Novel Amphiphilic Diphosphines: Synthesis, X-ray Structure, Rhodium Complexes, Use in Hydroformylation, and Rhodium Recycling

Armin Buhling, Paul C. J. Kamer, and Piet W. N. M. van Leeuwen*

University of Amsterdam, Van't Hoff Research Institute, Inorganic Chemistry, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Jaap W. Elgersma

University of Amsterdam, Amsterdam Institute for Molecular Studies, Laboratory for Analytical Chemistry, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Kees Goubitz and Jan Fraanje

University of Amsterdam, Amsterdam Institute for Molecular Studies, Department of Crystallography, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received January 30, 1997[⊗]

Three novel amphiphilic diphosphines have been synthesized: bis[2-(phenyl(3-pyridyl)-phosphino)ethyl] ether (POPpy) and bis[2-((4-((diethylamino)methyl)phenyl)phenylphosphino)-ethyl] ether (POPam), based on bis[2-(diphenylphosphino)ethyl] ether (POP), and 4,6-bis[bis(4-((diethylamino)methyl)phenyl)phosphino]-10,10-dimethylxanthene (xantham), based on 4,6-bis(diphenylphosphino)-10,10-dimethylxanthene (Xantphos). The crystal structure of xantham has been determined. Solution structures of rhodium xantham complexes have been studied using NMR and IR spectroscopy. When POPam is used in the hydroformylation of oct-1-ene, a linear/branched ratio (l/b) of 7.3 is achieved (88% nonanal) without isomerization to oct-2-ene. The use of POPpy results in an activity that is twice as high, a higher l/b-ratio of 9, and 0.7% isomerization. When xantham is used in the hydroformylation of hex-1-ene, oct-1-ene, and dodec-1-ene (80 °C, 20 bar of syngas, toluene), l/b-ratios of 50 have been achieved (94% nonanal) together with 4% of isomerized octenes. The pH-dependent distribution characteristics of the free ligands have been determined, and it is shown that POPpy, POPam, and xantham can be extracted for 40% from a Et_2O solution into an aqueous solution of H_2SO_4 at pH values of, respectively, 2.5, 5, and 5. Rhodium recycling experiments using POPam and xantham show that rhodium can be extracted into an aqueous layer at pH 5−5.5 for more than 99.95%, as determined by ICP-AES analysis, which allows complete separation of the product aldehydes and catalyst. After neutralization of the aqueous phase containing protonated POPam with an aqueous solution of $NaHCO_3$, only 65% of the rhodium can be re-extracted into fresh toluene. In the case of xantham, 98% of the rhodium is re-extracted. Pressurizing the recovered rhodium and excess xantham to 20 bar at 80 °C resulted in regeneration of the original active hydride complex, as judged by the retention of activity of up to 86%. POPpy has proved inappropriate for the recycling of rhodium.

Introduction

Since the discovery that rhodium phosphine complexes[1−3] enable hydroformylation of propene at much lower temperatures and pressures than cobalt,[4] they have replaced cobalt catalysts in nearly all major plants producing lower aldehydes, despite the higher price of rhodium.[5−7] Apart from the isononyl alcohol process by Mitsubishi Chemical Company,[8] no major commercial process for the hydroformylation of longer chain alkenes exploits rhodium phosphine complexes. The development of such a process faces two challenges. First of all, a highly efficient method for recovering the expensive rhodium catalyst from the high-boiling aldehydes is imperative. Secondly, a highly selective rhodium catalyst is required that can limit the formation of branched aldehydes and suppress isomerization of the feedstock alkenes. Ideally, isomerization should be absent since the isomerized alkenes build up in the reactor as a consequence of feed recycle.

The concept of biphasic catalysis has emerged as an important method for achieving easy separation and reuse of homogeneous metal catalysts.[9−15] The solubility of higher alkenes in water, however, is limited, which

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) Osborn, J. A.; Young, J. F.; Wilkinson, G. *J. Chem. Soc.* **1965**, 17.

(2) Slaugh, L. H.; Mullineaux, R. D. (Shell) U.S. Patent 3 239 566, 1966.

(3) Evans, D.; Osborn, J. A.; Wilkinson, G. J. *J. Chem. Soc. A* **1968**, 3133.

(4) Yagupski, G.; Brown, C. K.; Wilkinson, G. J. *J. Chem. Soc. A* **1970**, 1392.

(5) Bahrmann, H.; Bach, H. W. In *Ullmann's Encyclopedia of Industrial Chemistry*; Verlagsgesellschaft mbH: Weinheim, Germany, 1991; Vol. A18 pp 321−326.

(6) Cornils, B. In *Hydroformylation: New Syntheses with Carbon Monoxide*; J. Falbe, Ed.; Springer Verlag: Berlin, 1980.

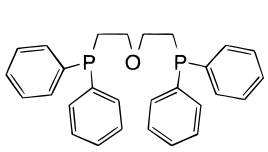
(7) Weissermel, K.; Arpe, H.-J. *Industrielle Organische Chemie*; Verlagsgesellschaft mbH: Weinheim, Germany, 1988.

(8) Onada, T. *CHEMTECH* **1993**, *23*(Sept), 34.

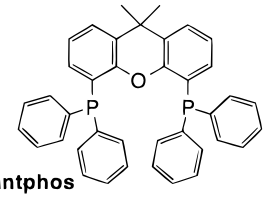
S0276-7333(97)00068-X CCC: $14.00

would result in low reaction rates due to the approximate first-order dependency of the hydroformylation reaction in alkene concentration.[16−18] We focused on a known catalyst recycling strategy, analogous to that of the Kuhlmann process,[6] using amphiphilic phosphines.[19−23] Thus, the hydroformylation is performed under conventional homogeneous conditions in an organic medium at high alkene concentrations. After (partial) conversion of the alkene, the catalyst is extracted into an acidic aqueous phase, thus allowing separation of the organic products, and re-extracted into a fresh organic phase upon neutralization of the aqueous phase. Previously, we investigated this system using a series of functionalized triphenylphosphines[24,25] and succeeded in the almost quantitative recovery of rhodium. Amphiphilic ligands based on 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl (BISBI) formed highly active and selective rhodium catalysts, but the rhodium recycling experiments were less successful.[26]

As part of our search for more effective catalysts, we decided on functionalisation of two other interesting ligands for the hydroformylation reaction, namely Xantphos, developed in our research group,[27] and bis[2-(diphenylphosphino)ethyl] ether (POP). The rigid Xant-



POP

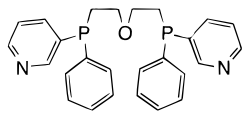


Xantphos

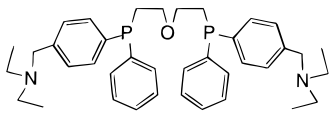
phos ligand induces the highest linearity in the hydroformylation reaction known so far, while the degree of isomerization is low. Extremely high selectivity is also obtained with diphosphite ligands,[28−31] but these systems are not suitable for aqueous work-up. The very flexible chelating POP ligand also provides an improved linearity in the hydroformylation of 1-decene, 1,9-decadiene, and 1,5-hexadiene when compared to PPh_3.[32] Moreover, the observed isomerization of the starting alkenes is extremely low. Brown *et al.* suggested that POP has the capacity to coordinate to the active rhodium hydride in both a bis(equatorial) and equatorial−axial fashion.[33] 1,5-Bis(diphenylphosphino)-pentane can easily lead to cyclometallation giving a Rh(III) complex, as reported by Shaw *et al.* for 1,5-bis-[bis(*tert*-butyl)phosphino]pentane,[34,35] which is prevented by the central oxygen atom in POP and Xantphos.

Phosphino ethers are potentially both oxygen- and phosphorus-donor ligands. Complexes have been reported in which POP only functions as a cis-coordinated phosphorus bidentate ligand, such as in [(POP)-$NiCl_2$],[36−38] [(POP)Rh(COD)][ClO_4],[39] and [(POP)Pd-$(CH_3CN)_2$][BF_4]$_2$.[40] However, POP can also serve as a terdentate ligand with additional oxygen coordination, as found in [(POP)Pd{η^1-(σ-alkenyl)}][PF_6],[41] [(POP)Pd-(PEt_3)][BF_4]$_2$,[40] [(POP)Rh(H)$_2$(MeOH)][BF_4],[33] and [(POP)-Rh(CO)][PF_6].[42] All of these complexes contain metal cations. In neutral, stable rhodium phosphine hydride species, we expect that coordination of oxygen is not significant, although it might play a role in transient species.

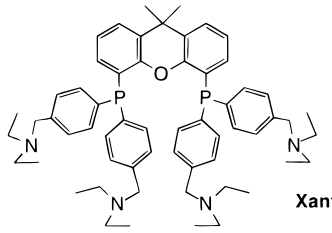
Here, we present a study of the novel amphiphilic ligands xantham, POPpy, and POPam. Their coordina-



POPpy (1)



POPam (2)

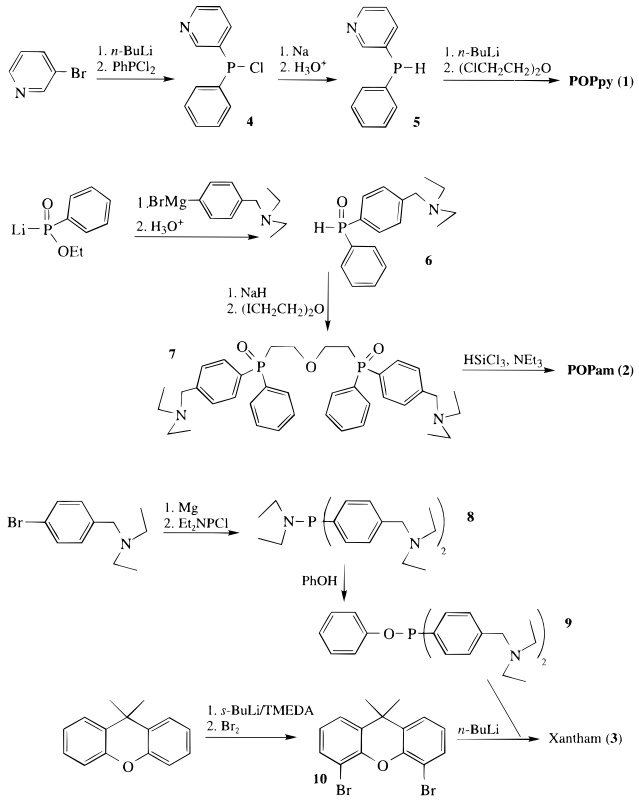


Xantham (3)

tion behavior in some rhodium complexes is discussed. These ligands are active and highly selective in the hydroformylation reaction. Additionally, xantham enables an efficient rhodium recycling.

