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Synthesis of a new family of water-soluble tertiary phosphine ligands and of their rhodium(I) complexes; olefin hydrogenation in aqueous and biphasic media

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Abstract

The series of phosphonium phosphines $[Ph_2P(CH_2)_nPMe_3]X$ ($n = 2$, 3, 6, 10; $X = NO_3^-$, Cl^-, PF_6^-), henceforth II-, III-, VI- and X-phosphos, respectively, have been prepared and characterized. The ligands react with $[NBDRhCl]_2$ (NBD = norbornadiene) to form the complexes [NBDRhCl(n-phosphos)]X, one of which, [NBDRhCl(II-phophos)]PF_6, has been characterized crystallographically. The 1:1 complexes [NBDRhCl(*n*-phophos)]X react with a second equivalent of ligand to form the complexes [NBDRh(*n*-phophos)$_2$]X, which form very active olefin hydrogenation catalysts in aqueous and aqueous–organic biphasic systems. The effect of chain length on activity is very significant, the complex of VI-phophos forming the most active catalyst.

Introduction

The potentially significant advantages of homogeneous over heterogeneous catalysts with respect to activity and selectivity are well documented [1], but problems of separation of product(s) from catalyst may present major impediments to industrial applications. Attractive solutions to this problem revolve around "heterogenizing" a homogeneous catalyst, either by anchoring the catalyst or catalyst precursor to an inert support, or by utilizing a liquid–liquid biphasic system, in which solutions of the catalyst and of the substrate are separated by a phase barrier [2].

We have earlier contributed to the literature in this field by reporting a series of rhodium complexes of the water-soluble, cationic phosphine ligand (2-diphenylphosphinoethyl)trimethylammonium nitrate ($Ph_2PCH_2CH_2NMe_3^+NO_3^-$, or amphos nitrate) [3]. It was shown that treatment of the rhodium(I) compound $[NBDRhCl]_2$ (NBD = norbornadiene) with four equivalents of amphos nitrate results in the facile formation of the water-soluble catalyst precursor $[NBDRh(amphos)_2]^{3+}$. Aqueous solutions of the latter were shown to catalyze the hydrogenation of water-soluble olefins, and the hydrogenation and hydroformyla-

tion of water-immiscible olefins dissolved in n-pentane, dichloromethane and ethyl ether. In addition, samples of $[NBDRh(amphos)_2]^{3+}$ sorbed onto a strong acid cation exchange resin very efficiently catalyzed the hydrogenation and hydroformylation of olefins in acetone solutions. It was suggested that the catalyst was bound ionically to the resin via the tetraalkylammonium groups.

In an effort to determine the effect of ligand chain length on catalyst properties, we have now prepared a series of similar ligands of the type $Ph_2P(CH_2)_nPMe_3^+$ ($n = 2, 3, 6, 10$; hereafter referred to as II-, III-, VI- and X-phophos, respectively). Tetraalkylphosphonium rather than tetraalkylammonium salts were chosen in part because of anticipated greater synthetic ease, in part because of the potential for utilizing ^{31}P NMR spectroscopic measurements to characterize the phosphonium environment in biphasic systems.

In this paper, we describe syntheses of the above-mentioned ligands and of a series of rhodium precursor complexes $[NBDRh(n\text{-phophos})_2]^{3+}$ ($n = 2, 3, 6, 10$). We also describe a series of experiments which demonstrate the high catalytic activity and some practical limitations of the rhodium-phophos system. In subsequent publications, we shall describe the catalytic properties of the supported complexes, and the results of a ^{31}P NMR investigation of the supported catalysts.

Experimental section

All reactions were carried out under an atmosphere of purified nitrogen in dried, deoxygenated solvents. NMR spectra were run on a Bruker AM-400 NMR spectrometer, IR on a Bruker IFS-85 FTIR spectrometer. The complex $[NBDRhCl]_2$ was prepared as in the literature [4]. Elemental analyses of the new ligands were carried out by Canadian Microanalytical Service Ltd., Delta, B.C., and data are listed in Table 1.

Preparation of $[PPh_2(CH_2)_2PMe_3]NO_3$ (II-phophos)

A solution of 16.5 mL (0.21 mol) of 1,2-dichloroethane in 50 mL of toluene was treated with a 50 mL solution of $LiPPh_2$ (0.84 *M*). Solvent and unreacted 1,2-dichloroethane were then removed under reduced pressure, giving a white solid of reasonably pure $Cl(CH_2)_2PPh_2$. To the latter was added 30 mL each of water and toluene, and the mixture was stirred. The organic phase was separated, and the aqueous phase was extracted with 30 mL of toluene; the two toluene fractions were combined, dried with sodium sulfate and filtered, after which the

Table 1

Elemental analyses

Compound	% Carbon		% Hydrogen	
	Found	Calc.	Found	Calc.
[II-phophos]PF_6	46.62	47.02	5.39	5.34
[III-phophos]PF_6	48.93	48.23	5.73	5.62
[VI-phophos]PF_6	51.49	51.44	6.35	6.37
[X-phophos]NO_3 [a]	64.82	64.78	8.32	8.48

[a] Found: N, 3.17. Calc.: N, 3.02%.

solvent was reduced under reduced pressure to give the product as a pale yellow oil (7.2 g, 29 mmol, 70% yield). ^{1}H NMR of $Cl(CH_2)_2PPh_2$ in $CDCl_3$: δ 2.54 (2H, m, CH_2); 3.56 (2H, m, CH_2); 7.34 (10H, m, Ph). $^{13}C\{^1H\}$ NMR in $CDCl_3$: δ 32.1 (d, J(PC) = 15.4 Hz, CH_2); 41.4 (d, J(PC) = 28.3 Hz, CH_2); 128.4 (d, J(PC) = 6.9 Hz, Ph); 128.7 (s, Ph); 132.5 (d, J(PC) = 19.4 Hz, Ph); 136.8 (d, J(PC) = 13.1 Hz, Ph).

