Tris(2-pyridyl)phosphine Complexes of Ruthenium(II) and Rhodium(I). Hydroformylation of Hex-1-ene by Rhodium Complexes †

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Complexes of ruthenium(II) and rhodium(I) containing tris(2-pyridyl)phosphine [P(py)$_3$] are described, examples being RuHCl[P(py)$_3$]$_3$ and RhCl[P(py)$_3$]$_2$. In certain cases, as in these, the nitrogen atom of one of the 2-pyridyl groups can act as a donor to give a P,N chelate ligand. In the presence of an excess of P(py)$_3$, and at low CO + H$_2$ (1 : 1) pressures, the complex RhH(CO)(PPh$_3$)[P(py)$_3$]$_2$ acts as a catalyst for the selective hydroformylation of hex-1-ene to n-heptanal.

THERE have been several attempts to overcome the difficulty of separating reactants and products from transition-metal complexes in homogeneous catalyst systems. The best studied procedure has been the ' heterogenising ' of homogeneous catalysts by anchoring them to supports.[1] Another approach has been to use reverse osmosis with selectively permeable membranes, which allow permeation of small molecules while retaining metal complexes.[2]

Finally, there has been the use[3-5] of two-phase systems where the metal complex is in a solvent such as water and the substrate and reaction products are in an immiscible organic phase, and the complex can act as its own phase-transfer catalyst. The difficulty here is that the metal complex may become distributed between the phases so that clean separations are impossible, as in the hydroformylation of alkenes using sulphonated arylphosphine complexes of rhodium.[3] A modification would be to use a metal complex in a homogeneous system and then remove the complex by extraction, *e.g.* with an aqueous solution. A patent[6] has claimed hydroformylation of alkenes by a cobalt carbonyl catalyst containing the amine-substituted phosphine, P(CH$_2$CH$_2$NEt$_2$)$_3$. The cobalt complex was said to be extractable into dilute mineral acid, from which it could be re-extracted into the organic solvent used after addition of base.

Rhodium complexes of arylphosphines are more effective catalysts for hydroformylation[7] than are those of cobalt but alkylphosphines are not satisfactory, giving neither high rates nor high selectivity for n-aldehyde production. The rhodium–triphenylphosphine system[8] is effective for ethylene, propylene, and possibly butenes, where the product aldehyde can be removed in the synthesis gas stream. However, it is not satisfactory for higher alkenes, since separation of the aldehyde would require a distillation step. This leads to difficulties since the complex RhH(CO)(PPh$_3$)$_3$ undergoes extensive decomposition on heating in solvents, giving benzene *via* cleavage of the P–C bond and several μ-diphenylphosphidorhodium carbonyl complexes.[9]

What is required, therefore, is not only a water-soluble phosphine complex, but one that retains the high steric bulk necessary for the selective formation of n-alkyl intermediates.[10] Although the sulphonated arylphosphines meet these criteria, as noted above, we have found them unsatisfactory. Different types of phosphine, fulfilling both requirements, are tris(pyridyl)phosphines.[11] We have synthesised rhodium and ruthenium complexes of tris(2-pyridyl)phosphine, and have studied the use of the rhodium system in hydroformylation.

Although selective hydroformylation to n-aldehydes can be achieved, as in the case of RhH(CO)(PPh$_3$)$_3$, in the presence of an excess of phosphine, we have still been unable to find a satisfactory way of removing the tris(pyridyl)phosphinerhodium complex from the products and solvent.

Attempts to make tris-3- and -4-pyridylphosphines from 3- and 4-bromopyridines failed to give clean products, although the mixtures did contain phosphines that gave evidence of complex formation with rhodium.

RESULTS AND DISCUSSION

Complexes of Tris(2-pyridyl)phosphine [P(py)$_3$].—A convenient route to rhodium and ruthenium complexes is direct substitution of P(py)$_3$ for PPh$_3$. In benzene, P(py)$_3$, PPh$_3$, and the PPh$_3$ complexes are soluble, while P(py)$_3$ complexes are not. The exchange reactions give products that may have a stoicheiometry different from that of the PPh$_3$ complex because P(py)$_3$ can also co-ordinate *via* the *ortho*-nitrogen atom.