(9) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.
(10) Herrmann, W. A.; Kohlpaintner, C. W.; Manetsberger, R. B.; Bahrmann, H.; Kottmann, H. *J. Mol. Catal.* **1995**, *97*, 65.
(11) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200.
(12) Fell, B.; Papadogianakis, G. *J. Prakt. Chem.* **1994**, *336*, 591.
(13) Fell, B.; Papadogianakis, G.; Konkol, W.; Weber, J.; Bahrmann, H. *J. Prakt. Chem.* **1993**, *335*, 75.
(14) Ding, H.; Hanson, B. E.; Bartik, T.; Bartik, B. *Organometallics* **1994**, *13*, 3761.
(15) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72.
(16) Cavalieri d'Oro, P.; Raimondi, L.; Pagani, G.; Montrasi, G.; Gregorio, G.; Andreetta, A. *Chim. Ind. (Milan)* **1980**, *62*, 572.
(17) van Rooy, A.; de Bruijn, N. H.; Roobeek, K. F.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1995**, *507*, 69.
(18) Gerritsen, L. A.; Klut, W.; Vreugdenhil, M. H.; Scholten, J. J. F. *J. Mol. Catal.* **1980**, *9*, 265.
(19) Tóth, I.; Hanson, B. E.; Davis, M. E. *J. Organomet. Chem.* **1990**, *396*, 363.
(20) Bayón, J. C.; Real, J.; Claver, C.; Polo, A.; Ruiz, A. *J. Chem. Soc., Chem Commun.* **1989**, 1056.
(21) Kurtev, K.; Ribola, D.; Jones, R. A.; Cole-Hamilton, D. J.; Wilkinson, G. J. *J. Chem. Soc., Dalton Trans.* **1980**, 55.
(22) Nagel, U. *Angew. Chem.* **1984**, *96*, 425.
(23) Andreetta, A.; Barberis, G.; Gregorio, G. *Chim. Ind. (Milan)* **1978**, *60*, 887.
(24) Buhling, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Mol. Catal.* **1995**, *98*, 69.
(25) Buhling, A.; Elgersma, J. W.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Mol. Catal. A: Chem.* **1997**, *116*, 297.
(26) Buhling, A.; Nkrumah, S.; Elgersma, J. W.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1996**, 2143.
(27) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081.
(28) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835.
(29) Billig, E.; Abatjoglou, A.; Bryant, D. R. (Union Carbide) U.S. Patent 4 769 49 8, 1988.
(30) Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *155*, 2066.
(31) Johnson, J. R.; Cuny, G. D.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1760.
(32) Goodall, B. L.; Grotenhuis, P. A. M.; van Leeuwen, P. W. N. M. GB Pat. Appl. 8722460, 1988.
(33) Brown, J. M.; Cook, S. J.; Kent, A. G. *Tetrahedron* **1986**, *42*, 5104.
(34) Shaw, B. L. *Adv. Chem. Ser.* **1982**, *196*, 101.
(35) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. L.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.
(36) Dapporto, P.; Sacconi, L. *J. Chem. Soc. A* **1971**, 1914.
(37) Dapporto, P.; Sacconi, L. *J. Am. Chem. Soc.* **1970**, *92*, 4133.
(38) Greene, P. T.; Sacconi, L. *J. Chem. Soc. A* **1970**, 866.
(39) Thewissen, D. H. M. W.; Timmer, K.; Noltes, J. G.; Marsman, J. W.; Laine, R. M. *Inorg. Chim. Acta* **1985**, *97*, 143.
(40) Steffey, B. D.; Miedaner, A.; Maciejewski-Farmer, M. L.; Bernatis, P. R.; Herring, A. M.; Allured, V. S.; Carperos, V.; DuBois, D. L. *Organometallics* **1994**, *13*, 4844.

Scheme 1. Synthesis of Ligands



Results and Discussion

Ligand Synthesis. POPpy was synthesized according to Scheme 1. 3-Pyridyllithium was synthesized[43,44] and isolated as a yellow solid. Direct addition to $PhPCl_2$ gave a mixture of $PhPCl_2$, Ph(3-pyridyl)PCl (**4**), and $PPh(3\text{-pyridyl})_2$. The use of a pyridylzinc intermediate[45] gave a similar isolated yield, though this procedure was more laborious. NaPPh(3-pyridyl), obtained by the slow reduction[45] of **4**, could be used *in situ* to react with bis(2-chloro)ethyl ether. Higher yields were obtained upon isolation and subsequent deprotonation of the secondary phosphine **5**. POPam was readily synthesized from the secondary phosphine oxide **6** and bis(2-iodo)ethyl ether. Dioxide **7** was readily reduced, and the pure diastereomeric mixture of POPam was obtained, albeit in low yield (42%) due to the formation of many decomposition products.

The synthesis of xantham starts with the highly water-sensitive phosphinous amide **8**. The common procedure to cleave the P−N bond with dry HCl to give the corresponding chlorophosphine[46] would lead to protonation of the benzylic amino groups by HCl. Therefore, we replaced the diethylamide group by an aryloxy group, which is also a potential leaving group. This was done with phenol in the absence of the usually required equivalent of acid.[47] Useful reaction rates were found when we used a large excess of phenol and higher temperatures (80−90 °C). The excess phenol could be easily removed by azeotropic distillation with mesitylene providing pure phosphinite **9** in 98% yield. 4,6-Dibromoxanthene **10** was prepared to cleanly generate the dilithio compound with 2 equiv of *n*-BuLi.[27,48−51] This compound did not react with the coproduct 1-bromobutane below 20 °C and smoothly substituted the phenoxy group in **9** at lower temperatures.

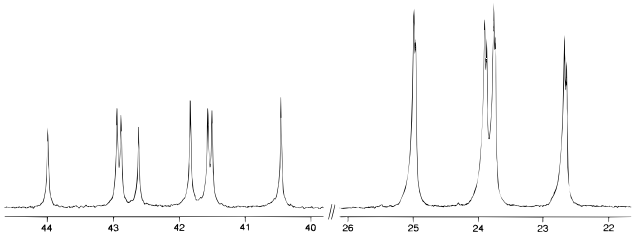


Figure 1. $^{31}P\{^1H\}$ NMR: spectrum for HRh(**4**)(CO)(PPh_3).

Rhodium Complexes. To establish the coordination chemistry of the novel ligands and the possible formation of P−N chelated complexes, solution structures of rhodium complexes were studied by means of NMR and IR spectroscopy.[45,52] Exchange of 1 equiv of xantham with $HRh(CO)(PPh_3)_3$ results in quantitative formation of HRh(xantham)(CO)(PPh_3). The $^{31}P\{^1H\}$ NMR spectrum, as shown in Figure 1, is typical of a structure in which both PPh_3 and xantham are equatorially coordinated, and it reveals the expected Rh−P and P−P coupling constants.[27] The additional fine structure in the spectrum is caused by second-order effects owing to the relatively small difference in chemical shifts of PPh_3 and xantham, as confirmed by simulation.

The relatively small H−P coupling constants in the ^1H NMR spectrum indicate coordination of the phosphines in a tris(equatorial) fashion. For the analogous Xantphos complex, it was shown that the rigid conformation of Xantphos, which is coordinated in the equatorial plane, leads to the inequivalence of the methyl groups in the xanthene bridge and the *ortho* hydrogens of the phenyl groups on the diphenylphosphino moieties. This was also observed for the xantham complex. In addition, the protons in the benzylic diethylamino groups are diastereotopic. The methyl protons of the ethyl groups give a multiplet, while the methylene protons are split into two overlapping multiplets. The methylene protons in the benzylic amine bridges give two separate resonances: an AB pattern and a singlet, both with the intensity of four protons. The AB pattern, which reveals geminal coupling constants of 14.3 Hz, can be accounted for by the "axial" positions that two of the phenyl groups assume in the rhodium complex, according to molecular modeling. This renders the two protons on the benzylic carbon diastereotopic. Formally, the benzylic hydrogens, situated on the "equatorial"

(41) Kataoke, Y.; Tsuji, Y.; Matsumoto, O.; Ohashi, M.; Yamagata, T.; Tani, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2099.
(42) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583.
(43) Rubinsztajn, S.; Zeldin, M.; Fife, W. K. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 495.
(44) Parham, W. E.; Piccirilli, R. M. *J. Org. Chem.* **1977**, *42*, 257.
(45) Budzelaar, P. H. M.; Frijns, J. H. G. *Organometallics* **1990**, *9*, 1222.
(46) Tóth, I.; Hanson, B. E.; Davis, M. E. *Organometallics* **1990**, *9*, 675.
(47) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357.
(48) Hillebrand, S.; Bruckmann, J.; Krüger, C.; Haenel, M. W. *Tetrahedron Lett.* **1995**, *36*, 75.
(49) Haenel, M. W.; Fieseler, H.; Jakubik, D.; Gabor, B.; Goddard, R.; Krüger, C. *Tetrahedron Lett.* **1993**, *34*, 2107.
(50) Haenel, M. W.; Jakubik, D.; Rothenberger, E.; Schroth, G. *Chem. Ber.* **1991**, *124*, 1705.
(51) Schwarz, E. B.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 10775.
(52) Lo Schiavo, S.; Rotondo, E.; Bruno, G.; Faraone, F. *Organometallics* **1991**, *10*, 1613.

phenyl groups and appearing as a singlet, are also diastereotopic, but they are accidentally degenerate.