To 13.4 g (0.054 mol) of $Cl(CH_2)_2PPh_2$ dissolved in 50 mL of toluene were added 10 mL (0.1 mol) of PMe_3. The mixture was refluxed for 3 days, during which a white solid, $[PPh_2(CH_2)_2PMe_3]Cl$ (II-phophos chloride), precipitated. The mixture was cooled, and the white, crystalline product was collected by filtration, washed with ethyl ether and dried (Yield 17.4 g, 100%). A solution of 0.34 g (1.0 mmol) of II-phophos chloride in 20 mL methanol was eluted through Amberlite IRA 400 anion exchange resin (40 g, nitrate form) with methanol to give a solution of $[PPh_2(CH_2)_2PMe_3]NO_3$ in about 150 mL methanol. On removal of most of the solvent under reduced pressure, the concentrated solution was tested for the presence of halide ion. There was none, and the product was precipitated by the addition of ethyl ether (0.28 g, 80% yield). This material was pure enough for syntheses of complexes (see below). For purposes of elemental analyses, metathesis of 1.0 g (2.8 mmol) of $[PPh_2(CH_2)_2PMe_3]NO_3$ with 0.5 g (3 mmol) of $NaPF_6$ in 20 mL of methanol resulted in the precipitation of $[PPh_2(CH_2)_2PMe_3]PF_6$, which was recrystallized from acetone/ethanol. ^{1}H NMR spectrum of [II-phophos]PF_6 in CD_3OD: δ 1.84 (9H, d, J(PH) = 14.4 Hz, Me); 2.22 (2H, m, CH_2); 2.31 (2H, m, CH_2); 7.44 (10H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of [II-phophos]PF_6 in acetone-d_6): δ 7.7 (d, J(PC) = 54.7 Hz, Me); 19.3 (dd, J(PC) = 4.2, 17.1 Hz, CH_2); 20.9 (dd, J(PC) = 21.7, 50.7 Hz, CH_2); 129.6 (d, J(PC) = 6.1 Hz, Ph); 130.1 (s, Ph); 133.5 (d, J(PC) = 19.4 Hz, Ph); 137.9 (d, J(PC) = 13.6 Hz, Ph). $^{31}P\{^1H\}$ NMR spectral data of various salts of II-phophos are listed in Table 2.

Preparation of $[PPh_2(CH_2)_3PMe_3]NO_3$ (III-phophos).

The preparation was carried out in similar fashion. ^{1}H NMR spectrum of $Cl(CH_2)_3PPh_2$ in $CDCl_3$: δ 1.86 (2H, m, CH_2); 2.17 (2H, m, CH_2); 3.57 (2H, t, J(HH) = 6.5 Hz, CH_2); 7.24–7.43 (10H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of $Cl(CH_2)_3PPh_2$ in $CDCl_3$: δ 25.2 (d, J(PC) = 13.2 Hz, CH_2); 28.9 (d, J(PC) = 17.8 Hz, CH_2); 45.7 (d, J(PC) = 14.6 Hz, CH_2); 128.4 (d, J(PC) = 6.7 Hz, Ph); 128.6 (s, Ph); 132.7 (d, J(PC) = 19.5 Hz, Ph); 138.0 (d, J(PC) = 13.2 Hz, Ph). ^{1}H NMR spectrum of [III-phophos]NO_3 in CD_3OD: δ 1.70 (2H, m, CH_2); 1.77 (9H, d, J(PH) = 14.5 Hz, 3Me); 2.24 (2H, t, CH_2); 2.36 (2H, m, CH_2); 7.38 (10H, m).

Table 2

$^{31}P\{^1H\}$ NMR data for salts of [II-phophos]X

X^-	Solvent	δ(PMe)	δ(PPh)	J(PP)
I^-	CD_3CN	30.9	−10.9	(47)
NO_3^-	D_2O	28.8	−12.9	(45)
Cl^-	MeOH	30.7	−11.1	(45)
Cl^-	D_2O	28.8	−12.8	(45)
PF_6^-	acetone	31.4	−11.0	(48)

$^{13}C\{^1H\}$ NMR spectrum of [III-phosphos]NO_3 in CD_3OD: δ 7.5 (d, $J(PC) = 54.7$ Hz, Me); 19.5 (d, $J(PC) = 19.7$ Hz, CH_2); 25.1 (dd, $J = 51.8$, 13.8 Hz, CH_2); 29.8 (m, CH_2); 129.7 (d, $J(PC) = 6.3$ Hz, Ph); 129.9 (s, Ph); 133.7 (d, $J(PC) = 19.2$ Hz, Ph); 139.2 (d, $J(PC) = 12.3$ Hz, Ph). $^{31}P\{^1H\}$ NMR spectrum of [III-phosphos]NO_3 in D_2O: δ 26.3 (PMe); -18.3 (PPh); of [III-phosphos]PF_6 in acetone-d_6: δ 28.8 (PMe); -16.9 (PPh).

Preparation of [$PPh_2(CH_2)_6PMe_3$]NO_3 (VI-phosphos)

A solution of 61 g (250 mmol) of 1,6-dibromohexane in 50 mL of toluene was treated with 5 mL (50 mmol) of PMe_3, and the mixture was stirred at room temperature for 72 h to yield a white precipitate of [$Br(CH_2)_6PMe_3$]Br. The latter (16.0 g, 50 mmol, 100% yield) was collected by filtration, washed with hexanes and dried under reduced pressure. ^1H NMR spectrum of [$Br(CH_2)_6PMe_3$]Br in $CDCl_3$: δ 1.48 (6H, m, $3CH_2$); 1.59 (2H, m, CH_2); 1.86 (9H, d, $J(PH) = 14.3$ Hz, 3Me); 2.20 (2H, m, CH_2); 3.43 (2H, t, $J = 6.6$ Hz, CH_2). $^{13}C\{^1H\}$ NMR spectrum of [$Br(CH_2)_6PMe_3$]Br in CD_3OD: δ 8.15 (d, $J(HP) = 55$ Hz, 3Me); 24.1 (d, $J(HP) = 53$ Hz, CH_2); 30.6 (d, $J(HP) = 16$ Hz, CH_2); 22.2 (d, $J(HP) = 4$ Hz, CH_2); 28.4 (s, CH_2); 33.5 (s, CH_2); 34.5 (s, CH_2). $^{31}P\{^1H\}$ NMR spectrum of $Br(CH_2)_{10}PMe_3^+Br^-$ in $CDCl_3$: δ 28.0.