Ruthenium. Purple-red RuHCl(PPh$_3$)$_3$ and RuCl$_2$(PPh$_3$)$_3$ both give yellow tris(pyridyl)phosphine complexes as benzene solvates. Thus suggests an 18-electron configuration for Ru^{II} and octahedral co-ordination,[12] achieved by one phosphine acting as a chelate. Thus for RuHCl[P(py)$_3$]$_3$ the ^{1}H and $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ n.m.r. spectra show that the three mutually-*cis* P atoms are non-equivalent, and that the hydride is *trans* to the P atom of the chelating phosphine, as in (1). Thus, as with *ortho*-metallated complexes[13] of C$_6$H$_4$PPh$_2$ where a four-membered ring is formed, the chemical shift of the P atom of the chelated P(py)$_3$ is to very low frequency.

The dichloride is evidently RuCl$_2$[P(py)$_3$]$_2$, probably with a structure of type (2); there is an appropriate very high-field $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ signal. This is a complex multiplet, suggesting a mixture of isomers in solution.

Rhodium. The complex RhCl[P(py)$_3$]$_2$ can be obtained from either RhCl(PPh$_3$)$_3$ or from [RhCl(C$_8$H$_{12}$)]$_2$ with an excess of P(py)$_3$. The complex is monomeric in dichloromethane and it probably has the structure (3).

From RhH(CO)(PPh$_3$)$_3$ and a six-fold excess of P(py)$_3$

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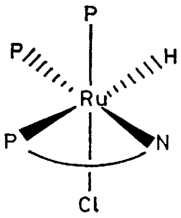
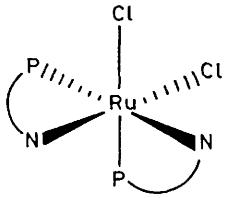
† No reprints available.

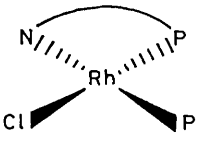
is obtained a yellow compound which appears to be RhH(CO)(PPh$_3$)[P(py)$_3$]$_2$, since the i.r. spectrum has bands at 745s and 699s cm^{-1}, due to the monosubstituted rings of PPh$_3$.



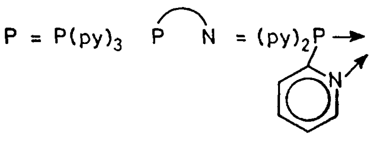
(1)



(2)



(3)



Other complexes appear to be similar to their PPh$_3$ analogues, *viz.*, *trans*-RhCl(CO)[P(py)$_3$]$_2$, RhCl(C$_8$H$_{12}$)-[P(py)$_3$]$_2$, and [Rh(C$_8$H$_{12}$){P(py)$_3$}$_2$][PF$_6$].

All these rhodium complexes are soluble to some extent in water, rather more soluble in dilute mineral acid, and soluble in solvents such as CH$_2$Cl$_2$. They are insoluble in aromatic and saturated hydrocarbons. We have also prepared from RhH(CO)(PPh$_3$)$_3$ the diphenyl-2-pyridylphosphine complex RhH(CO)[PPh$_2$(py)]$_3$ but it is insoluble in water and dilute acid.

Catalytic Studies.—Attempts to hydrogenate alkenes in either homogeneous or two-phase systems at ambient temperature and 3 atm pressure using RhCl[P(py)$_3$]$_2$, [Rh(C$_8$H$_{12}$){P(py)$_3$}$_2$][PF$_6$], or RuHCl[P(py)$_3$]$_3$ were unsuccessful, doubtless due to the chelating action of the pyridyl groups in blocking the co-ordination sites required.