In the $^{13}C\{^1H\}$ NMR spectrum of the ^{13}CO-enriched HRh(xantham)(CO)(PPh_3) complex, the ^{13}CO ligand gives an apparent double quartet at 205.9 ppm. The multiplet hydride signal in the ^1H NMR spectrum revealed a C−H coupling of 37.5 Hz, which is consistent with values found in other trans-^{13}CO hydride complexes.[53,54]

Bubbling CO through a solution of the HRh(xantham)(CO)(PPh_3) complex resulted in partial formation of HRh(xantham)$(CO)_2$, the presumed catalytically active species under hydroformylation conditions. Also in this complex, xantham is bis(equatorially) coordinated as judged by the neat doublet in the $^{31}P\{^1H\}$ NMR spectrum and the small H−P coupling constant. The hydride signal unveils a H−Rh coupling constant of 6.6 Hz.

The $^{13}C\{^1H\}$ NMR spectrum of the crude ^{13}CO-enriched HRh(xantham)$(CO)_2$ reveals only one CO resonance as a double triplet, owing to coupling with rhodium and two phosphorus atoms. The hydride signal also reveals coupling with two equivalent ^{13}CO ligands. Low-temperature NMR showed that the observed resonance is a time-averaged signal of an axial and equatorial CO which are rapidly exchanging. The CO signal loses its multiplicity at −60 °C and is very broad at −80 °C. Apparently, the complex is subject to fluxional processes even at low temperatures. This was previously reported for the analogous complex of BISBI.[54] Unlike the flexible BISBI, the rigid xantham ligand does not allow Berry pseudorotations[55] to occur. A "turnstile" transformation, as reported by Meakin *et al.*,[56,57] is more likely since the P−Rh−P entity can then maintain its integrity throughout the operation. The relatively low value for the P−C coupling constant can be accounted for by averaging a negative apical J_{P-C} of about −30 Hz and a positive J_{P-C} of about +10 Hz.[58] The same applies for the low C−H coupling constant. Xantham has been shown to give similar complexes as Xantphos and, hence, does not engage in P−N chelated rhodium complexes.

The catalytically active HRh$(CO)_2$(xantham) complex can also be prepared under hydroformylation conditions from Rh(acac)$(CO)_2$ and xantham under syngas pressure. The rhodium acetylacetonato complex formed prior to syngas admission was also studied with NMR and IR spectroscopy.

Upon addition of 1 equiv of xantham to Rh(acac)$(CO)_2$, immediate evolution of CO is observed and a yellow solution is formed. The IR spectrum exhibits a very strong band at 1968 cm^{-1}, which is indicative of a Rh−CO species. The ^{31}P NMR spectrum at room temperature reveals a broad doublet at 11.7 ppm with a Rh−P coupling constant of 90.9 Hz. The complex concerned is most likely Rh(acac)(CO)(xantham), in which xantham is coordinated in a bidentate fashion as no ^{31}P signals are observed without coupling to ^{103}Rh. Apparently, xantham is reluctant to form the expected Rh(acac)(xantham) complex, analogous to the known Rh(acac)$(PPh_3)_2$ complex.[59,60] The natural bite angle of xantham (about 115°) may be the driving force for the formation of a five-coordinate rhodium species incorporating one CO ligand. The bite angle in this complex, presumably possessing a square pyramidal or distorted trigonal bipyramidal structure, is still somewhat wrenched, which can explain the relatively low Rh−P coupling constant. According to the ^1H NMR spectrum, the acetylacetonate ligand is symmetrically coordinated, thus, in a bidentate fashion. The spectrum further shows that the methyl and benzylic amino groups and the *ortho* phenyl protons in xantham are equivalent, which suggests that the rhodium complex is involved in rapid fluxional processes. At lower temperatures, line broadening is indeed observed, leading to a very broad singlet at −80 °C. NMR measurements at lower temperatures have not been performed.

Bubbling ^{13}CO through the solution containing the complex resulted in the formation of a complex which reveals a double triplet in the ^{13}C NMR spectrum at 191.5 ppm. The Rh−C and P−C coupling constants of, respectively, 77.0 and 12.1 Hz are typical of a structure which possesses an apical CO facing two phosphorus atoms in an equatorial plane. Upon standing under an atmosphere of ^{13}CO, other complexes including Rh(acac)$(^{13}CO)_2$ (doublet at 184.6 ppm, $J_{Rh-C} = 72.4$ Hz) are formed.

The Rh(acac)(CO)(xantham) complex is thermally stable and was not converted to the Rh(acac)(xantham) complex by heating the solution at 80 °C for 2 h[59,60] or by carefully evacuating the solution, as judged by the unchanged IR and ^{31}P NMR spectra.

Rh(acac)(CO)PP complexes, in which PP functions as a bidentate ligand, have been recently reported for diphosphites[61] but, to our knowledge, have never been reported for diphosphines.

Crystal Structure of Xantham. The crystal structure of the xantham ligand is shown in Figure 2. When compared with that of Xantphos,[27] it is clear that the benzylic amino groups, although located at the *para* positions, cause a significant distortion of the overall structure. In contrast with Xantphos, the flat xanthene backbone of xantham does not possess a mirror plane (through O, C7, C14, C15). Due to steric congestion, the diphenylphosphino moieties point into different directions. Hence, the energetically favorable conformation in which two of the phenyl groups are aligned ("π-stacking"), as was observed in Xantphos, is lost. Also, the distance between the phosphorus atoms has increased from 4.080 for Xantphos to 4.383 Å for xantham. According to molecular modeling calculations,[27] this results in a somewhat larger bite angle for xantham (115°) than for Xantphos (111.7°) in the rhodium complexes.

Catalysis. Ligand Effects. The new diphosphines have been tested in the rhodium-catalyzed hydroformylation of oct-1-ene. The HRh$(CO)_2$PP complex is formed

(53) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1597.
(54) Casey, C. P.; Whiteker, W. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.
(55) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(56) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5271.
(57) Meakin, P.; Jesson, J. P.; Tebbe, F. N.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 1797.
(58) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Chem. Commun*, **1982**, 723.
(59) Trzeciak, A. M.; Ziólkowski, J. J. *J. Organomet. Chem.* **1992**, *429*, 239.
(60) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156.
(61) Buisman, G. J. H.; Vos, E. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1995**, 409.

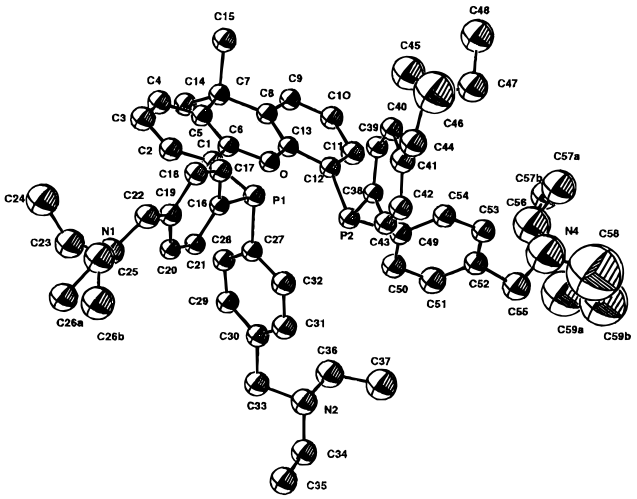


Figure 2. Molecular structure (ORTEP plot) of xantham. For clarity hydrogen atoms are omitted.

in situ from $Rh(acac)(CO)_2$ and a 10-fold excess of the diphosphine. Table 1 lists the hydroformylation results for the novel ligands, as obtained under standard conditions, and also includes the results for unmodified POP and Xantphos, which have been used under the same conditions for the sake of comparison. As can be seen in Table 1, POP and its amphiphilic derivatives give rise to mainly linear aldehydes (88−89%). Although the selectivity for linear aldehydes is moderate as compared to Xantphos, virtually no isomerization is observed. Until now, the coordination chemistry of rhodium catalysts modified with POP under hydroformylation conditions has not been thoroughly investigated, but it is tempting to speculate on the reasons for the absence of isomerization products. It is reasonable to assume that the coordinated POP ligand is capable of fast intramolecular occupation of formed vacant sites in the rhodium complexes, since the phosphorus bidentate ligand can span a wide range of bite angles; POP may act as a hemilabile terdentate ligand in an unsaturated transient species, in which the bridging oxygen atom also coordinates (Figure 3). In this way, β-H-elimination might be suppressed. The steric bulk around the rhodium center in the alkene hydride intermediate and the preference for bite angles around 110° may explain the increased regioselectivity in comparison with that of PPh_3.

The amino groups in POPam have no effect on the catalytic properties since both selectivity and activity are similar to those obtained with unmodified POP. The catalyst derived from POPpy, however, is almost twice as fast as the one derived from POP. This has been observed earlier for pyridyl-modified arylphosphines[24] and has been ascribed to the electron-withdrawing capacity of the pyridyl ring. π-Accepting ligands result in a weaker bonding of CO molecules to the rhodium center, thereby facilitating alkene coordination. In addition, owing to the higher electrophilicity, the rhodium alkyl species reacts less readily with CO. This results in an increased tendency toward β-H-elimination and thus to some isomerization (0.7%). This in turn partly accounts for the low yields of branched aldehyde relative to that found for POP and POPam; the branched alkyl species is more prone to undergo β-H-elimination than the linear alkyl species because of the higher number of available β-hydrogen atoms and the increased steric hindrance.

It can be seen that the rhodium catalyst derived from xantham and Xanthphos gives rise to an even higher yield of linear aldehyde owing to both a high l/b-ratio and a relatively low activity for isomerization. This is ascribed to the well-defined template structure of both rigid ligands which preferentially occupy two equatorial sites in the catalytically active rhodium hydride owing to their relatively large natural bite angle. This geometry leads to a higher proportion of *linear* aldehyde formation as compared to geometries with axial−equatorial chelates.[27,53] Xantphos and xantham give similar results in the hydroformylation of oct-1-ene. The reaction rate of the xantham-derived catalyst, however, is somewhat higher despite the electron-donating effect of the four aminomethyl groups, which has a negative effect on the reaction rate.[62,63] The different geometry of xantham, as shown for the free ligand in the X-ray structure, in the active rhodium hydride is held responsible for a faster replacement of a CO molecule by an alkene.

Hydroformylation of hex-1-ene and dodec-1-ene using xantham as a ligand shows very similar results.