A solution of 8.0 g (25 mmol) of $Br(CH_2)_6PMe_3^+Br^-$ in 50 mL of THF was treated with 4.8 g (25 mmol) of $LiPPh_2$. The solvent was then removed under reduced pressure and the residue was recrystallized from methanol/ethyl ether to give white crystals of $Ph_2P(CH_2)_6PMe_3^+Br^-$ (9.5 g, 22.3 mmol, 89% yield). The latter was then dissolved in 50 mL of methanol and eluted through an Amberlite IRA-400 anion exchange column (NO_3^- form) to give 7.4 g (18.1 mmol, 81% yield of [$Ph_2P(CH_2)_6PMe_3^+$]NO_3^-. ^1H NMR spectrum of [VI-phophos]NO_3 in acetone-d_6: δ 1.51 (6H, m, $3CH_2$); 1.67 (2H, m, CH_2); 2.05 (9H, d, $J(HP) = 15$ Hz, 3Me); 2.10 (2H, m, CH_2); 2.34 (2H, m, CH_2); 7.4 (10H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of [VI-phophos]NO_3 in CD_3CN: δ 8.6 (d, $J(PC) = 55$ Hz, Me); 21.7 (s, CH_2); 23.7 (d, $J(PC) = 53$ Hz, CH_2); 26.7 (d, $J(PC) = 16$ Hz, CH_2); 27.8 (d, $J(PC) = 11$ Hz, CH_2); 30.5 (d, $J(PC) = 16$ Hz, CH_2); 30.7 (d, $J(PC) = 14$ Hz, CH_2); 129.5 (d, $J(PC) = 6.4$ Hz, Ph); 129.6 (s, Ph); 133.5 (d, $J(PC) = 18$ Hz, Ph); 140.1 (d, $J(PC) = 13.7$ Hz, Ph). $^{31}P\{^1H\}$ NMR spectrum of [VI-phophos]NO_3 in $CDCl_3$: δ 29.0, -15.5.

Preparation of [$PPh_2(CH_2)_{10}PMe_3$]NO_3 (X-phophos)

The preparation was carried out in similar fashion utilizing 1,10-diiododecane prepared from 1,10-dichlorodecane. Sodium iodide (64 g, 0.43 mol), dried at 70 °C and 0.5 mmHg for 12 h, and 1,10-dichlorodecane (25 mL, 0.12 mol) were added to 300 mL of acetone and the mixture was refluxed under a nitrogen atmosphere for 24 h. The solvent was then removed under reduced pressure, and dichloromethane (5×30 mL) was used to extract the product, the sodium iodide and chloride being removed by filtration. The solvent was then removed under reduced pressure to give 1,10-diiododecane (41.3 g, 0.10 mol, yield 90%) as a yellow solid which was dried at 50 °C and 0.5 mmHg. ^1H NMR spectrum of 1,10-diiododecane in $CDCl_3$: δ 3.18 (t, $J = 8$ Hz, 4H, CH_2); 1.81 (m, 4H, CH_2); 1.37 (m, 4H, CH_2); 1.28 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$: δ 7.26, 28.37, 29.18, 30.36, 33.43.

^{1}H NMR spectrum of $[I(CH_2)_{10}PMe_3]I$ in $CDCl_3$: δ 3.11 (2H, t, $J = 7$ Hz, CH_2); 2.44 (2H, m, CH_2); 2.14 (9H, d, J(PH) = 14 Hz, Me); 1.73 (2H, m, CH_2); 1.49 (2H, m, CH_2); 1.40 (2H, m, CH_2); 1.20 (10H, m, $5CH_2$). $^{13}C\{^1H\}$ NMR spectrum of $[I(CH_2)_{10}PMe_3]I$ in $CDCl_3$: δ 7.5 (s, CH_2); 9.3 (d, J(PC) = 54 Hz, Me); 21.5 (d, J(PC) = 4 Hz, CH_2); 23.5 (d, J(PC) = 54 Hz, CH_2); 28.2 (s, CH_2); 28.7 (s, CH_2); 28.9 (s, CH_2); 29.0 (s, $_2$); 30.2 (s, CH_2); 30.3 (s, CH_2); 33.3 (s, CH_2). $^{31}P\{^1H\}$ NMR spectrum of $[I(CH_2)_{10}PMe_3]I$ in $CDCl_3$: δ 27.15. ^{1}H NMR spectrum of [X-phophos]NO_3 in $CDCl_3$: δ 1.13 (8H, m, $4CH_2$); 1.30 (6H, m, $3CH_2$); 1.39 (2H, m, CH_2); 1.86 (9H, d, J(PH) = 14 Hz, 3Me); 1.93 (2H, m, CH_2); 2.18 (2H, m, CH_2); 7.2–7.8 (10H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of [X-phophos]NO_3 in $CDCl_3$: δ 7.6 (d, J(PC) = 54 Hz, Me); 21.2 (d, J(PC) = 4.5 Hz, CH_2); 23.2 (d, J(PC) = 51.8 Hz, CH_2); 25.2 (d, J(PC) = 15.3 Hz, CH_2); 28.4 (s, CH_2); 28.6 (s, CH_2); 28.7 (s, CH_2); 28.8 (s, CH_2); 29.8 (s, CH_2); 30.0 (s, CH_2); 30.3 (d, J(PC) = 12.8 Hz, CH_2); 127.8 (d, J(PC) = 14.4 Hz, Ph); 128.1 (s, Ph); 132.0 (d, J(PC) = 17.6 Hz, Ph); 133.5 (d, J(PC) = 12 Hz, Ph). ^{31}P NMR spectrum of [X-phophos]I in $CDCl_3$: δ 27.1 (PMe); −15.5 (PPh); of [X-phophos]NO_3 in $CDCl_3$: δ 27.9 (PMe); −15.6 (PPh).

