As



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xantarsine and the mixed xantphosarsine ligands are even superior to the xantphos ligands.[40]

Results

Ligand synthesis

The xantamine ligands **1b**, **2b**, and **6** were prepared by a modification of the Ullmann reaction employing 18-crown-6 as a phase transfer catalyst (Scheme 1).[41] Boiling 2,7-di-*t*-butyl-4,5-diiodo-9,9-dimethylxanthene **5** and diphenylamine or phenoxazine, in the presence of copper powder, potassium carbonate and a catalytic amount of 18-crown-6 under reflux overnight in *o*-dichlorobenzene gave compounds **1b**, **2b**, and **6** in 58, 52, and 58% yield, respectively. Compound **5** was obtained in high yield *via* dilithiation of 4,5-dibromo-2,7-di-*t*-butyl-9,9-dimethylxanthene **4** and subsequent reaction of the formed dilithio compound with 1,2-diiodoethane.[42] Monolithiation of xantamine **6** followed by reaction with chlorodiphenylphosphine gave xantphosamine ligand **1d** in 62% yield.

The syntheses of the xantarsine and xantphosarsine ligands **1c**, **2c** and **1e** were performed *via* a procedure similar to the syntheses of the xantphos ligands **1a** and **2a** (Scheme 1).[43] Reaction of dilithiated **4** with chlorodiphenylarsine or 10-chlorophenoxarsine gives ligands **1c** and **2c** in 83 and 64% yield, respectively. Chlorodiphenylarsine and 10-chlorophenoxarsine were prepared according to literature procedures.[44,45] Xantphosarsine ligand **1e** was obtained in 49% yield by monolithiation of xantphos **7** and consequent reaction of the lithiated compound with chlorodiphenylarsine. Compound **7** was synthesized by monolithiation of **4**, followed by reaction with chorodiphenylphosphine. The yield obtained is only 48%, which is relatively high keeping in mind that the statistical yield for this reaction is 50%.

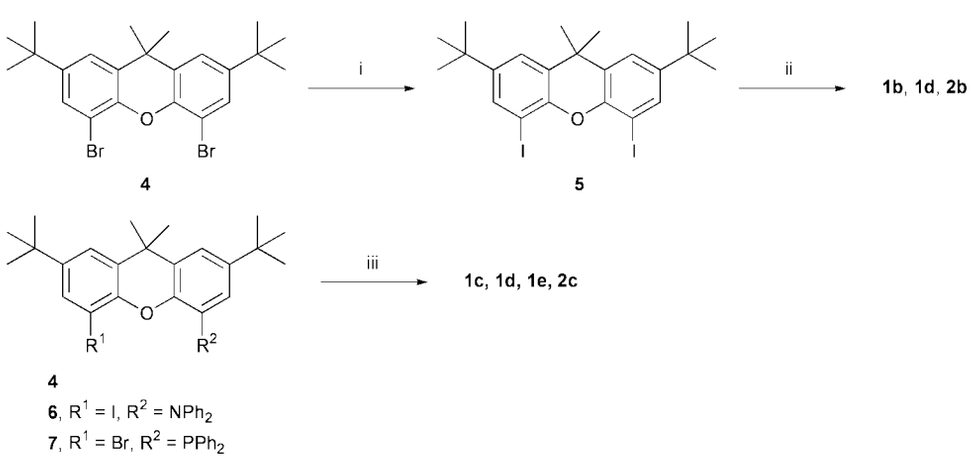
Table 1 Natural bite angles and flexibility ranges for the xantamine-, xantarsine-, and xantphos ligands

Ligand	E, E′	Natural bite angle (β_n)[a]/°	Flexibility range[a]/°
1a	P, P	110.1	98–134
2a	P, P	121.4	107–138
1b	N, N		
2b	N, N		
1c	As, As	112.9	98–132
2c	As, As	123.0	107–142
1d	N, P		
1e	As, P	111.4	97–130
3	P, P	102.0	92–120

[a] The natural bite angle (β_n) and the flexibility range were calculated as by Casey and Whiteker.[34] β_n is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles. The flexibility range is defined as the accessible range of bite angles within 12.6 kJ mol^{-1} excess strain energy from the calculated natural bite angle.

Rhodium complexes

We used IR and NMR spectroscopy to study the rhodium complexes that are formed upon mixing the ligands and $Rh(CO)_2(acac)$ under an atmosphere of CO/H_2 (1 : 1). The high pressure (HP) IR spectra obtained for the xantamine ligands **1b** and **2b** did not show the formation of the corresponding (ligand)$Rh(CO)_2H$ complexes, the catalyst's resting state in rhodium–diphosphine catalysed hydroformylation.[46] Instead, the $Rh(CO)_2(acac)$ was slowly converted into poorly soluble rhodium–carbonyl clusters and the xantamine ligands **1b** and **2b** do not seem to co-ordinate to rhodium at all. The three absorption bands in the carbonyl region of the IR spectrum (2073, 2043, and 1820 cm^{-1}) observed for the reaction using ligand **1b** can fully be ascribed to the hexanuclear rhodium–carbonyl cluster $Rh_6(CO)_{16}$.[47,48] For ligand **2b** five carbonyl absorptions (2074, 2068, 2043, 1886, and 1820 cm^{-1}) were displayed in the IR spectrum, indicating that both the hexanuclear as well as the tetranuclear rhodium–carbonyl cluster, $Rh_4(CO)_{12}$, were formed. The latter is most likely an intermediate in the formation of the larger rhodium–carbonyl cluster.[49] Compared to ligands **1b** and **2b**, $Rh(CO)_2(acac)$ was converted much faster in the HP IR experiment using the xantphosamine ligand **1d**. The HP IR spectrum for ligand **1d** again showed the



Scheme 1 Ligand synthesis. (i) *n*-BuLi/ICH_2CH_2I/THF/−20 °C; (ii) R_2NH/Cu/K_2CO_3/18-crown-6/$C_6H_4Cl_2$/220 °C; (iii) *n*-BuLi/R_2AsCl or Ph_2PCl/THF/−60 °C.

Table 2 ^{31}P-{^{1}H} NMR Data of the (ligand)Pt($SnCl_3$)Cl complexes[a]

	Ligand	% *cis*[b]	^{1}J(Pt,$P_{trans Cl}$)/Hz	^{1}J(Pt,$P_{trans Sn}$)/Hz	^{1}J(Pt,$P_{trans P}$)/Hz	^{2}J(P,P)/Hz
	1	67	3706	3046	1954	14.3
	1e	74	3697	2660	—	—
	3[c]	100	3840	3117	—	13.0

[a] In CD_2Cl_2 at −73 °C. [b] Percentage of the complex in which the ligand is co-ordinated *cis* to platinum. [c] T = −50 °C.