Conditions. The influence of temperature on the hydroformylation of oct-1-ene is shown in Table 2. As expected, the turn-over frequencies considerably decrease with lower temperature, whereas the l/b-ratios slightly increase. The isomerization activities also decrease, especially in the case of xantham, resulting in the production of 96.9% nonanal. At 100 °C, POPpy gives rise to an increased proportion of 2/3-octenes. This is in sharp contrast with POPam for which no isomerization can be detected, not even at 100 °C. When xantham is used at 100 °C, the selectivity with regard to both isomerization and linearity only slightly decreases while the reaction rate increases to synthetically attractive values. This effect was also found for Xantphos and was ascribed to the rigidity of the diphosphines stabilizing chelated complexes, even at elevated temperatures. In contrast, ligand systems such as BISBI and PPh_3 give rise to rhodium complexes with a less rigidly defined geometry, which leads to a significant increase in isomerization at higher temperatures.[26]

A few preliminary experiments have been performed to study the effect of the partial pressures of CO and H_2 for the catalyst system containing POPam (Table 3). Variation of the partial pressure of CO (entries 1 and 2) has a moderate effect on the turn-over frequencies. This seems to indicate that the hydroformylation of oct-1-ene using POPam only has a small negative order in CO concentration and does not involve a simple rate equation comprising merely CO replacement by alkene. The variation in H_2 concentration (entry 3) suggests that the last step in the hydroformylation cycle, hydrogenolysis of the acyl rhodium complex, is not rate determining. Remarkably, the selectivity of the hydroformylation reaction is not affected by variations in the composition of the used syngas. Even at CO pressures as low as 5 bar, POPam fully suppresses isomerization.

Distribution Characteristics of the Free Ligands. For functionalized triphenylphosphines and BISBI de-

(62) Moser, W. R.; Papite, C. J.; Brannon, D. A.; Duwell, R. A. *J. Mol. Catal.* **1987**, *41*, 271.
(63) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19.

Table 1. Hydroformylation under Standard Conditions[a]

				selectivity (%)				
ligand	alkene	time (h)	conversion (%)[b]	isomers[c]	l-aldehyde	b-aldehyde	l/b[d]	TOF[e]
POP	oct-1-ene	1	4.8	0.0	87.7	12.3	7.1	239
		4.5	19.4	0.0	88.0	12.0	7.3	215
		20	67.0	0.0	88.2	11.8	7.5	168
POPpy	oct-1-ene	1	9.1	0.8	89.3	9.9	9.0	449
		4.5	34.0	0.6	89.5	9.9	9.0	372
		20	88.0	0.7	89.3	10.0	8.9	207
POPam	oct-1-ene	1	5.0	0.0	88.0	12.0	7.3	251
		4.5	21.5	0.0	88.0	12.0	7.3	238
		21	71.5	0.0	88.0	12.0	7.3	178
xantphos	oct-1-ene	1	3.8	3.9	94.2	1.9	49	179
		4.5	16.0	3.9	94.1	2.0	48	170
		24	61.6	3.9	94.1	2.0	46	123
xantham	oct-1-ene	1	4.1	3.9	94.2	1.9	50	196
		4.5	16.9	4.0	94.1	1.9	49	181
		24	67.9	4.0	94.1	1.9	49	137
	hex-1-ene	1	4.3	3.9	94.2	1.9	49	205
		4.5	17.7	3.9	94.1	2.0	48	189
		24	71.0	3.8	94.2	2.0	48	143
	dodec-1-ene	1	4.0	4.1	94.1	1.8	51	193
		4.5	16.6	4.2	94.0	1.8	52	179
		24	66.9	4.2	94.0	1.8	51	134

[a] Conditions: 20 bar of H_2/CO (1:1), 80 °C, toluene (20 mL), [L] = 17 × 10^{-4} M, [Rh] = 1.7 × 10^{-4} M, [alkene] = 0.84 M. [b] Percentage of 1-alkene converted. [c] Percentage of 2-, 3-, and 4-alkenes formed. [d] Linear/branched ratio. [e] Turn-over-frequency in mol or aldehyde per mol of Rh per h, averaged over the time given.

Table 2. Variation of Reaction Temperature in the Hydroformylation of Oct-1-ene[a]

				selectivity (%)				
ligand	temp (C)	time (h)	conversion (%)	isomers	l-aldehyde	b-aldehyde	l/b	TOF
POPpy	60	4	5.7	0.4	89.7	9.7	9.2	71
		56	64.9	0.3	89.7	9.8	9.1	58
	100	0.2	9.5	1.5	88.3	10.2	8.7	2350
		0.7	31.5	1.3	88.4	10.3	8.6	2250
		2	64.0	1.4	88.3	10.3	8.6	1567
POPam	40	70	5.1	0.0	88.8	11.2	7.9	4
	60	4	3.0	0.0	88.4	11.6	7.6	37
		64	33.2	0.0	88.5	11.5	7.7	26
	100	0.5	12.5	0.0	86.1	13.9	6.2	1250
		2.2	42.0	0.0	86.1	13.9	6.2	1066
		4.5	78.0	0.0	86.3	13.7	6.3	866
xantham	40	24	4.4	1.4	96.7	1.9	51	10
		72	13.7	1.4	96.9	1.8	53	9
	60	48	29.5	3.5	94.6	1.9	51	30
		96	50.7	3.4	94.7	1.9	51	26
	100	1	18.0	4.3	93.6	2.1	44	866
		2	34.5	4.2	93.6	2.2	43	830
		4.5	68.5	4.1	93.7	2.2	43	732

[a] Conditions: 20 bar of H_2/CO (1:1), toluene (20 mL), [L] = 17 × 10^{-4} M, [Rh] = 1.7 × 10^{-4} M, [oct-1-ene] = 0.84 M. See Table 1 for definitions.

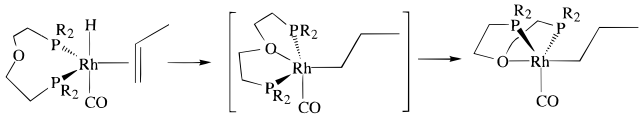


Figure 3. Possible role of the bridging oxygen in the prevention of β-H-elimination.

rivatives, the pH-dependant distribution characteristics of the free amphiphilic ligand have been shown to be comparable to that of the corresponding rhodium complex.[25,26] The distribution coefficient D is defined as

$$D = \frac{C_{H2O}}{C_{H2O} + C_{org}} \times 100\%$$

In Figure 4, the D−pH plots for POPpy, POPam, and xantham are depicted. POPpy is located mostly in the Et_2O layer at pH values of 4−7. Extraction of the ligand into the aqueous phase occurs at pH 3 and is complete at pH 1. The curve closely resembles that of PhP(3-pyridyl)$_2$.[25] The recorded extraction curves for POPam and xantham are almost the same and closely resemble that of PhP($C_6H_4CH_2NEt_2$)$_2$.[25] Both ligands are completely located in the organic layer at pH 7, but are extracted for more than 60% at pH 4.5. Extraction is complete at the relatively high pH of 2.5.

Rhodium Recycling Experiments. Table 4 shows the results of the recycling experiments in which the novel ligands are used. The rhodium contents of the aqueous and organic layers were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The recycled rhodium was reused in a second hydroformylation run, and the observed reaction rate as measured by the turn-over frequency (TOF) was compared with that of the TOF in the first run. Since the hydroformylation reaction is first-order in oct-1-ene concentration, the quotient of both turn-over frequencies is a measure of the recovery of catalytically active rhodium and is referred to as the retention of activity (RA).[25,26]

Table 3. Variations in P(CO) and P(H_2) in the Hydroformylation of Oct-1-ene with POPam[a]

					selectivity (%)				
entry	P_{H_2}	P_{CO}	time (h)	conversion (%)	isomers	l-aldehyde	b-aldehyde	l/b	TOF
1	10	5	0.6	3.6	0.0	88.0	12.0	7.3	297
			4.5	25.9	0.0	88.1	11.9	7.4	288
			20	80.4	0.0	87.9	12.1	7.3	201
2	10	30	1	4.4	0.0	88.0	12.0	7.3	222
			4.5	18.6	0.0	88.1	11.9	7.4	207
			20	66.4	0.0	87.7	12.3	7.1	166
3	5	10	1	4.8	0.0	87.6	12.4	7.0	241
			4.5	20.6	0.0	88.1	11.9	7.2	229
			19	67.6	0.0	88.1	11.9	7.2	178

[a] Conditions: 80 °C, toluene (20 mL), [L] = 17 × 10^{-4} M, [Rh] = 1.7 × 10^{-4} M, [oct-1-ene] = 0.84 M. See Table 1 for definitions.

Table 4. Results of the Recycling Experiments; Rhodium Measurements by ICP-AES and Retention of Activity[a]

			rhodium content (μg)					
entry	ligand	conditions	first organic layer	aqueous layer	new organic layer	Rh recovery[b] (%)	Rh balance[c] (%)	R. A.[d] (%)
1	POPpy	6 acidic extractions at pH 2.5 neutralization to pH 7	30	1010	183	15	99	13
2	POPpy	8 acidic extractions at pH 3 neutralization to pH 6−6.5	30	996	216	17	100	16
3	POPam	6 acidic extractions at pH 5 neutralization to pH 7	< 0.7[e]	489	707	59	97	51
4	POPam	8 acidic extractions at pH 5−5.5 neutralization to pH 6.5−7	<0.7[e]	432	791	65	99	58
5	xantham	7 acidic extractions at pH 5 neutralization to pH 7	<0.7[e]	37	1194	97	100	66
6	xantham	9 acidic extractions at pH 5−5.5 neutralization to pH 6.5−7	<0.7[e]	26	1193	98	99	86

[a] The 95% confidence interval of the mean measured values is ±4.5% for contents >10 μg, otherwise ±10%. [b] Rhodium recovered in the new organic layer as percentage of the total amount measured. [c] Rhodium mass balance defined as the total amount of rhodium measured as a percentage of the starting amount (= 1235 μg). [d] Retention of activity (see text). [e] The detection limit is 0.7 μg (based upon 3σ of the blank solution).