Preparation of [NBDRhCl(II-phophos)]PF_6

A solution of 0.46 g (1.0 mmol) of $[NBDRhCl]_2$ in 20 mL of methanol was treated with a solution of 0.70 g (2 mmol) of II-phophos nitrate in 20 mL of methanol. The solution was stirred at room temperature for 3 h, and then was treated with a solution of 0.35 g of $NaPF_6$ to give an orange precipitate of the product. ^{1}H NMR spectrum of [NBDRhCl(II-phophos)]PF_6 in acetone-d_6: δ 1.36 (2H, m, NBD CH_2); 2.08 (9H, d, J(HP) = 14.2 Hz, 3Me); 2.83 (2H, m, CH_2); 2.98 (2H, m, CH_2); 3.75 (2H, s, NBD bridgehead); 4.2 (4H, br, NBD olefinic); 7.50 (4H, m, Ph); 7.65 (6H, m, Ph). $^{13}C\{^1H\}$ NMR of [NBDRhCl(II-phophos)]PF_6 in acetone-d_6: δ 7.7 (d, J(PC) = 54.8 Hz, Me); 19.5 (d, J(PC) = 19.0 Hz, CH_2); 20.3 (d, J(PC) = 47.4 Hz, CH_2); 51.3 (s, NBD bridgehead); 64.4 (s, NBD–CH_2); olefinic carbons not detected; 129.3 (d, J(PC) = 8.9 Hz, Ph); 131.3 (s, Ph); 131.6 (d, J(PC) = 41.5 Hz, Ph); 133.8 (d, J(PC) = 10.2 Hz, Ph). $^{31}P\{^1H\}$ NMR spectrum of [NBDRhCl(II-phophos)]PF_6 in acetone-d_6: 32.0 (complex m, 2P); −142.9 (septet, PF_6^-).

Recrystallization from acetone/ethanol resulted in the formation of crystals suitable for structure determination.

X-Ray crystal structure of [NBDRhCl(II-phophos)]PF_6

The title compound crystallizes in space group $P2_1/n$ with $a = 25.973(4)$, $b = 11.361(2)$, $c = 9.341(6)$ Å, $\beta = 90.25(4)°$, $V = 2756.2$ Å^3; $Z = 4$, $D_{calc} = 1.598$ Mg m^{-3}, $\mu = 9.29$ cm^{-1}. A yellow crystal, 0.55 × 0.10 × 0.10 mm, was used for the collection of intensity data on an Enraf–Nonius CAD-4 diffractometer. The unit cell parameters were obtained by a least-squares analysis of 25 centered reflections in the range $20.2 < 2\theta < 28.5$. The data were collected by the θ–2θ scan technique, with variable scanning rate, using monochromated Mo-K_α radiation. A total of 4841 unique reflections were measured in the range $1.0 < 2\theta < 50$, of which 3140 were considered observed, i.e. $I \geqslant 3\sigma(I)$. Three standard reflections were measured every 7200 s of radiation time and showed no significant variation during the course of data collection. The intensities were corrected for Lorentz and polariza-

Table 3

Positional parameters and esd's for the compound [NBDRhCl(II-phophos)]PF_6

Atom	x	y	z	B (Å^2) [a]
Rh	0.71303(3)	0.22679(9)	0.91907(8)	3.24(1)
Cl	0.7418(1)	0.2276(3)	1.1597(3)	5.92(7)
P1	0.62970(9)	0.2829(2)	0.9617(3)	2.96(5)
P2	0.6217(1)	−0.0107(3)	1.2391(3)	3.77(6)
P3	0.4379(1)	0.1582(3)	0.2555(3)	4.12(6)
F1	0.4161(3)	0.2277(7)	0.3911(8)	7.1(2)
F2	0.4618(3)	0.0659(7)	0.3655(8)	7.1(2)
F3	0.4887(3)	0.2312(8)	0.2620(8)	8.5(2)
F4	0.4615(3)	0.0839(8)	0.1295(7)	7.7(2)
F5	0.4117(3)	0.2465(7)	0.1513(9)	8.7(2)
F6	0.3867(3)	0.0793(6)	0.2506(8)	6.7(2)
C1	0.7909(4)	0.223(1)	0.822(1)	5.0(3)
C2	0.7745(4)	0.110(1)	0.840(1)	4.9(3)
C3	0.7481(5)	0.081(1)	0.700(1)	5.1(3)
C4	0.7767(4)	0.151(1)	0.590(1)	4.7(3)
C5	0.7715(4)	0.265(1)	0.678(1)	5.0(3)
C6	0.7143(4)	0.270(1)	0.701(1)	4.0(2)
C7	0.6986(4)	0.152(1)	0.719(1)	4.2(2)
C8	0.6142(4)	0.4049(8)	1.0797(9)	2.8(2)
C9	0.5653(4)	0.443(1)	1.097(1)	4.5(3)
C10	0.5537(5)	0.531(1)	1.195(1)	5.8(3)
C11	0.5897(5)	0.590(1)	1.268(1)	5.8(3)
C12	0.6406(5)	0.554(1)	1.252(1)	5.9(3)
C13	0.6537(4)	0.462(1)	1.154(1)	4.7(3)
C14	0.5942(3)	0.3162(9)	0.8015(9)	2.8(2)
C15	0.5678(4)	0.2287(9)	0.725(1)	3.9(2)
C16	0.5448(4)	0.258(1)	0.589(1)	4.8(3)
C17	0.5480(4)	0.369(1)	0.537(1)	4.6(3)
C18	0.5736(5)	0.455(1)	0.613(1)	4.9(3)
C19	0.5967(4)	0.4309(9)	0.745(1)	4.0(2)
C20	0.5918(4)	0.1609(8)	1.0414(9)	3.1(2)
C21	0.6110(4)	0.1403(9)	1.198(1)	4.3(3)
C22	0.6635(5)	−0.075(1)	1.113(1)	6.8(3)
C23	0.5635(5)	−0.090(1)	1.241(1)	5.3(3)
C24	0.6514(5)	−0.015(1)	1.412(1)	6.8(4)
H1	0.8108	0.2701	0.8887	5
H2	0.2148	0.9687	0.0761	5
H3	0.7454	−0.0035	0.6749	5
H4a	0.7558	0.1562	0.5000	4
H4b	0.1875	0.8437	0.4218	4
H5	0.2832	0.1875	0.1152	4
H6	0.1738	0.1875	0.1523	4
H7	0.8359	0.6250	0.8066	4
H9	0.0253	0.0937	0.5371	4
H10	0.5172	0.5498	1.2078	6
H11	0.4316	0.3437	0.6523	6
H12	0.6682	0.5911	1.2092	5
H13	0.8105	0.9375	0.3457	4
H15	0.4316	0.8750	0.2304	3
H16	0.9726	0.6875	0.9609	4
H17	0.5390	0.4062	0.4218	4
H18	0.9179	0.0312	0.9218	5
H19	0.6074	0.5000	0.8066	4
H20a	0.5527	0.1875	0.0371	3
H20b	0.4042	0.9375	0.000	3