However, using RhH(CO)(PPh$_3$)[P(py)$_3$]$_2$ in the presence of an excess of tris(pyridyl)phosphine we achieved selective hydroformylation of hex-1-ene, as a representative alkene, as with the system RhH(CO)(PPh$_3$)$_3$ + PPh$_3$ studied previously.[14]

Tables of the effects of the variation of pressure, temperature, H$_2$: CO ratio, metal and P(py)$_3$ concentration on the ratio of straight- to branched-chain aldehyde are deposited as Supplementary Publication No. SUP 22611 (5 pp.).* Conversion (%) *vs.* metal concentration, the variation of conversion with solvent, and the decrease in pressure in the reaction vessel as a function of time, which shows essentially complete conversion in two hours, are also deposited in SUP 22611.

The results show that the selectivity to heptanal increases (*a*) when large excesses of phosphine ligand are used, as before,[14] and (*b*) with low CO + H$_2$ pressure. Optimum results were obtained using acetophenone as solvent, 2 atm of CO + H$_2$ (1 : 1), temperature 60 °C, with a twenty-fold excess of P(py)$_3$ over RhH(CO)(PPh$_3$)-[P(py)$_3$]$_2$. Under these conditions, with a complex : hexene ratio of 1 : 100, the ratio of 1- to 2-aldehyde is *ca.* 13 : 1. In each case a small amount ($<2\%$) of 2-ethylpentanal is also produced, evidently *via* hydroformylation of isomerised hex-1-ene; the small amount of unreacted alkene present at the end of a run is a mixture of *cis*- and *trans*-hex-2-ene. There is no evidence for hydrogenation to give hexane, or of reduction of aldehyde to alcohol.

The rate of reaction of the P(py)$_3$ system is similar to that of the PPh$_3$ system under similar conditions in the same solvent. Hydroformylation will occur with the P(py)$_3$ complex in water with hex-1-ene alone and the selectivity is unaffected, though the rate is much lower.

Attempts to recover the rhodium–phosphine complex after completion of a hydroformylation run by extraction with water were unsuccessful. The use of dilute HCl or HBF$_4$ resulted in rapid evolution of gas (H$_2$) and loss of the high-field line in the ^{1}H n.m.r. spectrum due to Rh–H; also about half the rhodium now remains in the organic phase (orange) and cannot be extracted. Attempts to adsorb the complex from the hydroformylation solutions on to ion-exchange resins were also unsuccessful.

The addition of petroleum to the reaction mixtures does precipitate most of the rhodium complex and the recovered material can be re-used. However, we have never been able to recover more than *ca.* 95%.

EXPERIMENTAL

Microanalyses were by the Butterworth Microanalytical and Imperial College laboratories. Infrared spectrometers: Perkin-Elmer PE 457 and 597. N.m.r. spectrometers: Perkin-Elmer R-12 (60 MHz), R32 (90 MHz), and Varian Associates XL-100 [^{31}P{^{1}H} Fourier-transform referenced to external 85% H$_3$PO$_4$ (δ 0.0) at 40.5 MHz; 28 °C]. G.l.c.: Perkin-Elmer F33 using Carbowax 20-M on a Chromosorb W column. All operations were carried out under nitrogen and solvents were freed from peroxides and degassed before use. The petroleum used has b.p. 40—60 °C.

Analytical data are collected in the Table.

Catalytic studies were made normally using methods as previously described.[3,4] Gases were from British Oxygen Co., and were used as received. All pressures are absolute.

Infrared spectra reported below are from Nujol mulls and are in cm^{-1}; ^{1}H n.m.r. spectra (δ values) in CD$_2$Cl$_2$ unless otherwise stated.