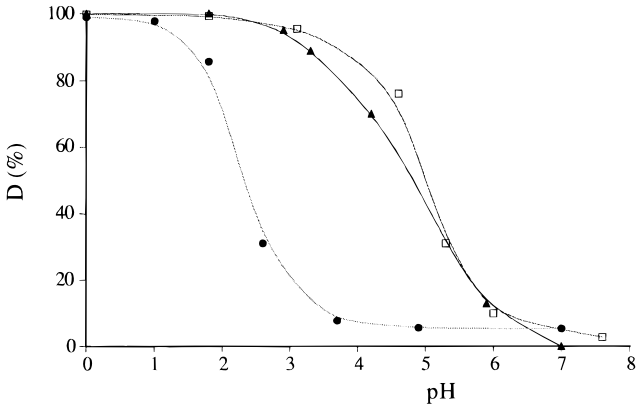


Figure 4. Extraction curves of POPpy (●), POPam (□) and xantham (▲).

Optimum conditions for the recycling procedure were established in previous experiments[25,26] using the amphiphilic derivatives of PPh_3 and BISBI. The catalytic mixture of POPpy was titrated with an aqueous H_2SO_4 solution of pH 1.8 to an effective pH of 2.5, although at pH 3, the aqueous layer had already turned slightly yellow. These observations are in agreement with the extraction curve depictured in Figure 4. Six extractions at pH 2.5 rendered a combined bright-yellow aqueous layer and a colorless toluene layer, which contained only 30 μg of rhodium (2.4% of the total rhodium amount, entry 1). Upon neutralization to pH 7, the aqueous phase remained yellow. Analysis confirmed that the majority of the rhodium amount remained in the aqueous phase. The recovered toluene phase accordingly showed a low retention of activity (13%). An experiment done under milder conditions, acidic extraction at pH 3 and subsequent neutralization to pH 6−6.5 (entry 2), gave similar results. Evidently, POPpy is inapt for rhodium reuse, as observed earlier for pyridyl-modified PPh_3 and BISBI ligands.[25,26]

Six extractions at pH 5 of the catalytic mixture of POPam resulted in a bright-yellow aqueous layer and a colorless toluene layer having a rhodium contamination below the detection limit (entry 3). Upon neutralization to pH 7, the aqueous layer became turbid and toluene extractions recovered only 59% of the total amount of rhodium charged. No improvement was observed when milder conditions were applied (entry 4).

Successive extraction of the catalytic mixture of xantham at pH 5, at which free xantham is extracted for more than 40% (Figure 4), effected the quantitative extraction of rhodium (entry 5). Neutralization and successive toluene extractions rendered an aqueous phase contaminated with only 36 μg Rh. Although the overall rhodium recovery was almost quantitative (97%), the retention of activity amounted to only 66%. However, a substantial elevation to 86% was observed (entry 6) when the acidic titration procedure was done at pH 5−5.5. This result equals the success of $PhP(C_6H_4CH_2NEt_2)_2$.[25] To study the rhodium species involved throughout the rhodium recycling procedure using xantham, a small scale experiment was done at higher concentrations and monitored by IR and NMR spectroscopy. The organic reaction medium in the autoclave, which was shown to contain the previously characterized HRh(xantham)$(CO)_2$ complex, was extracted with a solution of H_2SO_4 in D_2O. ^{31}P NMR analysis of the deep yellow

aqueous layer revealed the presence of several unknown rhodium species. Apart from the sharp resonance assigned to free ligand, several very broad signals between −10 and +20 ppm were observed. After neutralization, the aqueous phase was extracted with toluene-d_8. The ^{31}P spectrum of this layer showed the presence of several phosphorus containing compounds. The IR spectrum showed bands at 1970 and 1988 cm^{-1}, which were also found for the active hydride complex. This experiment conclusively showed that the catalytically active hydride completely decomposes upon acidic extraction in the absence of syngas.

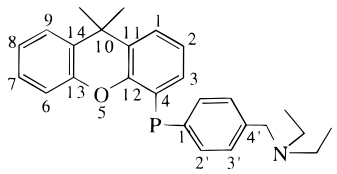
Conclusion

Rhodium catalysts modified with the novel amphiphilic diphosphines are highly active and selective. The use of POPam ensures complete suppression of isomerization of the substrate alkene. Although unable to fully recycle rhodium, POPam enables complete separation of the rhodium catalyst, to the extent of 99.95%, from the organic reagents by simple acidic extraction. Xantham is very promising for the use as a ligand in a rhodium catalyzed hydroformylation process of higher alkenes. This ligand gives rise to a rhodium catalyst that is as selective and even somewhat more active as the catalyst derived from the hydrophobic Xantphos ligand. Moreover, rhodium and ligand can be recycled by extraction and re-extraction at nearly neutral pH, which implies a minimum amount of salt waste. For commercial application in a commodity aldehyde producing process, a rhodium recovery of 99.98% is mentioned in the literature.[64] Rhodium and excess xantham can be extracted from the organic reagents by simple acidic extraction to the extent of 99.95%, while the overall rhodium recovery amounts to 98%. Given the basic experimental setup we used, these are promising figures. The 86% retention of activity is high but far from satisfactory from an industrial point of view. The spectroscopic study showed that the active hydride decomposes upon recycling. The majority of the eventually recycled rhodium species, whose structures have not yet been elucidated, act as precursors for the active catalyst. Avoiding *ir*reversible decomposition could be envisaged by performing all recycling steps under syngas pressure. Finally, the present recovery procedure in combination with the xantham ligand may already be applied to the batchwise hydroformylation of fine chemicals.

Experimental Section

General Considerations. All reactions were carried out in flame-dried glasswork using standard Schlenk techniques under an argon atmosphere. Toluene, THF, and diethyl ether were distilled from sodium/benzophenone; CH_2Cl_2 was dried over P_2O_5 and distilled from CaH_2. All solvents used in the preparation or handling of phosphines were degassed prior to use. Solvents and reagents were distilled prior to use. Mesitylene and methyl iodide were freshly distilled from sodium and anhydrous $CaCl_2$, respectively. All chemicals were purchased from Acros Chimica or Aldrich Chemical Co. Bis(2-iodoethyl) ether,[65] bis[2-(diphenylphosphino)ethyl] ether,[39] Cl_2PNEt_2,[66] and (4-bromobenzyl)diethylamine[24] were prepared according to literature procedures. For column chromatography, both silica gel 60 (Merck, 230−400 mesh) and aluminium oxide (activated neutral, 50−200 micron, Acros) were used. ^1H NMR (300 MHz, TMS as standard), ^{31}P NMR (121.5 MHz, H_3PO_4 as standard), and ^{13}C NMR (75.5 MHz, TMS as standard) spectra were measured on a Bruker AMX 300 spectrometer in $CDCl_3$ unless otherwise stated. IR spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Melting points were determined on a Gallenkamp MFB-595 apparatus. GCMS was measured on a HP 5890/5971 spectrometer. For exact mass determination, a JEOL JMS-SX/SX102A spectrometer was used. Hydroformylation reactions were carried out in a homemade 200 mL stainless steel autoclave. Gas chromatographic analyses were run on a Carlo Erba GC 6000 Vega Series apparatus (split/splitless injector; J&W Scientific; DB1 30m column; film thickness 3.0 μm; carrier gas 70 kPa He; FID detector) equipped with a HP 3396 integrator. Syngas 3.0 was purchased from UCAR. The 1-alkenes were freshly filtered over a short column of aluminum oxide before use to remove hydroperoxides (activated neutral, 50−200 micron, Acros). UV spectra were measured on a Varian Cary 4 single-beam apparatus. The pH values were measured on a Corning 240 pH meter. ICP-AES measurements were done using a sequential Jarrell Ash upgraded (Model 25) Atomscan model 2400 ICP scanning monochromator. Sulphuric acid calibration solutions of rhodium were prepared by dilution of a rhodium standard ($RhCl_3$ in 20% HCl) from Johnson Matthey. Experimental conditions of the ICP-AES analysis are described in ref. 25. Elemental analysis was performed by the Department of Micro-Analyses at the University of Groningen.

NMR simulation was done with Softshell NMR software.[67] The following labeling was used in the NMR assignments of the POP-related compounds: PPh (C_{i-p}), P(Ph−amino) ($C_{i'-p'}$), and P(3-pyridyl) (C_{2-6}). For the xantham-related compounds, the following labeling was used in the NMR assignments and nomenclature:



Chlorophenyl(3-pyridyl)phosphine (4). A 2.5 M solution of *n*-butyllithium in hexane (0.150 mol, 62.3 mL) was cooled to −78 °C. A solution of 3-bromopyridine (0.150 mol, 14.45 mL) in Et_2O (120 mL) was added in 1 h, and stirring was continued for 1 h. The yellow suspension was quickly filtered and washed first with cold hexanes (−78 °C, 2 × 35 mL) and then with hexanes at room temperature (50 mL). The dark yellow solid was suspended in THF (200 mL). In a second flask, a solution of dichlorophenylphosphine (0.30 mol, 40.5 mL) in Et_2O (100 mL) was cooled to −78 °C and the suspension was added in 1 h in portions through a glass joint. The reaction mixture was then allowed to warm to room temperature overnight. The solvents were evaporated, and the brown residue was distilled at reduced pressure, giving a forerun of dichlorophenylphosphine and the product (bp 110 °C, 0.09 mmHg). The yellowish liquid product contained 5 wt % lithium chloride, which sublimed from the residue during distillation. Yield: 33% (0.050 mol, 11.0 g).

^1H NMR: δ 8.72 (m, 1H, H_2), 8.56 (d, 1H, J = 4.8 Hz, H_6), 7.78 (dist. t, 1H, J = 7.9 Hz, H_4), 7.57 (m, 2H, aromatic), 7.37 (m, 3H, aromatic), 7.24 (m, 1H, H_5). $^{31}P\{^1H\}$ NMR: δ 75.4. ^{13}C NMR: δ 152.3 (d, J = 31.7 Hz, C_2), 151.2 (C_6), 140.0 (d, J = 17.4 Hz, C_4), 137.7 (d, J = 31.7 Hz, C_i), 136.2 (d, J = 38.5 Hz, C_3), 132.3 (d, J = 25.7 Hz, C_o), 131.5 (C_p), 129.5 (d, J =

(64) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570.
(65) Metzger, L.; Kuhnen, O. P. *Z. Naturforsch. B* **1957**, *12*, 28.
(66) Issleib, K.; Seidel, W. *Chem. Ber.* **1959**, *92*, 2681.
(67) Budzelaar, P. H. M. *geNMR 3.5M*; Ivorysoft: Amsterdam, The Netherlands.