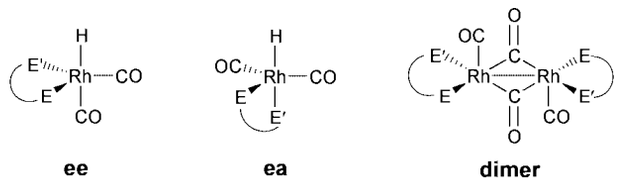


Fig. 1 Structures of **ee**, **ea**, and dimeric complexes.

Fig. 2 *cis* and *trans* complexes (ligand)Pt($SnCl_3$)(Cl).

formation of the hexanuclear rhodium–carbonyl cluster along with the formation of another rhodium–carbonyl complex. The structure of this complex is not clear, however the absence of a rhodium–hydride signal in the ^{1}H NMR spectrum of the complex mixture excludes the desired (ligand)Rh$(CO)_2$H complex. The ^{31}P-{^{1}H} NMR spectrum of the complex mixture shows one broad doublet at δ 41.6, with a relatively large rhodium–phosphorus coupling constant (^{1}J(Rh,P)) of 184 Hz. The composition of the complex mixture was not affected by the addition of 1-octene.

Xantarsine ligand **2c** reacted very slowly with Rh$(CO)_2$(acac). In the HP IR spectrum formation of the hexanuclear rhodium–carbonyl cluster and of another complex with carbonyl absorptions at 2060, 2045, 2027, and 1795 cm^{-1} was observed. The latter complex is most likely a rhodium–carbonyl cluster of the type $Rh_x(CO)_y$(**2c**)$_n$.[47,48] The HP IR spectrum of the complexes obtained with xantarsine ligand **1c** clearly showed the four carbonyl absorptions that can be assigned to two isomers of the rhodium–hydride complex Rh$(CO)_2$(**1c**)H (2036, 1998, 1971, and 1953 cm^{-1}), in which the ligand is co-ordinated in the equatorial–equatorial (**ee**) and in the equatorial–apical (**ea**) fashion, respectively (Fig. 1).[46] Predominantly, however, formation of the rhodium–dimer complex [Rh$(CO)_2$(**1c**)]$_2$ (see Fig. 1) was observed (2012, 1981, 1768, 1756 cm^{-1}).[43,50,51] The formation of the rhodium–hydride complex was confirmed by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum the rhodium–hydride signal is observed at δ −9.68 as a doublet with a rhodium–proton coupling constant (^{1}J(Rh,H)) of 11.1 Hz.‡ Also for the xantphosarsine ligand **1e** both the rhodium–hydride complex Rh$(CO)_2$(**1e**)H (2037, 1998, 1978, 1953 cm^{-1}, mixture of **ee** and **ea** isomers) and the rhodium–dimer complex [Rh$(CO)_2$(**1e**)]$_2$ (1974, 1767, 1754 cm^{-1}) were formed according to the IR spectrum, but with this ligand the dimer complex is formed in a considerably smaller amount. In the ^{1}H NMR spectrum of Rh$(CO)_2$(**1e**)H the rhodium–hydride signal appears as a double doublet at δ −8.65 with a rhodium–proton coupling constant of 8.4 Hz and a relatively large phosphorus–proton coupling constant (^{2}J(P,H)) of 78 Hz. The ^{31}P-{^{1}H} NMR spectrum of Rh$(CO)_2$(**1e**)H exhibits a doublet at δ 26.9 with a rhodium–phosphorus coupling constant (^{1}J(Rh,P)) of 112 Hz. Both the intensities of the carbonyl vibrations in the IR spectrum and the heteronuclear coupling constants in the NMR spectra of Rh$(CO)_2$(**1e**)H indicate that the **ea** complex isomer is favoured over the **ee** isomer.[46]

‡ The Rh$(CO)_2$(**1c**)H complex consists of a mixture of **ee** and **ea** isomers that is in dynamic equilibrium on the NMR timescale and, therefore, only one rhodium–hydride signal is observed in the ^{1}H NMR spectrum. This dynamic behaviour is consistent with that of xanthene-type (diphosphine)Rh$(CO)_2$H complexes, and cannot be frozen out even at 200 K.[7,43,46]

Platinum complexes

The (ligand)Pt($SnCl_3$)Cl complexes of ligands **1a**, **1d**, and **1e** were investigated using ^{31}P-{^{1}H} NMR spectroscopy to elucidate the co-ordination mode of the ligands. For comparison also the platinum/tin complex of homoxantphos[7] **3** was measured. The platinum–phosphorus coupling constants (^{1}J(Pt,P)) of the square-planar (ligand)Pt($SnCl_3$)Cl complexes are tools to differentiate between *cis* and *trans* co-ordination of phosphine ligands (see Fig. 2). The platinum–phosphorus coupling constants of the *trans* platinum(II) complexes are usually considerably lower than those of the *cis* complexes.[25,26,52,53] The (ligand)Pt($SnCl_3$)Cl complexes were prepared *in situ* in CD_2Cl_2 from $PtCl_2$(cod), ligand and anhydrous tin(II) chloride. In general broad signals were observed in the ^{1}H and ^{31}P-{^{1}H} NMR spectra at room temperature, indicating the occurrence of dynamic processes on the NMR timescale. These dynamic processes were frozen at low temperature. The platinum–phosphorus coupling constants of the complexes of ligands **1a**, **1e**, and **3** measured at −73 or −50 °C are summarised in Table 2.