(1) *Tris(2-pyridyl)phosphine.*—This was prepared by a modification of a reported procedure.[15] A solution of n-butyl-lithium (50 ml of a 1.6M hexane solution, 80 mmol) in diethyl ether (70 ml) was cooled to −90 °C and 2-bromopyridine (12.6 g, 80 mmol) in diethyl ether (30 ml) at −90 °C was added quickly and the dark red solution stirred

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, **Index issue**

Analytical data

Compound	Found (%)					Calculated (%)					
	C	H	N	P	Cl	C	H	N	P	Cl	M.p. (°C)
$RuHCl[P(py)_3]_3 \cdot C_6H_6$	61.7	4.8	10.6	9.0	3.5	60.3	5.1	12.5	9.2	3.4	138
$RuCl_2[P(py)_3]_2$	52.0	3.6	12.5	8.9	11.9	51.3	3.4	12.0	8.8	10.1	258 (decomp.)
$RhCl[P(py)_3]_2$	52.8	3.6	13.5	7.6	5.3	53.8	3.6	12.6	9.3	5.3	*ca.* 200
$RhCl(CO)[P(py)_3]_2$	53.9	3.5	11.7	8.5	4.8	53.7	3.4	12.1	8.9	5.1	185—200 (decomp.)
$RhH(CO)(PPh_3)[P(py)_3]_2$	62.8	4.4	8.9	11.4		63.6	4.3	9.1	10.1		145
$RhCl(cod)[P(py)_3]$	53.9	4.6	7.3	5.1	6.7	54.0	4.7	8.2	6.1	7.0	156
$[Rh(cod)\{P(py)_3\}][PF_6]$	49.8	3.9	9.1	10.4		51.5	4.1	9.5	10.5		110
$RhH(CO)[PPh_2(py)]_3$	67.3	4.6	3.2	9.6		67.8	4.7	4.6	10.1		150

cod = cyclo-octa-1,5-diene.

at –100 °C (4 h). A solution of PCl_3 (2.3 ml, 27 mmol) in diethyl ether (50 ml) was added dropwise during 1 h at −90 °C and the solution stirred at −90 °C (2 h) before warming slowly to room temperature. The tan-coloured mixture was extracted with H_2SO_4 (100 ml, 2M) and the extract made alkaline with saturated NaOH solution. The solid product was collected, washed with H_2O (100 ml) and petroleum (4 × 10 ml), and recrystallised twice from acetone-petroleum (1 : 1); yield 4.30 g, *ca.* 60%. The phosphine was stored under nitrogen since it is readily oxidised to $OP(py)_3$ ($\nu_{max.}$ at 1 212 and 553 cm^{-1}). It is soluble in acetone but insoluble in petroleum.

The use of triphenyl phosphite in place of PCl_3 gave only 25% yields and the use of tetrahydrofuran instead of Et_2O gave only very low yields. The use of a 2 : 1 mol ratio of n-butyl-lithium to 2-bromopyridine gave only a 20% yield of $P(py)_3$.

(2) *Chlorohydridotris[tris(2-pyridyl)phosphine]ruthenium*(II).—$RuHCl(PPh_3)_3$ (0.3 g, 0.325 mmol) and $P(py)_3$ (0.52 g, 1.95 mmol) in benzene (10 ml) were stirred for 2 h at room temperature. The yellow precipitate was collected, washed with benzene (10 ml) and petroleum (10 ml), and dried *in vacuo*; yield 0.18 g, 60%; $\nu_{max.}$ at 3 035s, 1 984s, 1 570vs, 1 555s (sh), 1 282m, 1 275m, 1 230m, 1 150m, 1 081m, 1 045m, 986s, 770vs, 760vs, 740vs, 710m, 696s, 687s, 618w, 545s, 518vs, 508vs, 494s, 460m, 436m, 422m, 410m, 390m, 312w, and 286 w; δ_H 6.7—8.7 [br, 36 H, $P(py)_3$]; 7.27 (s, 6 H, C_6H_6); −7.2 ddd (1 H, Ru-*H*, $^2J_{P-H}$ 126, 29, and 23 Hz); $^{31}P\{^1H\}$ 74.7 (dd, J_{P-P} 13.0 and 36.4 Hz); 14.8 (dd, J_{P-P} 23.4 and 13.0 Hz); and −11.7 (m).