7.6 Hz, C_m), 124.3 (br s, C_5). Exact mass (FAB): 186.0456 ($M - Cl)^+$ (calcd for $C_{11}H_9NP$, 186.0473).

Phenyl(3-pyridyl)phosphine (5). Small pieces of sodium (137 mmol, 3.15 g) and ca. 20 mg of 4,4′-di-*tert*-butylbiphenyl were added to a solution of chlorophenyl(3-pyridyl)phosphine **4** (66.6 mmol, 14.7 g) in THF (120 mL). The initially colorless mixture was refluxed until all the sodium had reacted, which took approximately 5 days. Then the dark red reaction mixture was quenched with water (40 mL) at 0 °C and Et_2O (50 mL) was added. The organic layer was separated and evaporated. The resulting dark red residue was azeotropically dried with toluene (3 × 50 mL) and distilled at reduced pressure (bp 106 °C, 0.20 mmHg). Yield: 53% (6.6 g, 35.3 mmol) of a colorless liquid.

^{1}H NMR: δ 8.70 (m, 1H, H_2), 8.54 (d, 1H, J = 5.6 Hz, H_6), 7.73 (m, 1H, H_4), 7.48 (m, 2H, aromatic), 7.34 (m, 3H, aromatic), 7.22 (m, 1H, H_5), 5.22 (d, 1H, J_{P-H} = 220.4 Hz, HP). ^{31}P NMR: δ −49.6 (d, J_{P-H} = 220 Hz). ^{13}C NMR: δ 155.4 (d, J = 18.1 Hz, C_2), 150.9 (C_6), 142.6 (d, J = 15.9 Hz, C_4), 135.5 (d, J = 17.4 Hz, C_o), 134.5 (d, J = 9.1 Hz, C_i), 132.7 (d, J = 15.1 Hz, C_3), 130.4 (C_p), 130.2 (d, J = 6.8 Hz, C_m), 125.0 (br s, C_5).

Bis[2-(phenyl(3-pyridyl)phosphino)ethyl] Ether (POPpy, 1). A solution of phenyl(3-pyridyl)phosphine, **5** (4.9 mmol, 0.92 g), in THF (10 mL) was cooled to −78 °C. A 2.5 M solution of *n*-butyllithium in hexane (4.9 mmol, 2.0 mL) was added in 30 min, and stirring was continued at room temperature for 1 h. A solution of bis(2-chloroethyl) ether (2.45 mmol, 0.29 g) in THF (15 mL) was added dropwise at −78 °C to the resulting deep red-brown solution. The reaction mixture was then allowed to warm to room temperature overnight. After the reaction mixture was concentrated, an aqueous 4 M solution of NaOH (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were evaporated, and the resulting oil was purified by column chromatography (silica gel, 10% MeOH/CH_2Cl_2). Yield: 69% of a yellowish oil (1.7 mmol, 0.76 g).

^{1}H NMR: δ 8.61 (m, 2H, H_2), 8.53 (d, 2H, J = 4.7 Hz, H_6), 7.64 (dist t, 2H, J = 7.0 Hz, H_4), 7.50−7.35 (m, 10H, aromatic), 7.23 (m, 2H, H_5), 3.52 (q, 4H, J_{P-H} = 7.6, J_{H-H} = 7.6 Hz, CH_2O), 2.34 (dist t, 4H, J_{P-H} < 3, J_{H-H} = 7.4 Hz, CH_2P). ^{31}P{^{1}H} NMR: δ −26.8. ^{13}C NMR: δ 152.9 (d, J = 22.6 Hz, C_2), 149.3 (C_6), 139.7 (d, J = 15.1 Hz, C_4), 136.4 (d, J = 12.1 Hz, $C_{i/3}$), 134.7 (d, J = 18.1 Hz, $C_{i/3}$), 132.6 (d, J = 19.6 Hz, C_o), 128.9 (C_p), 128.5 (d, J = 6.8 Hz, C_m), 123.2 (C_5), 67.6 (d, J = 22.8 Hz, CH_2O), 28.2 (d, J = 13.0 Hz, CH_2P). Exact mass (FAB): 445.1553 (M + H) (calcd for $C_{26}H_{27}N_2OP_2$, 445.1599), Anal. Calcd for $C_{26}H_{26}N_2OP_2$: C, 70.26; H, 5.90; N, 6.30. Found: C, 69.46; H, 6.15; N, 6.19.

Phenylphosphinic acid ethyl ester was prepared from dichlorophenylphosphine, ethanol, and water by the method of Emmick.[68] Yield: 86% (literature yield 59%), bp 91−92 °C, 0.3 mmHg. ^{31}P NMR: δ 25.1 (d, J_{P-H} = 563 Hz). ^{1}H NMR: δ 7.77−7.71 (m, 2H, aromatic), 7.54 (d, J_{P-H} = 561.3 Hz), 7.53−7.41 (m, 3H, aromatic), 4.13 (m, 2H, CH_2), 1.34 (t, 3H, J = 7.0 Hz).

[4-((-Diethylamino)methyl)phenyl]phenylphosphine oxide (6). A solution of (4-bromobenzyl)diethylamine (25 mmol, 6.05 g) in THF (60 mL) was added dropwise to magnesium (25.5 mmol, 0.625 g), which was preactivated by 1,2-dibromoethane, allowing a gentle reflux. The reaction mixture was refluxed for an additional period of 3 h. In another flask, a solution of phenylphosphinic acid ethyl ester (25 mmol, 4.25 g) in THF (80 mL) was cooled to −78 °C. A 2.5 M solution of *n*-butyllithium in hexane (25 mmol, 10.0 mL) was added in 1 h, resulting in a light yellow solution. After the mixture was stirred at room temperature for $^1/_2$ h, the phosphide anion was added at 0 °C to the Grignard reagent in $^1/_2$ h. The reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and a saturated aqueous solution of NH_4Cl (75 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic phases were evaporated. The resulting yellow oil was purified by column chromatography (silica gel, 55% THF/40% toluene/5% NEt_3). The resulting oil was dissolved in an aqueous 0.05 M solution of H_2SO_4 (100 mL) for further purification. This solution was washed with CH_2Cl_2 (3 × 50 mL) and then neutralized with a saturated aqueous solution of $NaHCO_3$. Extraction with CH_2Cl_2 (2 × 75 mL) and evaporation of the organic phases gave a colorless oil. Yield: 69% (34.5 mmol, 9.9 g).

^{1}H NMR: δ 8.07 (d, 1H, J_{P-H} = 480.5 Hz, HP), 7.75−7.45 (m, 9H, aromatic), 3.59 (s, 2H, CH_2N), 2.51 (q, 4H, J = 7.1 Hz, CH_2CH_3), 1.03 (t, 6H, J = 7.1 Hz, CH_3). ^{31}P NMR: δ 22.1 (dm, J_{P-H} = 479 Hz). ^{13}C NMR: δ 133.0 (C_p), 132.1 (d, J = 101.2 Hz, $C_{i+i'}$), 131.3 (d, J = 3.8 Hz, $C_{o/o'}$), 131.1 (d, J = 4.5 Hz, $C_{o/o'}$), 130.7 ($C_{p'}$), 129.7 (d, J = 12.8 Hz, $C_{m/m'}$), 129.4 (d, J = 12.8 Hz, $C_{m/m'}$), 57.9 (CH_2N), 47.4 (CH_2CH_3), 12.3 (CH_3). GCMS *m/e* 287 (M^+), 272 ($M^+ - CH_3$), 215 ($M^+ - N(CH_2CH_3)_2$). Exact mass (FAB): 286.1337 ($M - H)^+$ (calcd for $C_{17}H_{21}ONP$, 286.1361).

Bis[2-((4-((diethylamino)methyl)phenyl)phenylphosphino)ethyl] Ether Dioxide (7). A solution of **6** (9.5 mmol, 2.72 g) in THF (25 mL) was slowly added to a suspension of sodium hydride (10.0 mmol, 0.30 g) in THF (10 mL) at room temperature. The resulting yellow solution was added to a solution of bis(2-iodoethyl) ether (4.7 mmol, 1.54 g) in THF (40 mL) at −78 °C in $^1/_2$ h. The reaction mixture was allowed to warm to room temperature overnight. It was then poured into an aqueous phosphate buffer solution (pH 7, 200 mL), and Et_2O (50 mL) was added. The phases were separated, and the aqueous layer was washed with CH_2Cl_2 (2 × 80 mL). The combined organic phases were dried on Na_2SO_4 and evaporated. The resulting yellow oil was purified by column chromatography (silica gel, 60% THF/35% toluene/5% NEt_3). For further purification, water (100 mL) and an aqueous 0.1 M solution of H_2SO_4 was added at 0 °C until the pH was 2−3 and the oil dissolved. This solution was washed with CH_2Cl_2 (3 × 60 mL) and toluene (60 mL) and neutralized with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was then extracted with CH_2Cl_2 (3 × 60 mL). The organic phases were dried on Na_2SO_4 and evaporated, resulting in a colorless glassy oil. Yield 56% (2.64 mmol, 1.7 g).

^{1}H NMR: δ 7.75−7.52 (m, 9H, aromatic), 7.50−7.41 (m, 9H, aromatic), 3.65 (q, 4H, J_{P-H} = 8.3, J_{H-H} = 8.3 Hz, CH_2O), 3.59 (s, 4H, CH_2N), 2.50 (q + m, 12H, J = 7.1 Hz, $CH_2CH_3 + CH_2P$), 1.03 (t, 12H, J = 7.1 Hz, CH_3). ^{31}P{^{1}H} NMR: δ 29.9. ^{13}C NMR: δ 132.7 (d, J = 99.7 Hz, $C_{i+i'}$), 131.6 (C_p), 130.5 (d, J = 3.8 Hz, $C_{o/o'}$), 130.4 (d, J = 3.0 Hz, $C_{o/o'}$), 130.2 ($C_{p'}$), 128.9 (d, J = 12.1 Hz, $C_{m/m'}$), 128.4 (d, J = 12.1 Hz, $C_{m/m'}$), 63.9 (CH_2O), 56.9 (CH_2N), 46.6 (CH_2CH_3), 30.4 (d, J = 70.7 Hz, CH_2P), 11.3 (CH_3).