Table 3 (continued)

Atom	x	y	z	B (Å^2) [a]
H21a	0.5820	0.1562	1.2695	4
H21b	0.6415	0.1901	1.2034	4
H22a	0.6894	−0.1562	1.1542	6
H22b	0.6879	−0.0135	1.0796	6
H22c	0.6447	−0.0986	1.0297	6
H23a	0.5683	−0.1562	1.3085	5
H23b	0.5347	−0.0410	1.2714	5
H23c	0.5542	−0.1190	1.1466	5
H24a	0.6640	−0.0937	1.4238	6
H24b	0.6274	−0.0069	1.4869	6
H24c	0.6796	0.0425	1.4188	6

[a] Hydrogen atoms were refined anisotropically.

tion effects. A numerical absorption correction was applied. The minimum, maximum and average correction factors were 0.721, 0.780 and 0.747, respectively.

The structure was solved by direct methods using the program MULTAN80 [5]. Difference Fourier map calculations revealed the positions of 20 of the hydrogen atoms. The remaining ones were calculated. The hydrogen atoms were assigned temperature factors equal in magnitude to the equivalent isotropic values of their parent atoms, and were included in the calculations but not refined. Full-matrix least-squares refinement minimizing the function $\Sigma w \| F_o | - | F_c \|^2$, where $w = 1/\sigma^2(|F_o|)$ resulted in $R = 0.063$ and $R_w = 0.096$. The esd of an observation of unit weight was 2.554; the maximum shift to error ratio was 0.00. The scattering factors used were those of Cromer and Waber [6]. The anomalous dispersion coefficients were taken from Cromer [6]. The final atomic coordinates are given in Table 3, bond lengths and bond angles in Table 4. All calculations were performed on a PDP 11/23 computer using the structure determination package of Enraf–Nonius, SDP [7]. The program ORTEP [8] was used for the preparation of the illustrations.

Preparation of catalyst precursors

A solution of 0.46 g (1.0 mmol) of $[NBDRhCl]_2$ in 15 mL of THF was treated with a solution of 0.34 g (2.0 mmol) of silver nitrate in 5:1 ethanol/water. The mixture was stirred at room temperature for 30 min, and then the precipitated silver chloride was removed by filtration and 1.41 g (4.0 mmmol) of II-phophos nitrate in 25 mL of methanol was added to the filtrate. The orange solution was stirred for 30 min, and the solvent was removed under reduced pressure and the resulting product, $[NBDRh(II\text{-}phophos)_2](NO_3)_3$, as an orange powder, was obtained. The compounds $[NBDRh(III\text{-}phophos)_2](NO_3)_3$, $[NBDRh(VI\text{-}phophos)_2](NO_3)_3$ and $[NBDRh(X\text{-}phophos)_2](NO_3)_3$ were prepared in an analogous fashion. All were unambiguously characterized spectroscopically (see below for ^1H and $^{13}C\{^1H\}$, Table 5 for $^{31}P\{^1H\}$ NMR data), and utilized as obtained in the catalytic runs described below.

^1H NMR spectrum of $[NBDRh(II\text{-}phophos)_2](NO_3)_3$ in methanol-d_4: δ 1.59 (2H, s, NBD CH_2); 1.69 (18H, d, $J(PH) = 14.5$ Hz, 6Me); 2.06 (4H, m, CH_2); 2.25 (4H, m, CH_2); 4.06 (2H, s, NBD bridgehead); 5.11 (4H, s, NBD olefinic); 7.30 (8H,

Table 4

Bond lengths (Å)

Rh–Cl	2.366(2)	C1–C5	1.515(11)
Rh–P1	2.293(2)	C2–C3	1.514(10)
Rh–C1	2.220(6)	C3–C4	1.499(10)
Rh–C2	2.206(7)	C3–C7	1.530(10)
Rh–C6	2.095(6)	C4–C5	1.544(10)
Rh–C7	2.089(6)	C5–C6	1.503(9)
P1–C8	1.817(6)	C6–C7	1.413(9)
P1–C14	1.794(5)	C8–C9	1.352(9)
P1–C20	1.857(6)	C8–C13	1.395(9)
P2–C21	1.780(7)	C9–C10	1.386(10)
P2–C22	1.764(8)	C10–C11	1.332(11)
P2–C23	1.762(7)	C11–C12	1.392(12)
P2–C24	1.789(7)	C12–C13	1.436(11)
P3–F1	1.598(5)	C14–C15	1.401(9)
P3–F2	1.592(5)	C14–C19	1.408(8)
P3–F3	1.560(5)	C15–C16	1.445(9)
P3–F4	1.575(5)	C16–C17	1.353(9)
P3–F5	1.553(5)	C17–C18	1.384(10)
P3–F6	1.603(4)	C18–C19	1.397(10)
Cl–C2	1.369(11)	C20–C21	1.557(6)
Cl–Rh–P1	97.40(6)	C14–P1–C20	102.7(3)
Cl–Rh–C1	96.0(2)	C21–P2–C22	110.5(4)
Cl–Rh–C2	95.3(2)	C21–P2–C23	111.4(4)
P1–Rh–C6	97.0(2)	C21–P2–C24	106.8(4)
P1–Rh–C7	95.9(2)	C22–P2–C23	109.0(4)
C8–P1–C14	103.3(3)	C22–P2–C24	109.1(4)
C8–P1–C20	101.9(3)	C23–P2–C24	110.0(4)