At low temperature three signals were observed in the ^{31}P-{^{1}H} NMR spectrum for the (ligand)Pt($SnCl_3$)(Cl) complex containing xantphos **1a**. Based on the mutual phosphorus–phosphorus coupling ^{2}J(P,P), the doublets at δ 16.4 and 4.3 are assigned to the *cis* isomer.[26] From the chemical shifts and the platinum–phosphorus coupling constants it can be concluded that the doublet at δ 16.4 belongs to the phosphine positioned *trans* to tin, and that at δ 4.3 to the phosphine positioned *trans* to chlorine. The singlet at δ 15.2 is assigned to the *trans* complex. According to the relative intensities of the signals in the NMR spectrum, the *cis*:*trans* isomer ratio of the complex Pt($SnCl_3$)(Cl)(**1**) is 2:1. The complex of xantphosarsine **1e** exhibited two signals in the ^{31}P-{^{1}H} NMR spectrum with relative intensities of 3:1. The relatively large platinum–phosphorus coupling constant and the relatively small tin–phosphorus coupling constant ($^{2}J_{avg}$(Sn,P))[54] of 212 Hz of the major signal at δ 2.1 are indicative of a phosphine positioned *trans* to chlorine and *cis* to tin and, hence, is assigned to a *cis* complex. The platinum–phosphorus coupling constant of the minor signal at δ −2.6 is in between those of *cis* and *trans* complexes. Considering the absence of a small *cis* tin–phosphorus coupling constant, however, it is assigned to the other *cis* complex isomer in which arsenic is positioned *trans* to chlorine. The 3:1 ratio of the *cis* complexes is in agreement with the relative *trans* influences of the phosphorus and arsenic. The *cis* complex in which phosphorus is positioned *trans* to chlorine is favoured, since phosphorus has a larger *trans* directing effect than arsenic.[55] For homoxantphos **3** it is clear that only the *cis* complex isomer is formed. In the ^{31}P-{^{1}H} NMR spectrum of the complex Pt($SnCl_3$)(Cl)(**3**) only two doublets with relatively large platinum–phosphorus coupling constants are observed.

Table 3 Results of the rhodium-catalysed hydroformylation of 1-octene at 80 °C[a]

Ligand	% Conversion[b]	l:b ratio[b]	% Linear aldehyde[b]	% Isomerisation[b]	tof[b,c]
—	96	1.9	21	68	180
1a[d]	22	50	94	3.9	240
2a[e]	30	67	89	10	1600
1b	55	3.0	21	72	90
2b	62	3.0	21	71	94
1c	90	2.9	65	12	500
2c	55	3.5	52	33	200
1d	96	2.7	52	28	450
1e	17	8.9	87	3.2	84
3[f]	30	8.5	88	1.4	37

[a] Conditions: $P(CO/H_2)$ (1:1) = 20 bar, ligand:Rh = 5:1, substrate:Rh = 637:1, [Rh] = 1.00 mM, number of experiments = 3. Hydrogenation was observed in none of the experiments. [b] Percent conversion, l:b ratio, percent linear aldehyde, percent isomerisation to 2-octene, and turnover frequency were determined after 1 h by GC analysis. [c] Averaged turnover frequency = (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}. [d] The reaction was analysed after 0.5 h. [e] The reaction was analysed after 6 min. [f] The reaction was analysed after 4.5 h.

As was the case for rhodium, xantphosamine **1d** forms other platinum/tin complexes than the arsine and phosphine ligands. According to the ^{31}P-{^1H} NMR spectrum, two platinum complexes are formed in a 9:2 ratio using ligand **1d**. The major complex displays two signals at δ 22.9 and −0.05 with platinum–phosphorus coupling constants of 3081 and 3601 Hz, respectively. This strongly indicates that in this complex *two* xantphosamine ligands are co-ordinated to platinum only *via* the phosphine moieties, which are probably in mutually *cis* positions. The formation of $(ligand)_2MCl_2$ complexes starting from $MCl_2(cod)$ and ligand has been observed before for other mixed phosphorus/nitrogen ligands.[56,57] For the minor complex only one signal is observed, which has a large platinum–phosphorus coupling constant of 5721 Hz. The structure of this complex is unclear, but the large platinum–phosphorus coupling constant could be indicative of the chelate complex $Pt(SnCl_3)Cl$(**1d**) with the phosphine and the nitrogen group in mutual *trans* positions.

For ligands **1a** and **3** the platinum/tin–diphosphine complexes present during hydroformylation conditions were also studied using HP IR spectroscopy. The catalyst precursor complexes $(ligand)Pt(SnCl_3)(CO)H$ were prepared *in situ* by stirring the solutions of the $(ligand)Pt(SnCl_3)Cl$ complexes in CH_2Cl_2 at 60 °C under an atmosphere of 40 bar of CO/H_2 (1:1). Formation of the $(ligand)Pt(SnCl_3)(CO)H$ complexes was evidenced by the observation of a single platinum–carbonyl vibration in the carbonyl region of the IR spectrum. The IR carbonyl bands for xantphos ligands **1a** and **3** are at 2049 and 2041 cm^{-1}, respectively. The platinum–hydride vibration was not observed for either complex. The $(ligand)Pt(SnCl_3)(CO)H$ complex proved to be the catalyst resting state for ligand **3**, since the addition of 1-octene to the reaction mixture did not lead to the formation of new complexes. The occurrence of the hydroformylation reaction was clearly evidenced by the decay of the absorption of 1-octene at 1639 cm^{-1}, and the rise of the strong acyl absorption of 1-nonanal at 1724 cm^{-1}. Upon the addition of 1-octene to the platinum–hydride complex of ligand **1a** the platinum–carbonyl absorption band of this complex disappeared completely and two new absorptions at 1828 and 1683 cm^{-1} emerged. The band at 1683 cm^{-1} can be ascribed to the platinum–acyl complex, *trans*-$Pt(SnCl_3)(COC_8H_{17})$(**1a**).[26,27] The vibration at 1828 cm^{-1} is characteristic of the presence of bridging carbon monoxide ligands and thus suggests the formation of oligomeric platinum–acyl complexes $[Pt(SnCl_3)(COC_8H_{17})(CO)_n$(**1a**)$]_m$ in which xantphos **1a** and or the carbonyl ligand bridge two platinum centres. The formation of oligomeric platinum–acyl complexes has been reported before by Scrivanti *et al.*[26]

Hydroformylation of 1-octene

(a) Rhodium. The rhodium-catalysed hydroformylation of 1-octene was performed at 80 °C and 20 bar of 1:1 CO/H_2 using a 1.0 mM solution of rhodium diphosphine catalyst prepared from $Rh(CO)_2(acac)$ and five equivalents of ligand. The production of octene isomers, nonanal, and 2-methyloctanal was monitored by gas chromatography. The results of the experiments with ligands **1**–**3** are shown in Table 3.