Bis[2-((4-((diethylamino)methyl)phenyl)phenylphosphino)ethyl] Ether (POPam, 2). Dioxide **7** (2.64 mmol, 1.7 g) was dissolved in acetonitrile (80 mL), and triethylamine (15.9 mmol, 2.2 mL) was added. Trichlorosilane (15.9 mmol, 1.6 mL) was added dropwise at 0 °C. The heterogeneous reaction mixture was stirred for 2 h at room temperature. The clear reaction mixture obtained was concentrated to ca. 20 mL, and toluene (20 mL) and an aqueous 20% solution of KOH (30 mL) were added at 0 °C. The turbid organic phase was separated, and the aqueous phase was washed with Et_2O (20 mL). The combined organic phases were evaporated, and the resulting brown oil was purified by column chromatography (silica gel, 20% THF/75% toluene/5% NEt_3). Yield 42% of a yellowish oil (1.1 mmol, 0.67 g).

^{1}H NMR: δ 7.43−7.30 (m, 18H, aromatic), 3.56 (s, 4H, CH_2N), 3.49 (q, 4H, J_{P-H} = 7.9, J_{H-H} = 7.9 Hz, CH_2O), 2.52 (q, 8H, J = 7.1 Hz, CH_2CH_3), 2.33 (dist t, 4H, J_{P-H} < 5, J_{H-H} = 8.0 Hz, CH_2P), 1.04 (t, 12H, J = 7.1 Hz, CH_3). ^{31}P{^{1}H} NMR: δ −22.6. ^{13}C NMR: δ 140.7 ($C_{p'}$), 138.3 (d, J = 12.8 Hz, $C_{i/i'}$), 135.8 (d, J = 12.1 Hz, $C_{i/i'}$), 132,4 (d, J = 18.9 Hz, $C_{o/o'}$), 128.7

(68) Emmick, T. L.; Letsinger, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 3459.

(d, J = 6.8 Hz, $C_{m/m'}$), 128.3 (C_p), 128.2 (d, J = 6.8 Hz, $C_{m/m'}$), 67.8 (d, J = 24.9 Hz, CH_2O), 57.0 (CH_2N), 46.6 (CH_2CH_3), 28.7 (d, J = 12.7 Hz, CH_2P), 11.6 (CH_3). Exact mass (FAB): 613.3429 (M + H) (calcd for $C_{38}H_{51}N_2OP_2$, 613.3477). Anal. Calcd for $C_{38}H_{50}N_2OP_2$: C, 74.48; H, 8.23; N, 4.57. Found: C, 74.52; H, 8.25; N, 4.48.

Bis[4-((diethylamino)methyl)phenyl]phosphinous Diethylamide (8). A solution of (4-bromobenzyl)diethylamine (25 mmol, 6.05 g) in THF (50 mL) was added to magnesium (26 mmol, 0.63 g), which was activated by 1,2-dibromoethane, at such a rate that the reaction mixture refluxed gently. After the addition, the reaction mixture was refluxed for an additional 2 h. At −78 °C, a solution of dichlorophosphonous diethylamide, Cl_2PNEt_2 (12.5 mmol, 2.17 g), in THF (10 mL) was added in 30 min. The reaction mixture was allowed to warm to room temperature overnight. The THF was evaporated and hexane (35 mL) was added. The suspension was filtered, and the solid was washed with another 20 mL of hexane. The filtrate was evaporated, resulting in a viscous yellow oil, which was sufficiently pure for further synthesis. Yield: 92% (11.5 mmol, 4.92 g).

^{1}H NMR: δ 7.40−7.28 (m, 8H, aromatic), 3.58 (s, 4H, CH_2N), 3.12−3.02 (dq, 4H, J_{PH} = 9.4, J_{H-H} = 7.1 Hz, CH_2NP), 2.54 (q, 8H, J = 7.1 Hz, CH_2CH_3), 1.06 (t, 12H, J = 7.1 Hz, CH_3), 0.94 (t, 6H, J = 7.1 Hz, CH_3CH_2NP). ^{31}P NMR: δ 61.1. ^{13}C NMR: δ 138.5 (d, J = 13.6 Hz, $C_{1'}$), 138.3 ($C_{4'}$), 131.6 (d, J = 20.4 Hz, $C_{2'}$), 128.5 (d, J = 6.0 Hz, $C_{3'}$), 57.0 (CH_2N), 46.6 (CH_2CH_3), 44.1 (d, J = 15.1 Hz, CH_2NP), 14.3 (d, J = 3.3 Hz, CH_3CH_2-NP), 11.5 (CH_3).

Bis[4-(N,N-diethylaminomethyl)phenyl]phenoxyphosphine (9). Phenol (67 mmol, 6.3 g) was azeotropically dried three times with 25 mL of toluene. A solution of **8** (16.8 mmol, 7.2 g) in THF (50 mL) and mesitylene (60 mL) was added, and the reaction mixture was stirred at 80 °C overnight. The solvents were distilled from the reaction mixture at 90 °C. The excess phenol was removed by repeated codistillation with mesitylene (5 × 30 mL). The resulting yellow oil was free of phenol and 100% pure. Yield: 98% (16.5 mmol, 7.39 g).

^{1}H NMR: δ 7.54 (approximate t, 4H, J = 7.7 Hz, aromatic), 7.38 (approximate d, 4H, J = 7.4 Hz, aromatic), 7.27 (approximate t, 2H, J = 8.5 Hz, aromatic), 7.13 (m, 2H, aromatic), 7.01 (t, 1H, J = 7.3 Hz, aromatic), 3.58 (s, 4H, CH_2N), 2.53 (q, 8H, J = 7.1 Hz, CH_2CH_3), 1.05 (t, 12H, J = 7.1 Hz, CH_3). ^{31}P NMR: δ 111.0. ^{13}C NMR: δ 157.2 (d, J = 9.8 Hz, C_i), 140.8 ($C_{4'}$), 139.1 (d, J = 16.6 Hz, $C_{1'}$), 130.5 (C_m), 130.4 (d, J = 22.6 Hz, $C_{2'}$), 129.0 (d, J = 6.8 Hz, $C_{3'}$), 119.6 (C_p), 118.7 (d, J = 10.6 Hz, C_o), 56.9 (CH_2N), 46.4 (CH_2CH_3), 11.2 (CH_3).

4,6-Dibromo-10,10-dimethylxanthene (10). 9.9′-Dimethylxanthene (4.8 mmol, 1.0 g), TMEDA (14 mmol, 2.09 mL), and Et_2O (45 mL) were cooled to −78 °C. A 1.3 M solution of *sec*-butyllithium in hexane (14 mmol, 10.8 mL) was added, and the reaction mixture was stirred at room temperature for 20 h. A solution of bromine (15.9 mmol, 0.82 mL) in pentane (10 mL) was added dropwise at −78 °C, after which the reaction mixture was allowed to warm to room temperature overnight. Then a 20% aqueous solution of sodium bisulphite (20 mL) was added. The organic phase was separated, and the aqueous phase was washed with Et_2O (20 mL). The combined organic phases were washed with the sulphite solution (15 mL) and water (30 mL), dried over $MgSO_4$, and evaporated. The orange oil was purified by flash column chromatography (silica gel, 3% EtOAc/hexane), resulting in a yellow oil which solidified overnight. Yield: 70% (3.3 mmol, 1.22 g).

^{1}H NMR: δ 7.49 (dd, 2H, J = 7.9, 1.4 Hz, H_3), 7.36 (dd, 2H, J = 7.9, 1.4 Hz, H_1), 7.00 (t, 2H, J = 7.9 Hz, H_2), 1.63 (s, 6H, CH_3). ^{13}C NMR: δ 147.1 (C_{12}), 131.7 (C_{11}), 131.2 (aromatic), 124.7 (aromatic), 124.2 (aromatic), 110.8 (C_4), 35.1 (C_{10}), 31.7 (CCH_3). GCMS m/e 368 (M^+), 353 ($M^+ - CH_3$), 273 ($M^+ - CH_3$, −Br). Mp 53−54 °C.

4,6-Bis[bis(4-((diethylamino)methyl)phenyl)phosphino]-10,10′-dimethylxanthene (xantham, 3). A 2.5 M solution of *n*-butyllithium in hexane (6.15 mmol, 2.46 mL) was cooled to −25 °C. A solution of **10** (3.0 mmol, 1.1 g) in Et_2O (35 mL) was added in 30 min, and stirring was continued at +15 °C for another 30 min. Then a solution of **9** (6.0 mmol, 2.68 g) in Et_2O (20 mL) was added dropwise at −20 °C. The reaction mixture was allowed to warm to room temperature overnight and poured in an aqueous 0.15 M solution of H_2SO_4 (100 mL). The aqueous phase was separated, washed with CH_2Cl_2 (3 × 50 mL) and toluene (50 mL), and neutralized with a saturated aqueous solution $NaHCO_3$. Extraction with CH_2Cl_2 (4 × 50 mL) and evaporation of the combined organic phases resulted in a yellow oil. This crude oil was further purified by flash column chromatography (silica gel, 55% EtOAc/40% hexane/5% NEt_3). Crystallization from acetonitrile gave white crystals suitable for crystal structure determination. Yield: 74% (2.2 mmol, 2.0 g)

^{1}H NMR: δ 7.39 (d, 2H, J = 7.4 Hz, H_3), 7.25−7.17 (m, 16H, $P(C_6H_4)$), 6.95 (d, 2H, J = 7.6 Hz, H_2), 6.59 (d, 2H, J = 7.1 Hz, H_1), 3.57 (s, 8H, CH_2N), 2.55 (q, 16H, J = 7.1 Hz, CH_2CH_3), 1.66 (s, 6H, CH_3), 1.07 (t, 24H, J = 7.1 Hz, CH_2CH_3). ^{31}P NMR: δ −18.9. ^{13}C NMR: δ 152.2 (t, J = 9.8 Hz, C_{12}), through-space P−P coupling constant ≥45 Hz, 139.7 ($C_{4'}$), 135.5 (t, J = 6.0 Hz, $C_{1'}$), 133.7 (t, J = 10.6 Hz, $C_{2'}$), 131.8 (C_3), 129.5 (C_{11}), 128.5 (br s, $C_{3'}$), 126.3 (t, J = 10.2 Hz, C_4), 126.0 ($C_{1/2}$), 122.9 ($C_{1/2}$), 57.1 (CH_2N), 46.6 (CH_2CH_3), 34.2 (C_{10}), 31.9 (CCH_3), 11.6 (CH_2CH_3). Mp 286−288 °C. Anal. Calcd for $C_{59}H_{76}N_4OP_2$: C, 77.09; H, 8.34; N, 6.09. Found: C, 76.99; H, 8.43; N, 6.03.