m, Ph); 7.41 (12H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of [NBDRh(II-phophos)$_2$](NO$_3$)$_3$ in methanol-d_4: δ 7.15 (d, J(PC) = 54.0 Hz, 6Me); 16.9 (m, CH$_2$); 19.5 (d, J(PC) = 49.5 Hz, CH$_2$); 55.3 (s, NBD bridgehead); 70.0 (s, NBD CH$_2$); 85.5 (s, NBD olefinic); 128.0 (d, J(PC) = 37.0 Hz, Ph); 130.3 (s, Ph); 132.4 (s, Ph); 134.2 (s, Ph).

^1H spectrum of [NBDRh(III-phophos)$_2$](NO$_3$)$_3$ in methanol-d_4: δ 1.61 (2H, s, NBD–CH$_2$); 1.75 (4H, m, CH$_2$); 1.80 (18H, d, J(PC) = 14.5 Hz, 6Me); 2.03 (4H, m, CH$_2$); 2.23 (4H, m, CH$_2$); 4.07 (2H, s, NBD bridgehead); 4.96 (4H, s, NBD olefinic); 7.45 (8H, m, Ph); 7.53 (12H, m, Ph). $^{13}C\{^1H\}$ NMR spectrum of

Table 5

^{31}P NMR data for new rhodium complexes in D$_2$O

Compound	δ(PPh$_2$)(J(RhP))	δ(PMe$_3$)
[NBDRh(II-phophos)$_2$](NO$_3$)$_3$ [a]	21.9 (158 Hz)	31.7
[NBDRh(III-phophos)$_2$](NO$_3$)$_3$	20.8 (151 Hz)	28.1
[NBDRh(VI-phophos)$_2$](NO$_3$)$_3$	21.2 (156 Hz)	28.3
[NBDRh(X-phophos)$_2$](NO$_3$)$_3$	21.0 (154 Hz)	28.5
[NBDRh(amphos)$_2$](NO$_3$)$_3$	15.7 (152 Hz)	

[a] J(PP) = 46 Hz.

[NBDRh(III-phophos)$_2$](NO$_3$)$_3$ in acetonitrile-d_3: δ 7.52 (d, J(PC) = 54.3 Hz, 6Me); 18.0 (s, CH_2); 24.5 (d, J(PC) = 50.2 Hz, CH_2); 26.7 (m, CH_2); 55.1 (s, NBD bridgehead); 69.9 (s, NBD–CH_2); 84.8 (s, NBD olefinic); 129.9 (s, Ph); 130.4 (d, J(PC) = 38.0 Hz, Ph); 131.2 (s, Ph); 133.7 (s, Ph).

^{1}H NMR spectrum of [NBDRh(VI-phophos)$_2$](NO$_3$)$_3$ in methanol-d_4: δ 1.26 (8H, m, 4CH_2); 1.43 (8H, m, 4CH_2); 1.57 (2H, s, NBD–CH_2); 1.75 (18H, d, J(PH) = 14.5 Hz, 6Me); 1.79 (4H, m, 2CH_2); 2.08 (4H, m, 2CH_2); 3.96 (2H, s, NBD bridgehead); 4.80 (4H, s, NBD olefinic); 7.35 (8H, m, Ph); 7.41 (12H, m, Ph). ^{13}C{^{1}H} NMR spectrum of [NBDRh(VI-phophos)$_2$](NO$_3$)$_3$ in acetone-d_6: δ 8.05 (d, J(PC) = 55.2 Hz, 6Me); 21.67 (d, J(PC) = 4.1 Hz, CH_2); 23.43 (d, J(PC) = 52.4 Hz, CH_2); 25.57 (s, CH_2); 26.50 (d, J(PC) = 23.6 Hz, CH_2); 30.39 (d, J(PC) = 16.2 Hz, CH_2); 30.78 (d, J(PC) = 11.5 Hz, CH_2); 52.1 (s, NBD bridgehead); 66.6 (s, br, NBD–CH_2); 73.7 (s, br, NBD olefinic); 129.8 (s, Ph); 131.6 (s, Ph); 131.9 (d, J(PC) = 37.2 Hz, Ph); 133.7 (s, Ph).

^{1}H NMR spectrum of [NBDRh(X-phophos)$_2$](NO$_3$)$_3$ in methanol-d_4: δ 1.17 (8H, br, 4CH_2); 1.33 (12H, br, 6CH_2); 1.43 (8H, br, 4CH_2); 1.58 (6H, br, 2CH_2 + NBD–CH_2); 1.86 (18H, d, J(PC) = 14.5 Hz, 6Me); 2.21 (4H, m, 2CH_2); 4.00 (2H, s, NBD bridgehead); 4.80 (4H, s, NBD olefinic); 7.45 (8H, m, Ph); 7.50 (12H, m, Ph). ^{13}C{^{1}H} NMR spectrum of [NBDRh(X-phophos)$_2$](NO$_3$)$_3$ in acetone-d_6: δ 7.65 (d, J(PC) = 55.1 Hz, 6Me); 22.3 (s, CH_2); 22.4 (s, CH_2); 23.9 (d, J(PC) = 52.4 Hz, CH_2); 26.5 (s, CH_2); 27.3 (d, J(PC) = 12.7 Hz, CH_2); 29.7 (s, CH_2); 29.8 (s, CH_2); 30.3 (d, J(PC) = 5.7 Hz, CH_2); 31.6 (d, J(PC) = 16.6 Hz, CH_2); 32.2 (d, J(PC) = 6.3 Hz, CH_2); 54.5 (s, NBD bridgehead); 69.4 (s, NBD CH_2); 83.1 (s, NBD olefinic); 130.1 (s, Ph); 132.1 (s, Ph); 134.1 (s, Ph).