For the xantamine ligands **1b** and **2b** almost the same selectivity for linear aldehyde formation and the same extent of isomerisation are observed as for hydroformylation experiments without added ligand. The application of ligands **1b** and **2b** only leads to a slight increase of the l:b ratio and a lower hydroformylation rate. The xantphosamine ligand **1d** clearly forms an active hydroformylation catalyst. The high activity displayed by this ligand is, however, accompanied by a considerable amount of isomerisation and a low l:b ratio, resulting in a low selectivity for linear aldehyde formation of 52%. These results are comparable to those reported for other phosphorus/nitrogen ligands.[58–60]

The results obtained with the xantarsine ligands **1c** and **2c** and the xantphosarsine ligand **1e** show that substituting phosphine for arsine gives less selective but equally active catalysts. While substitution of one diphenylphosphine group for one diphenylarsine group decreases the hydroformylation rate by a factor of three, substitution of both diphenylphosphine groups for diphenylarsine groups doubles the activity. For the xantphos ligands the substitution of the diphenylphosphine moieties for phosphacyclic groups results in enhanced catalytic activity.[43] The phosphacyclic xantphos **2a** is more than six times as active as xantphos **1a**. The opposite effect is observed for the xantarsine ligands. The arsacyclic ligand **2c** proves to be only half as active as the non-cyclic xantarsine **1c**. The mixed xantphosarsine ligand **1e** proves to be the most selective arsine modified ligand. Although ligand **1e** is less selective and active than xantphos ligands **1a** and **2a**, it is equally selective and more than twice as active as xantphos ligand **3**.

(b) Platinum/tin. The platinum/tin-catalysed hydroformylation of 1-octene was performed at 60 °C and 40 bar of 1:1 CO/H_2 using a 2.5 mM solution of platinum/tin–diphosphine catalyst prepared from $PtCl_2(cod)$, two equivalents of ligand, and two equivalents of $SnCl_2$. The production of octene isomers, nonanal, and 2-methyloctanal was monitored by gas chromatography. The results of the experiments with ligands **1a**, **1d**, **1e** and **3** are shown in Table 4. Averaged turnover frequencies were determined at 20–30% conversion. A relatively

small natural bite angle appeared to be beneficial for the reaction rate. Ligand **3**, having a natural bite angle of 102°, is 40 times as active as ligand **1a**, which has a natural bite angle of 110°. The increase in activity, however, is accompanied by a considerable increase of the isomerisation rate. It is striking that the selectivities for linear aldehyde obtained for ligands **1a** and **3** are virtually identical to those obtained in the rhodium-catalysed hydroformylation.

Remarkably, the substitution of one phosphine group of ligand **1a** for arsine increases the hydroformylation activity twentyfold, without losing the excellent selectivity for linear aldehyde formation. To the best of our knowledge the high activity and selectivity displayed by the mixed xantphosarsine ligand **1e** under these mild conditions is unprecedented. Usually, the hydrogenation and isomerisation rates increase along with the hydroformylation activity. Substituting both phosphine groups for arsine results in a twelvefold increase of the hydroformylation rate compared to xantphos **1a**. Xantarsine ligand **1c** is still a very active ligand, but not as selective as xantphosarsine ligand **1e**. The xantamine ligand **1b** and the xantphosamine ligand **1d** gave very poor results in the platinum/tin-catalysed hydroformylation. The strong electron donating capacity of the diphenylamine group evidently renders the platinum/tin complexes unsuitable for efficient hydroformylation.

The high activities displayed by ligands **1c**, **1e**, and **3** in the platinum/tin-catalysed hydroformylation of 1-octene prompted us to test these ligands also in the platinum tin-catalysed hydroformylation of methyl *trans*-3-pentenoate. Meessen *et al*. have recently reported that in the hydroformylation of methyl *trans*-3-pentenoate the xantphos ligands display high regioselectivities toward linear aldehyde.[19] Selective linear hydroformylation of unsaturated carboxylic acid esters, such as methyl 3-pentenoate, is of great industrial interest, since it can provide new synthetic routes to polyamides and polyesters. The platinum/tin-catalysed hydroformylation of methyl *trans*-3-pentenoate was performed similarly to the hydroformylation of 1-octene only at a temperature of 80 °C and a pressure of 15 bar of 1 : 1 CO/H_2. The results of the experiments are shown in Table 5. Xantphos **3** shows a very good activity in the hydroformylation of methyl *trans*-3-pentenoate. The high activity, however, is accompanied by a substantial amount of hydrogenation. The xantarsine ligand **1c** and xantphosarsine ligand **1e** displayed less hydrogenation, but also lower hydroformylation activity compared to xantphos **3**.

Table 4 Results of the platinum/tin-catalysed hydroformylation of 1-octene at 60 °C[a]

Ligand	l : b ratio[b]	% Linear aldehyde[b]	% Isomerisation[b]	tof[b,c]
1a	230	95	4.5	18
1b	1.9	8.5	87	<1
1c	>250	92	8.0	210
1d	3.9	23	71	6.5
1e	200	96	3.1	350
3	>250	88	12	720

[a] Conditions: $P(CO/H_2)$ (1 : 1) = 40 bar, ligand : $SnCl_2$: Pt = 2 : 2 : 1, substrate : Pt = 255 : 1, [Pt] = 2.50 mM, number of experiments = 2. Hydrogenation was observed in none of the experiments. [b] l : b ratio, percent linear aldehyde, percent isomerisation to 2-octene, and turnover frequency were determined at 20% conversion. [c] Turnover frequency = (mol of aldehyde) (mol of Pt)$^{-1}$ h^{-1}.

Discussion

The results of the rhodium-catalysed hydroformylation with the (mixed) xanthamine, and xantarsine ligands are consistent with earlier work. The superiority of phosphines among the Group 15 ligand series was demonstrated before by Carlock in the rhodium-catalysed hydroformylation of 1-dodecene.[61] The fact that the xantamine and xantphosamine ligands **1b**, **2b**, and **1d** do not form selective hydroformylation catalysts is in agreement with the HP IR experiments. According to the IR spectra ligands **2b** and **2c** do not co-ordinate to rhodium at all and rhodium–carbonyl clusters are formed. The decreased hydroformylation rates found for these ligands can be explained by the fact that the ligands slow down the reaction of the rhodium–carbonyl clusters with hydrogen to form the $Rh(CO)_4H$ complex, which is the active catalyst in unmodified rhodium-catalysed hydroformylation. The IR and NMR data obtained for the rhodium complex containing ligand **1d** are inconclusive. The structure of the catalytic complex formed for ligand **1d** is unknown and no conclusions can be drawn whether, besides the phosphine, also the amine function of the ligand is co-ordinated to rhodium. Probably a dimeric or a cluster rhodium–carbonyl complex containing one or more ligands is formed.