HRh(xantham)(CO)(PPh_3) (11). This complex was prepared *in situ* by stirring a solution of xantham (40 mg, 0.044 mmol) and $HRh(CO)(PPh_3)_3$ (40 mg, 0.044 mmol) in benzene-d_6 (1 mL) overnight at 25 C.

^{1}H NMR: (C_6D_6) δ 7.91 (m, 4H, aromatic), 7.81 (m, 2H, aromatic), 7.71 (apparent q, J = 4.1 Hz, 4H, aromatic), 7.61 (m, 4H, aromatic), 7.46 (m, 8H, aromatic), 7.22 (m, 6H, aromatic), 7.11 (m, 25H, aromatic), 6.98 (m, 12H, aromatic), 6.85 (m, 2H, aromatic), AB (3.61 (d, $^1J_{H-H}$ = 14.3 Hz) + 3.52 (d, $^1J_{H-H}$ = 14.3 Hz), 4H, CH_2N), 3.43 (s, 4H, CH_2N), 2.48 (dm, 16H, J = 7.1 Hz, CH_2CH_3), 1.49 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.03 (m, 24H, J = 7.1 Hz, CH_2CH_3), −8.95 (dt, 1H, J_{Rh-H} = 1.5 Hz, J_{HP} = 12.2 Hz, $J_{H-P'}$ = 19.2 Hz, RhH). ^{31}P NMR: (C_6D_6): δ 42.2 (dt, $J_{Rh-P'}$ = 167.5 Hz, $J_{P-P'}$ = 131.6 Hz, PPh_3), 23.8 (dd, J_{Rh-P} = 148.1 Hz, $J_{P-P'}$ = 131.6 Hz, xantham). IR (ν(cm^{-1}), C_6D_6): 1996.6 (s), 1915.1 (w). Exact mass (FAB): 1314.5 (M + H) (calcd for $C_{78}H_{93}N_4O_2P_3Rh$, 1314.5).

HRh(xantham)($CO)_2$ (12). A gentle stream of CO was led through a solution of HRh(xantham)(CO)(PPh_3) in benzene-d_6, which was prepared as described above, in an NMR tube for 30 min. No quantitative conversion, about 70%, could be achieved due to the presence of excess PPh_3.

^{1}H NMR (C_6D_6): δ 7.86−6.76 (aromatic), 3.43 (s, 8H, CH_2N), 2.53 (q, 16H, J = 6.9 Hz, CH_2CH_3), 1.46 (s, 6H, CH_3), 1.07 (t, 24H, J = 7.0 Hz, CH_2CH_3), −8.46 (dt, 1H, J_{Rh-H} = 6.6 Hz, J_{HP} = 16.8 Hz, RhH). ^{31}P NMR (C_6D_6): δ 18.7 (d, J_{Rh-P} = 126.1 Hz). IR (ν(cm^{-1}), C_6D_6): 1989.9 (s), 1969.6 (s), 1937.9 (s).

HRh(xantham)(^{13}CO)(PPh_3). ^{13}CO-enriched **11** was prepared *in situ* by bubbling a stream of ^{13}CO very gently into a solution of **11** in an NMR tube for 10 s, after which the tube was sealed and thoroughly shaken. Low-temperature NMR: experiments were done with toluene-d_8 as the solvent.

^{13}C NMR (C_6D_6) δ 205.9 (dq, J_{Rh-C} = 54.4 Hz, J_{P-C} = 10.7 Hz, CO). ^{1}H NMR (C_6D_6): δ −8.93 (mp, J_{H-C} = 37.5 Hz, J_{Rh-H} = 1.5 Hz, J_{HP} = 12.2 Hz, $J_{H-P'}$ = 19.1 Hz, RhH).

HRh(xantham)(^{13}CO)$_2$. ^{13}CO-enriched **12** was prepared analogously to ^{13}CO-enriched **11** by the addition of ^{13}CO for 5 min.

^{13}C NMR (C_6D_6): δ 200.1 (dt, J_{Rh-C} = 64.9 Hz, J_{P-C} = 10.6 Hz, CO). ^{1}H NMR (C_6D_6): δ −8.45 (mp, J_{H-C} = 10.0 Hz, J_{Rh-H} = 6.4 Hz, J_{HP} = 16.6 Hz, RhH).

Rh(xantham)(CO)(acac). Xantham (35 mg, 0.038 mmol) and Rh(acac)$(CO)_2$ (9 mg, 0.035 mmol) were dissolved in

benzene-d_6 (0.8 mL) and stirred for 15 min. This complex was enriched with ^{13}CO by bubbling stream of ^{13}CO a very gently into the solution in an NMR tube for 2 min. Low-temperature NMR experiments were done with toluene-d_8 as the solvent.

X-ray Crystal Structure Determination of Xantham. A crystal with approximate dimensions of 0.35 × 0.50 × 0.50 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and ω-2θ scan. A total of 10 996 unique reflections was measured within the range $0 \le h \le 14$, $-19 \le k \le 19$, $-21 \le l \le 19$. Of these, 6153 were above the significance level of 2.5 σ (I). The maximum value of (sin θ)/λ was 0.63 Å^{-1}. Two reference reflections ($03\bar{3}$, 300) were measured hourly and showed no decrease during the 34 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 82°$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods. After isotropic refinement, some of the ethyl groups had rather high temperature factors. It was possible to distribute most of these atoms over two half-occupied positions which remained isotropic during the entire refinement (C26, C56, C57, and C59). No attempts were made to determine the hydrogen atoms of the disordered atoms. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms keeping the latter fixed at their calculated positions with a temperature factor of U = 0.10 Å^2, converged to $R = 0.080$, $R_w = 0.085$, $(\Delta/\sigma)_{max} = 0.86$, $S = 0.500(5)$. A weighting scheme $w = [14.8 + 0.0055*(\sigma(F_{obs}))^2 + 0.00004/(\sigma(F_{obs}))]^{-1}$ was used. The secondary isotropic extinction coefficient[69,70] refined to ext = 0.073(8). A final difference Fourier map revealed a residual electron density between −0.5 and 0.8 e Å^{-3}. Scattering factors were taken from Cromer and Mann (1968).[71,72] The anomalous scattering of P was taken into account. All calculations were performed with XTAL,[73] unless stated otherwise.

Hydroformylation. In a typical experiment, the autoclave was filled with a mixture of a 4 mM solution of Rh(acac)$(CO)_2$ in toluene (0.004 mmol, 1 mL), the ligand (0.04 mmol), and 19 mL of toluene under an atmosphere of argon. The autoclave was pressurized with syngas ($CO:H_2$ = 1:1) to 20 bar, and the temperature was raised to 80 °C in approximately 1 h. Subsequently, oct-1-ene (20 mmol, 3.14 mL) and decane (3 mmol, 0.6 mL) as internal standard were added under pressure. Samples were taken which were quenched with triphenylphosphite to deactivate the catalyst and analyzed by gas chromatography.

Table 5. Selected Wavelengths and Corresponding Extinction Coefficients

	organic solution		aqueous solution	
phosphine	λ/nm	$10^{-4}\epsilon$/dm^3 mol^{-1} cm^{-1}	λ/nm	$10^{-4}\epsilon$/dm^3 mol^{-1} cm^{-1}
POPpy	250	2.21	240	2.24
POPam	252	2.13	270	0.86
xantham	262	2.74	273	2.08

Distribution Measurements of the Free Ligands. The method for measuring the distribution characteristics of the free ligands have been described in a previous paper.[26] Table 5 lists the extinction coefficients of the ligands in Et_2O and in water.

Rhodium Recycling Experiments. Experimental details concerning the procedure of a typical titration experiment and rhodium analysis by ICP-AES were given elsewhere.[26] In the NMR/IR experiment, a small vessel was filled with Rh(acac)-$(CO)_2$ (0.027 mmol, 8.5 mg), xantham (0.11 mmol, 0.104 g), and toluene (2.5 mL) and placed in the autoclave. After 2 h under 20 bar of syngas at 80 °C, the reaction mixture was cooled to 10 °C and siphoned into a flask. Characterization of this organic mixture revealed the presence of the HRh-(xantham)$(CO)_2$ complex (^{31}P δ = 18.9 ppm, J_{Rh-P} = 127.6 Hz; IR 1988, 1970, and 1939 cm^{-1}). It was extracted into D_2O by titration with H_2SO_4 (pH 1) and neutralized with $NaHCO_3$ in the presence of toluene-d_8. The ^{31}P NMR spectrum of the toluene-d_8 layer contained the following signals: δ 27.0 (s, 0.06), 24.4 (d, 0.46, J = 8.7 Hz), 11.4 (br m, 0.05), 7.6 (double m, 0.2, J = 165 Hz), −0.4 (double m, 0.2, J = 152 Hz), −18.6 (xantham, 1.0), −22.7 (d, 0.4, J = 9.7 Hz).

Supporting Information Available: Tables of crystal data and collection parameters, atomic coordinates, bond lengths, bond angles, thermal parameters, and H atom coordinates and NMR spectra of HRH(xantham)$(CO)(PPh_3)$, HRh-(xantham)$(CO)_2$, HRH(xantham)$(^{13}CO)(PPh_3)$, HRh(xantham)-$(^{13}CO)_2$, Rh(xantham)(CO)(acac), and Rh(xantham)(^{13}CO)(acac) (25 pages). Ordering information is given on any current masthead page.

OM970068W

(69) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *A23*, 558.
(70) Larson, A. C. In *The inclusion of Secondary Extinction in Least-Squares Refinement of Crystal Structures. Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1969; pp 291−294.
(71) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321−324.
(72) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV; pp 55.
(73) *XTAL3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland: 1992.