Catalyst testing

Preliminary assessment of catalytic activities was carried out at 25 °C with maleic acid and $\approx 10^{-4}$ M solutions of [NBDRh(n-phophos)$_2$](NO$_3$)$_3$ (n = 2, 3) in D_2O with substrate : catalyst ratios of 100 : 1 to 500 : 1. A strong flow of hydrogen was maintained through a large glass frit, and the course of each reaction was monitored by ^{1}H NMR spectroscopy.

Testing of biphasic systems was carried out utilizing approximately millimolar concentrations of all four catalyst precursors, 1-hexene (neat and dissolved in ethyl or dichloromethane) as substrate, and substrate : catalyst ratios of 500 : 1 to 1000 : 1. Reactions were carried out in the glass vessel of a Parr Hydrogenation Apparatus at 25 °C and under 3 atm of hydrogen for 3 to 6 h; concentrations of reactants and products were subsequently determined utilizing a Hewlett Packard 5880A gas chromatograph.

Results and discussion

Preparation of ligands

Syntheses of the ligands II- and III-phophos were accomplished via the following sequence of steps:

$$Cl(CH_2)_nCl + LiPPh_2 \rightarrow Cl(CH_2)_nPPh_2 \quad (70\%) \qquad (1)$$

$$Cl(CH_2)_nPPh_2 + PMe_3 \rightarrow [PPh_2(CH_2)_nPMe_3]Cl \quad (100\%) \qquad (2)$$

$$[PPh_2(CH_2)_nPMe_3]Cl \xrightarrow[\text{Exchange}]{\text{Ion}} [PPh_2(CH_2)_nPMe_3]NO_3 \quad (80\%) \qquad (3)$$

$$[PPh_2(CH_2)_nPMe_3]NO_3 + NaPF_6 \underset{(n=2,3)}{\rightarrow} [PPh_2(CH_2)_nPMe_3]PF_6 \qquad (4)$$

The chloroalkylphosphine intermediate products were obtained as colourless oils which were characterized spectroscopically. Care had to be taken in the reaction of eq. 1 that the $LiPPh_2$ was added slowly and in deficiency lest significant formation of the diphosphines $PPh_2(CH_2)_nPPh_2$ occur. Also, the unreacted 1,2- and 1,3-dichloroalkanes had to be removed under reduced pressure to avoid reaction with trimethylphosphine in the next step. However, other than these provisos, all steps proceeded smoothly and good overall yields of the desired ligands $[PPh_2(CH_2)_nPMe_3]NO_3$ were obtained.

Unfortunately, the syntheses of VI- and X-phophos could not be prepared in the same way because the 1,6- and 1,10-dihaloalkanes left after the first step could not be readily removed; their vapour pressures are too low. The following route was therefore devised:

$$X(CH_2)_nX + PMe_3 \xrightarrow{\text{Toluene}} [X(CH_2)_nPMe_3]X \quad (100\%) \qquad (5)$$

$$[X(CH_2)_nPMe_3^+] + LiPPh_2 \xrightarrow{\text{THF}} [Ph_2P(CH_2)_nPMe_3]X \quad (89\%) \qquad (6)$$

$$[Ph_2P(CH_2)_nPMe_3]X + NO_3^- \xrightarrow[\text{Exchange}]{\text{Ion}} [Ph_2P(CH_2)_nPMe_3]NO_3 \quad (81\%) \qquad (7)$$

(n = 6, 10; X = Br, I; overall yield = 65–100%)

The bromo- and iodoalkylphosphonium intermediate products were obtained as colourless, crystalline solids which were characterized spectroscopically. Again, the desired ligands were obtained in excellent overall yields.

Preparation of rhodium complexes

By analogy with earlier work with the ligand amphos [3] 1:1 and 2:1 complexes of rhodium with the phophos ligands were prepared via the following sequence:

$$[NBDRhCl]_2 + 2n\text{-phophos}^+ \rightarrow 2[NBDRhCl(n\text{-phophos})]^+ \qquad (8)$$

$$[NBDRhCl(n\text{-phophos})]^+ + n\text{-phophos}^+ \rightarrow [NBDRh(n\text{-phophos})_2]^{3+} \qquad (9)$$

(n = 2, 3, 6, 10)

The products of eq. 8 could not generally be obtained analytically pure, but the structure of the derivative of II-phophos was determined utilizing X-ray crystallography. An ORTEP diagram is shown in Fig. 1, bond lengths and angles in Table 4. As expected, the compound was found to assume an essentially square planar structure with metal–ligand distances comparable to those of other rhodium(I) complexes [9]. Of particular interest is the observation that the Rh–C(olefin) bonds *trans* to phosphorus are significantly longer than those *trans* to chlorine, a result of the much greater *trans* influence of the tertiary phosphine [10]. The internal dimensions of the coordinated II-phophos and of the hexafluorophosphate ion are all normal.

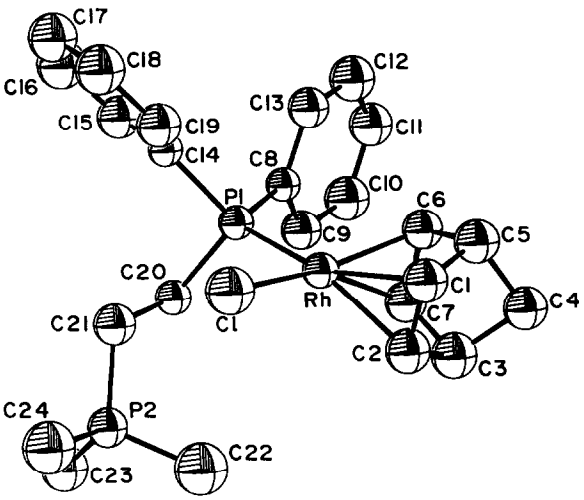
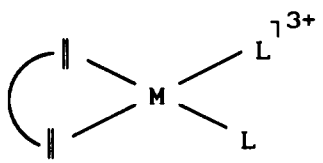


Fig. 1. ORTEP drawing of the compound [NBDRhCl(II-phophos)]PF_6.