Contrary to the xantamine ligands, the xantarsine and xantphosarsine ligands **1c** and **1e** give efficient rhodium hydroformylation catalysts. The activity of **1c** and the selectivity of **1e** resemble those of the xantphos ligands. This shows that diarsine or phosphine–arsine ligands can perform as well as diphosphine ligands. For these xantarsine ligands the same rhodium–hydride and the same dimeric rhodium complexes are formed as for the xantphos ligands. The poor results obtained for ligand **2c** are explained by the fact that this ligand, like **1d**, gives undefined rhodium–carbonyl clusters instead of the rhodium–hydride complex.

The HP IR and NMR spectra of the (ligand)$Rh(CO)_2H$ complex containing ligand **1e** indicate that, compared to xantphos **1a**, ligand **1e** shows an increased preference for **ea** co-ordination. This is best explained by the electronic dissimilarity of arsine and phosphorus. Based on the relatively small rhodium–phosphorus and large phosphorus–proton coupling constants, it can be concluded that in the **ea** isomer of $Rh(CO)_2$(**1e**)H the phosphine group is co-ordinated predominantly at the apical site of the trigonal bipyramidal complex, while the arsine group is located mainly in the equatorial plane. These results are consistent with the work of Casey *et al*. on electronically dissymmetric diphosphines, which give enhanced **ea** co-ordination with the stronger donor ligand on the apical position *trans* to the hydride ligand.[62] The relatively large rhodium–hydride coupling constant observed in the ^{1}H NMR spectrum of $Rh(CO)_2$(**1c**)H could be an indication

Table 5 Results of the platinum/tin-catalysed hydroformylation of methyl *trans*-3-pentenoate at 80 °C[a]

Ligand	*t*/h	% Conversion[b]	% Hydrogenation[b]	% 2-MP[b]	% Aldehyde[b]	l : b ratio[b,c]	tof[b,d]
1c	16	39	4.0	27	69	2.9	4.5
1e	16	36	3.4	29	68	3.7	3.9
3	16	95	16	19	65	3.4	10

[a] Conditions: $P(CO/H_2)$ (1 : 1) = 15 bar, ligand : $SnCl_2$: Pt = 2 : 2 : 1, substrate : Pt = 326 : 1, [Pt] = 2.50 mM, number of experiments = 2. [b] Percent conversion, -hydrogenation, -methyl 2-pentenoate (MP), -linear aldehyde, and l : b ratio were determined by GC analysis. [c] l : b ratio includes all branched aldehydes. [d] Averaged turnover frequency = (mol of aldehyde) (mol of Pt)$^{-1}$ h^{-1}.

that also xantarsine **1c** exhibits an increased preference for **ea** co-ordination. This cannot be confirmed by HP IR spectroscopy since the carbonyl absorptions of the $Rh(CO)_2$(**1c**)H complex are partly hidden under the intense absorption bands of the $[Rh(CO)_2(\mathbf{1c})]_2$ dimer.

The very good catalytic performances of xantarsine ligand **1c** and xantphosarsine ligand **1e** in the platinum/tin-catalysed hydroformylation are remarkable. Arsine ligands have been employed in platinum/tin-catalysed hydroformylation before, but like in the rhodium-catalysed hydroformylation, without exception they performed worse than phosphine ligands.[15,20,31] Especially the high hydroformylation activity and excellent selectivity for linear aldehyde formation displayed by ligand **1e** are striking. The xantphosarsine modified platinum/tin catalyst performs even better than the rhodium–xantphos catalysts in the hydroformylation of 1-octene. The low activity of xantphosamine ligand **1d** in the platinum/tin-catalysed hydroformylation is not surprising. As was demonstrated by Dekker *et al*. for other phosphine–amine ligands, the barrier for migratory insertion reactions in square-planar platinum(II) complexes is higher for this type of ligand than for symmetric diphosphine or diamine ligands.[57] Alternatively, it is likely that ligand **1d** does not form chelate complexes at all and during catalysis two ligands are co-ordinated to platinum only *via* the phosphine moieties. This is evidenced by the fact that according to NMR spectroscopy the complex $Pt(SnCl_3)Cl(\mathbf{1d})_2$ is formed to the greater extent when ligand **1d** is treated with $PtCl_2$(cod) and anhydrous tin chloride. The symmetric xantamine **1b** performs even worse than ligand **1d**. This can be explained by the strong electron donating capacity of the diphenylamine groups which have an unfavourable effect on the hydroformylation cycle.

In the platinum/tin-catalysed hydroformylation homoxantphos **3**, having the smaller natural bite angle, showed a higher activity than the xantphos ligand **1a**. These results are consistent with the previous work of Kawabata and Hayashi and co-workers.[13,16,63] It can be deduced from their work that in the platinum/tin–diphosphine catalysed hydroformylation the activity increases with increasing natural bite angles up to a value of approximately 102° (DIOP, 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane),[5] but for wider bite angles the activity drops abruptly. This suggests that the rate-determining step shifts from one point in the hydroformylation cycle to another. For diphosphines having narrow natural bite angles alkene co-ordination or carbon monoxide insertion could be rate limiting, while hydrogen addition could be rate determining for diphosphines with wide natural bite angles. This is confirmed by the hydroformylation experiments with xantphos ligands **1a** and **3** that were monitored by IR spectroscopy. The observation of the platinum–carbonyl complex as the catalyst resting state for ligand **3** suggests a rate-limiting step early in the catalytic cycle, while the platinum–acyl complexes observed for ligand **1a** indicate that the reaction with hydrogen is rate determining.

The shift of the rate-determining step is probably explained by the different reactivity of the *cis* and *trans* isomers of the platinum(II) complexes. In general *trans* co-ordination of phosphines in the square-planar platinum/tin–acyl complexes is thermodynamically favoured over *cis* co-ordination.[26,27,64] However, for the occurrence of migratory insertion reactions in the platinum/tin–hydride and –alkyl complexes and for hydrogenolysis of the platinum/tin–acyl complex to form the aldehyde, *cis* co-ordination of the phosphines is a prerequisite.[28,29,65] Diphosphines having narrow natural bite angles can only form the *cis* complexes due to bite angle constraints and give, therefore, active hydroformylation catalysts. Diphosphines with wide natural bite angles and monophosphines will give the more stable *trans* platinum/tin–acyl complexes. The hydrogenolysis rate of these complexes is slowed down considerably, since first an energetically unfavourable isomerisation of the *trans* to the *cis* complex has to occur. This clearly explains why for triphenylphosphine and for ligands with wide natural bite angles hydrogenolysis is found to be the rate determining step in the catalytic cycle.[16,27] The increased preference for *trans* co-ordination with increasing natural bite angle is demonstrated by the co-ordination behaviour of xantphos ligands **1a** and **3** in the (ligand)$Pt(SnCl_3)Cl$ complexes. Ligand **3** gives the *cis* complex exclusively according to the ^{31}P-$\{^1H\}$ NMR spectrum, while **1a** gives the *trans* complex in 33% yield.

The trend of increasing activity with increasing natural bite angle that is observed for the ligands possessing narrow natural bite angles[16] can be explained by both the step of alkene insertion and the step of carbon monoxide insertion. A theoretical study of Rocha and De Almeida on the complex $Pt(H)(PH_3)_2(SnCl_3)(C_2H_4)$ shows that upon alkene insertion the P–Pt–P bite angle increases from 106.8 to a maximum of 146.2°.[29] Based on these results it can be concluded that widening of the natural bite angle enhances the alkene insertion reaction and, therefore, the hydroformylation rate. The influence of the natural bite angle on the rate of carbon monoxide insertion has been demonstrated both experimentally and theoretically.[55,65,66]

Besides an effect on the activity, an effect of the natural bite angle on the selectivity for linear aldehyde formation is also observed. This bite angle effect is comparable to that observed in the rhodium–diphosphine catalysed hydroformylation, and can be explained in a similar way.[7,46] Widening of the bite angle will lead to an increase of the steric congestion around the platinum centre, and, hence, to more selective formation of the sterically less hindered linear platinum alkyl species. The major difference, however, between the platinum/tin- and rhodium-catalysed hydroformylation is the fate of the branched metal–alkyl species that is also formed in the hydroformylation cycle. The branched rhodium–alkyl species gives both branched aldehyde formation and isomerisation to 2-octene, while for the branched platinum–alkyl species isomerisation to 2-octene occurs almost exclusively.

The high activity of the xantphosarsine ligand **1e** in the platinum/tin-catalysed hydroformylation is thus explained by the fact that, despite a wide natural bite angle, this ligand gives *cis* co-ordination in the platinum/tin complexes, as was observed by ^{31}P-$\{^1H\}$ NMR. The enhanced preference for *cis* co-ordination of ligand **1d** compared to **1a** can be imposed by the electronic dissymmetry of the ligand. On the other hand, the high activity of xantarsine **1c** suggests that this symmetric ligand also is a better *cis* co-ordinating ligand than **1a**, which might be the result of the smaller *trans* directing influence of arsine compared to phosphine.[55] The wide natural bite angle of ligand **1d**, which is comparable to the one of xantphos **1a**, explains the high selectivity for linear aldehyde formation observed for this ligand.

Conclusion

Wide bite angle xantarsine and mixed xantphosarsine ligands give active and selective rhodium catalysts for the hydroformylation of 1-octene. The xanthene based amine ligands give very poor hydroformylation catalysts. Under hydroformylation conditions the xantamine ligands do not co-ordinate to rhodium at all, while the xantphosamine ligand behaves most likely as a monophosphine ligand instead of a chelating phosphorus/nitrogen ligand.

In the platinum/tin-catalysed hydroformylation the xantamine and xantphosamine ligands do not give active catalysts either. The xantarsine and xantphosarsine ligands on the other hand give very efficient catalysts for the selective hydroformylation of 1-octene. Especially the high activity and selectivity that is observed for the xantphosarsine ligand is remarkable. To the best of our knowledge these are the first examples of arsine based ligands that are superior to phosphine ligands in the platinum/tin-catalysed hydroformylation. The high activity

and selectivity of the xantphosarsine ligand is explained by the fact that it has approximately the same natural bite angle as xantphos, but has an enhanced preference for the formation of *cis* co-ordinated platinum/tin complexes.

Experimental

Computational details

The molecular mechanics calculations were performed using the CAChe WorkSystem version 4.0,[67] on an Apple Power MacIntosh 950, equipped with two CAChe CXP coprocessors. Calculations were carried out similarly to the method described by Casey and Whiteker,[34] using a Rh–P bond length of 2.315 Å and a Rh–As bond length of 2.415 Å.[68] Minimisations were done *via* the block-diagonal Newton–Raphson method, allowing the structures to converge fully with a termination criterion of a rms factor of 0.00042 kJ mol^{-1} $Å^{-1}$ or less.

Preparations

Ligand 1b. This compound was prepared *via* a modified version of the Ullmann reaction.[41] A slurry of 1.50 g of compound **5** (2.66 mmol), 1.35 g of diphenylamine (7.98 mmol), 2.5 g of copper (40 mmol), 11.0 g of potassium carbonate (80 mmol), and 0.10 g of 18-crown-6 (0.27 mmol) was boiled under reflux overnight in 20 ml of 1,2-dichlorobenzene. The reaction mixture was filtered and the residual solids were washed with dichloromethane. The filtrate was evaporated to dryness and the residue washed with hexanes and crystallised from ethanol–THF. Yield: 1.01 g white crystals of **1b** (58%). mp 259–260 °C. ^{1}H NMR ($CDCl_3$): δ 7.31 (d, ^4J(H,H) = 2.4, 2H; $H^{1,8}$), 7.00 (m, 10H; CH), 6.80 (t, ^3J(H,H) = 7.3, 4H; CH), 6.73 (d, ^3J(H,H) = 7.5 Hz, 8H; CH), 1.70 (s, 6H; CH_3) and 1.25 (s, 18H; *t*-butyl). Calc. for $C_{47}H_{48}N_2O$: C, 85.93; H, 7.37; N, 4.26. Found: C, 86.18; H, 7.43; N, 4.06%.

Ligand **2b** and compound **6** were prepared similarly to **1b**. Detailed descriptions of the syntheses and characterisations are included in the supplementary material.

Ligand 1c. At −60 °C 2.8 ml of *n*-butyllithium (2.5 M in hexanes, 6.9 mmol) were added dropwise to a stirred solution of 1.50 g of compound **4** (3.12 mmol) in 50 ml of THF. The resulting beige suspension was stirred for 1 h. Next a solution of 1.82 g of chlorodiphenylarsine (6.9 mmol) in 20 ml of THF was added and the reaction mixture slowly warmed to room temperature overnight. It was diluted with 25 ml of ethyl acetate and hydrolysed with 25 ml of a one to one mixture of brine and dilute hydrochloric acid. The water layer was removed and the organic layer dried over $MgSO_4$. The solvents were removed *in vacuo* and the residual off-white powder washed with hexanes and crystallised from ethanol–THF. Yield: 2.01 g white crystals of **1c** (83%). mp 207–208 °C. ^{1}H NMR ($CDCl_3$): δ 7.41 (d, ^4J(H,H) = 2.3, 2H; $H^{1,8}$), 7.27 (m, 20H; CH), 6.69 (d, ^4J(H,H) = 2.3 Hz, 2H; $C^{3,6}$), 1.72 (s, 6H; CH_3) and 1.15 (s, 18H; *t*-butyl). Calc. for $C_{47}H_{48}As_2O$: C, 72.49; H, 6.22. Found: C, 72.65; H, 6.25%. Ligands **1d**, **1e**, and **2c** and compound **7** were prepared similarly to **1c**. Detailed descriptions of the syntheses and characterisations are included in the supplementary material.