The 1:1 compounds [NBDRhCl(*n*-phophos)]$^+$ were readily reduced by molecular hydrogen (eq. 10), and thus could not function as useful hydrogenation catalysts.

$$[\text{NBDRhCl}(n\text{-phophos})]^+ + 2H_2 \rightarrow \text{norbornane} + \text{rhodium metal} + n\text{-phophos}^+ \quad (10)$$

On the basis of previous work [1–3], the 2:1 complexes formed as in eq. 9 are expected to act as good catalyst precursors, and were generally prepared in situ, after removal of the chloride ion with silver nitrate, by treating $[NBDRhCl]_2$ with four equivalents of the phosphine. While the products could not be obtained analytically pure, their structures were shown spectroscopically to be as in **A**.



A (L = n-phophos)

Thus the ^{31}P NMR parameters (Table 5) are very similar to those of a variety of similar tertiary phosphine complexes, including the amphos analogue [3]. The ^1H and ^{13}C NMR data were also consistent with the suggested structures. Hydrogenation of these complexes in turn is expected [1–3] to result in the formation of solvated complexes of the type $[Rh(n\text{-phophos})_2S_2]^{3+}$ (S = water, methanol), which function as the actual catalysts.

Catalyst studies

It was desirable to ascertain the properties of the new phophos-rhodium complexes as homogeneous catalysts for olefin hydrogenation in monophasic

systems. We therefore screened the two complexes $[NBDRh(n\text{-phophos})_2]^{3+}$ (n = 2, 3) for their abilities to catalyze the hydrogenation of a model water-soluble olefin, maleic acid, in D_2O. Similar data had been previously accumulated for water-soluble rhodium complexes of amphos [3] and other ligands [1,2], and comparisons with known systems were desirable.

Preliminary experiments were carried out utilizing approximately 10^{-4} M catalyst and substrate:catalyst ratios of 100:1 to 500:1, the hydrogen pressure of the experiments being maintained at 1 atm by bubbling through a large frit. Under these conditions, the substrate could be almost quantitatively hydrogenated within 10 to 15 min. In agreement with this very high level of activity, it was also found in several cases that the apparent activity of a catalyst solution varied greatly with the hydrogen flow rate, suggesting that catalytic activities were so high that diffusion of the hydrogen gas was rate-limiting. Although uncertainties concerning the possibility of hydrogen diffusion being rate-limiting therefore rendered detailed comparisons with other catalysts suspect, it is clear that the phophos-based catalysts exhibit very high catalytic activity.

Since highly active biphasic catalysts were the ultimate goal of this research, no effort was made to optimize or otherwise investigate the monophasic catalyst systems. Instead, given the encouraging results from the monophasic systems, we began an investigation of the properties of the complexes as biphasic olefin hydrogenation catalysts. The experimental protocol for these experiments involved the utilization of 2.5×10^{-3} M solutions of the complexes in distilled water and substrate:catalyst ratios of 500:1 to 100:1. The substrates were either neat or were dissolved in the water-immiscible solvent ethyl ether, and the catalytic reactions were carried out in the glass vessel of a Parr Hydrogenation Apparatus at 25 °C and under 3 atm of hydrogen.

Representative results are given in Table 6. As can be seen, all four catalysts exhibited high activity for the catalytic hydrogenation of 1-hexene and, although isomerization of 1-hexene was observed in most cases, the internal olefins were also hydrogenated and their formation did not appear to detract significantly from the efficiency of the catalysts. A clear effect of ligand chain length is apparent, although the reasons are not obvious since activities vary in the order VI-phophos

Table 6

Representative catalytic results; hydrogenation of 1-hexene in biphasic systems [a]

Exp. no.	Ligand	Products (%)			
		Hexane	1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene
1	II-phophos	23	55	13	9
2	II-phophos [b]	11	71	10	8
3	II-phophos [c]	2	96	0	2
4	III-phophos	70	0	24	6
5	III-phophos [b]	22	65	7	6
6	VI-phophos [d]	89	1	8	2
7	VI-phophos [e]	61	17	10	12
8	X-phophos	27	30	30	13
9	X-phophos [c]	7	89	1	3

[a] 20 mL of water; 6 mL of 1-hexene; 3 atm H_2; 6 h; substrate:catalyst 1000:1. [b] 20 mL of ethyl ether as co-solvent. [c] Phophos:Rh 3:1. [d] 3 h. [e] 20 mL dichloromethane co-solvent.

> X-phophos ≥ III-phophos > II-phophos. Interestingly, the activity of the II-phophos catalyst was within 30% of that of the amphos catalyst [3], seemingly confirming chain length as an important factor in determining catalyst activity. The VI-phophos system formed by far the most active catalyst, about 90% of the 1-hexene having been hydrogenated after only three hours. It is not clear why this should be, nor is it clear why the extent of substrate isomerization should also be minimized for this catalyst.

As anticipated, it was found that addition of free phophos to a catalytic mixture resulted in a significant decrease in activity; presumably the added phophos ligand competes with the olefin for a coordination site on the rhodium and activation is retarded under such circumstances. However, we were rather surprised to find that addition of water-immiscible co-solvents such as ethyl ether and dichloromethane also resulted in significant deactivation; such was not the case with the amphos system [3].

Unfortunately, the catalysts containing the longer chain ligands are quite prone to the formation of very stable emulsions, which are quite difficult to break. In large part for this reason, reproducibility of particularly the X-phophos system suffered. Thus the biphasic systems are not well-behaved as catalysts, and better systems, in which the catalysts are supported on cation exchange resins, will be reported separately.

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