Pt($SnCl_3$)Cl(1a) 11a. To a stirred solution of 3.7 mg of $PtCl_2$(cod) (10 μmol) and 7.6 mg of compound **1a** (11 μmol) in 0.75 ml of CD_2Cl_2 were added 2.1 mg of anhydrous $SnCl_2$ (11 μmol). After 1 h the reaction mixture was transferred to a 0.5 cm NMR tube and analysed. ^{1}H NMR (25 °C, CD_2Cl_2): δ 7.54 (bm, 6H; CH), 7.37 (bm, 6H; CH), 7.25 (bm, 12H; CH), 1.84 (s, 3H; CH_3), 1.81 (s, 3H; CH_3), 1.26 (s, 9H; *t*-butyl) and 1.22 (s, 9H; *t*-butyl). ^{31}P-{^{1}H} NMR (25 °C, CD_2Cl_2): δ 16.4 (^1J(Pt,P) = 2172 Hz, satellites). ^{31}P-{^{1}H} NMR (−73 °C, CD_2Cl_2): δ 18.1 (d, ^1J(Pt,P) = 3046 (satellites), ^2J(P,P) = 14.3, $P_{trans Sn}$), 15.2 (^1J(Pt,P) = 1954 (satellites), $^2J_{avg}$(Sn,P) = 234 (satellites), $P_{trans P}$) and 4.3 (d, ^1J(Pt,P) = 3706 (satellites), $^2J_{avg}$(Sn,P) = 117 (satellites), ^2J(P,P) = 14.3 Hz, $P_{trans Cl}$).

Pt(CO)($SnCl_3$)Cl(**1a**) **11b**. HP IR (CH_2Cl_2, carbonyl region, cm^{-1}): 2049 (PtCO).

Hydroformylation experiments

(a) Rhodium catalysed. Hydroformylation reactions were carried out in an autoclave, equipped with a glass inner beaker, a substrate inlet vessel, a liquid sampling valve, and a magnetic stirring rod. The temperature was controlled by an electronic heating mantle. In a typical experiment the 50 μmol of ligand were placed in the autoclave and the system was evacuated and heated to 50 °C. After 0.5 h the autoclave was filled with CO/H_2 (1 : 1) and a solution of 10 μmol $Rh(CO)_2$(acac) in 8.5 ml of toluene. The autoclave was pressurised to 16 bar, heated to 80 °C and stirred for 1.5 h to form the active catalyst. Then 1.0 ml of substrate (filtered over neutral activated alumina to remove peroxide impurities) and 0.5 ml of the internal standard *n*-decane were placed in the substrate vessel, purged with 10 bar CO/H_2 (1 : 1), and pressed into the autoclave with 20 bar CO/H_2 (1 : 1). After 1 h samples of the reaction mixture were taken, quenched with tri-*n*-butyl phosphite, and analysed by temperature-controlled gas chromatography.

(b) Platinum/tin-catalysed. The platinum/tin-catalysed hydroformylation experiments were performed similarly to the procedure described for rhodium. The catalyst complex (ligand)-Pt($SnCl_3$)Cl was preformed outside the autoclave by adding 9.5 mg of $SnCl_2$ (50 μmol) to a solution of 9.4 mg $PtCl_2$(cod) (25 μmol) and two equivalents of ligands in 8.5 ml of CH_2Cl_2. The reactions were stopped by cooling on ice.

HP FT IR experiments

(a) Rhodium complexes. In a typical experiment the HP IR autoclave was filled with two to five equivalents of ligand, 4 mg of $Rh(CO)_2$(acac), and 15 ml of cyclohexane. The autoclave was purged three times with 15 bar CO/H_2 (1 : 1), pressurised to approximately 18 bar, and heated to 80 °C. Catalyst formation was monitored in time by FT IR and was usually completed within one h.

(b) Platinum/tin complexes. In a typical experiment 14 mg of anhydrous $SnCl_2$ (75 μmol) were added to a stirred solution of 14 mg $PtCl_2$(cod) (38 μmol) and two equivalents of ligand in 15 ml of CH_2Cl_2. After 0.5 h the reaction was transferred to the HP IR autoclave. The autoclave was purged three times with 15 bar CO/H_2 (1 : 1), warmed to 60 °C and pressurised with CO/H_2 (1 : 1) to 40 bar. After 1 h 1.0 ml of 1-octene was added and the reaction monitored in time by FT IR.

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References

1 P. W. N. M. van Leeuwen and G. van Koten, in *Homogeneous Catalysis with Transition Metal Complexes*, eds. P. W. N. M. van Leeuwen and G. van Koten, Elsevier, Amsterdam, 1993, pp. 201 and 222.
2 M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17.
3 C. D. Frohning and C. W. Kohlpaintner, in *Applied Homogeneous Catalysis with Organometallic Compounds: a Comprehensive Handbook in Two Volumes*, eds. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. 1, pp. 27–104.

4 T. J. Devon, G. W. Phillips, T. A. Puckette, J. L. Stavinoha and J. J. Vanderbilt (to Eastman Kodak), *U.S. Pat.*, 4,694,109, 1987 (*Chem. Abstr.*, 1988, **108**, 7890).
5 C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney, Jr. and D. R. Powell, *J. Am. Chem. Soc.*, 1992, **114**, 5535.
6 M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Fraanje, *Organometallics*, 1995, **14**, 3081.
7 L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz and A. L. Spek, *Organometallics*, 2000, **19**, 872.
8 E. Billig, A. G. Abatjoglou and D. R. Bryant (to Union Carbide), *Eur. Pat.*, 213,639, 1987 (*Chem. Abstr.*, 1987, **107**, 7392r).
9 A. van Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman and A. L. Spek, *Organometallics*, 1996, **15**, 835.
10 M. E. Broussard, B. Juma, S. G. Train, W.-J. Peng, S. A. Laneman and G. Stanley, *Science*, 1993, **260**, 1784.
11 P. M. Burke, J. M. Garner, W. Tam, K. A. Kreutzer, A. J. J. M. Teunissen, C. S. Snijder and C. B. Hansen (to DSM/Du Pont), *WO Pat.*, 97/33854, 1997 (*Chem. Abstr.*, 1997, **127**, 294939r).
12 L. A. van der Veen, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 336.
13 Y. Kawabata, T. Hayashi and I. Ogata, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 462.
14 C.-Y. Hsu and M. Orchin, *J. Am. Chem. Soc.*, 1975, **97**, 3553.
15 I. Schwager and J. F. Knifton, *J. Catal.*, 1976, **45**, 256.
16 T. Hayashi, Y. Kawabata, T. Isoyama and I. Ogata, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3438.
17 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal.*, 1991, **66**, 37.
18 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal.*, 1990, **63**, 15.
19 P. Meessen, D. Vogt and W. J. Keim, *J. Organomet. Chem.*, 1998, **551**, 165.
20 S. C. Tang and L. Kim, *J. Mol. Catal.*, 1982, **14**, 231.
21 P. W. N. M. van Leeuwen, C. F. Roobeek, R. L. Wife and J. H. G. Frijns, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 31.
22 P. W. N. M. van Leeuwen and C. F. Roobeek, *New J. Chem.*, 1990, **14**, 487.
23 C. Botteghi, S. Paganelli, U. Matteoli, A. Scrivanti, R. Ciociaro and L. M. Venanzi, *Helv. Chim. Acta*, 1990, **73**, 284.
24 F. Agbossou, J.-F. Carpentier and A. Mortreux, *Chem. Rev.*, 1995, **95**, 2485.
25 J. K. Stille, H. Su, P. Brechot, G. Parrinello and L. S. Hegedus, *Organometallics*, 1991, **10**, 1183.
26 A. Scrivanti, C. Botteghi, L. Toniolo and A. Berton, *J. Organomet. Chem.*, 1988, **344**, 261.
27 M. Gomez, G. Muller, D. Sainz, J. Sales and X. Solans, *Organometallics*, 1991, **10**, 4036.
28 I. Tóth, T. Kegi, C. J. Elsevier and L. Kollar, *Inorg. Chem.*, 1994, **33**, 5708.
29 W. R. Rocha and W. B. De Almeida, *Organometallics*, 1998, **17**, 1961.
30 B. Cornils, in *Hydroformylation. Oxo Synthesis, Roelen Reaction*, ed. J. Falbe, Springer-Verlag, Berlin, 1980, pp. 1–225.
31 H. C. Clark and J. A. Davies, *J. Organomet. Chem.*, 1981, **213**, 503.
32 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
33 C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2953.
34 C. P. Casey and G. T. Whiteker, *Isr. J. Chem.*, 1990, **30**, 299.
35 P. C. J. Kamer, J. N. H. Reek and P. W. N. M. van Leeuwen, *Chemtech*, 1998, **28**, 27.
36 P. Dierkes and P. W. N. M. van Leeuwen, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1519.
37 M. Kranenburg, P. C. J. Kamer, D. Vogt and P. W. N. M. van Leeuwen, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2177.
38 W. Goertz, P. C. J. Kamer, P. W. N. M. van Leeuwen and D. Vogt, *Chem. Commun.*, 1997, 1521.
39 M. Kranenburg, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.*, 1998, 25.
40 L. A. van der Veen, P. K. Keeven, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 2000, 333.
41 S. Gauthier and J. M. J. Frechet, *Synthesis*, 1987, 383.
42 K. McWilliams and J. W. Kelly, *J. Org. Chem.*, 1996, **61**, 7408.
43 L. A. van der Veen, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 1999, **18**, 4765.
44 N. K. Bliznyuk, G. S. Levskaya and E. N. Matyukhina, *J. Gen. Chem. USSR*, 1965, **35**, 1253.
45 W. L. Lewis, C. D. Lowry and F. H. Bergheim, *J. Am. Chem. Soc.*, 1921, **43**, 893.
46 L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk and C. Bo, *J. Am. Chem. Soc.*, 1998, **120**, 11616.
47 R. Whyman, *Chem. Commun.*, 1970, 230.
48 B. L. Booth, M. J. Else, R. Fields and R. N. Haszeldine, *J. Organomet. Chem.*, 1971, **27**, 119.
49 P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 315.
50 B. R. James, D. Mahajan, S. J. Rettig and G. M. Williams, *Organometallics*, 1983, **2**, 1452.
51 A. Castellanos-Páez, S. Castillón, C. Claver, P. W. N. M. van Leeuwen and W. G. J. de Lange, *Organometallics*, 1998, **17**, 2543.
52 E. Paumard, A. Mortreux and F. Petit, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1380.
53 C. J. Cobley and P. G. Pringle, *Inorg. Chim. Acta*, 1997, **265**, 107.
54 The averaged value of $^{2}J(^{117}\mathrm{Sn,P})$ and $^{2}J(^{119}\mathrm{Sn,P})$.
55 G. K. Anderson and G. J. Lumetta, *Organometallics*, 1985, **4**, 1542.
56 G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.
57 G. P. C. M. Dekker, A. Buijs, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang and C. H. Stam, *Organometallics*, 1992, **11**, 1937.
58 S. Gladiali, L. Pinna, C. G. Arena, E. Rotondo and F. Faraone, *J. Mol. Catal.*, 1991, **66**, 183.
59 C. Abu-Gnim and I. Amer, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 115.
60 C. Basoli, C. Botteghi, M. A. Cabras, G. Chelucci and M. Marchetti, *J. Organomet. Chem.*, 1995, **488**, C20.
61 J. T. Carlock, *Tetrahedron*, 1984, **40**, 185.
62 C. P. Casey, E. L. Paulsen, E. W. Beuttenmueller, B. R. Proft, B. A. Matter and D. R. Powell, *J. Am. Chem. Soc.*, 1999, **121**, 63.
63 Actually, their reports are the first examples in which the catalytic performance can be related to the natural bite angle of diphosphine ligands.[36]
64 G. K. Anderson and R. J. Cross, *Acc. Chem. Res.*, 1984, **17**, 67.
65 N. Koga and K. Morokuma, *Chem. Rev.*, 1991, **91**, 823.
66 G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze and P. W. N. M. van Leeuwen, *Organometallics*, 1992, **11**, 1598.
67 CAChe WorkSystem, Version 4.0, CAChe Scientific Inc., Beaverton, OR, 1997.
68 According to the Cambridge Crystallographic Database, a distance of 2.415 Å is typical for Rh–As bond lengths.