(3) *Dichlorobis[tris(2-pyridyl)phosphine]ruthenium*(II).—As above but using $RuCl_2(PPh_3)_3$ (0.18 g, 0.19 mmol) and $P(py)_3$ (0.3 g, 1.13 mmol); yield 65%; benzene of solvation is lost *in vacuo* (10 h); $\nu_{max.}$ at 3 017m, 1 571s, 1 282w (sh), 1 276w, 1 150w, 1 125w, 1 083w, 1 045w, 1 016w, 978s, 765s, 743s, 618w, 545s, 525vs, 515vs (sh), 500s, 445w, 295vw, and 275vw; n.m.r., δ_H 6.5—8.8 [br, $P(py)_3$]; $^{31}P\{^1H\}$, −0.3, multiplet of at least 12 lines.

(4) *Chlorobis[tris(2-pyridyl)phosphine]rhodium*(I).— (*a*) $[Rh(C_8H_{12})Cl]_2$ (0.2 g, 0.28 mmol) and $P(py)_3$ (0.44 g, 1.67 mmol) were stirred in benzene (5 ml) for 10 h at ambient temperature. The orange precipitate was collected, washed with benzene (10 ml) and petroleum (10 ml), and dried *in vacuo*, yield 0.13 g, 70%; $\nu_{max.}$ at 3 030s, 1 578s, 1 560s (sh), 1 280s, 1 152s, 1 128w, 1 092s, 1 045m, 987s, 768s, 740s, 725m, 558vs, 530vs, 512vs, 475m, 438m, 418m, 332w, and 291m.

(*b*) As above, using $RhCl(PPh_3)_3$ (0.2 g) and $P(py)_3$ (0.6 g); yield *ca.* 95%.

(5) *Carbonylchlorobis[tris(2-pyridyl)phosphine]rhodium*(I).—As above using $RhCl(CO)(PPh_3)_2$ (0.2 g, 0.29 mmol) and $P(py)_3$ (0.31 g, 1.17 mmol); yield 72%; $\nu_{max.}$ at 3 040m, 1970vs (br), 1 570s, 1 560s, 1 420vs, 1 280m, 1 235m, 1 152m, 1 120w, 1 087m, 1 045m, 988s, 765vs, 747vs, 736s, 715w, 700w, 622w, 578s, 542m, 538vs, 528vs, 516vs, 505vs, 497s, 450m, 425m, 398m, and 307m.

(6) *Carbonylhydridotriphenylphosphinebis[tris(2-pyridyl)-phosphine]rhodium*(I).—$RhH(CO)(PPh_3)_3$ (0.7 g, 0.76 mmol) and $P(py)_3$ (0.6 g, 2.3 mmol) were stirred in a mixture of benzene (20 ml) and petroleum (20 ml) at ambient temperature (2 h). The yellow precipitate was collected, washed with toluene (10 ml) and petroleum (10 ml), and dried *in vacuo*; yield 0.68 g, 97%; $\nu_{max.}$ at 3 028s, 2 015s, 1 948s (br), 1 572vs, 1 560s, 1 419vs, 1 308w, 1 280m (br), 1 231m, 1 183w, 1 153m, 1 128w, 1 085m, 1 048m, 1 028w, 988s, 880w, 785m, 755m, 745vs, 723m, 699vs, 685m, 620m, 541m, 515vs (br), 463w, and 420m; δ_H 6.8—8.0 (br, 39 H); −9.8q (1 H, J_{P-H} 9.5 Hz).

(7) *Chloro(cyclo-octa-1,5-diene)[tris(2-pyridyl)phosphine]-rhodium*(I).—$[Rh(C_8H_{12})Cl]_2$ (0.19 g, 0.38 mmol) and $P(py)_3$ (0.2 g, 0.76 mmol) were stirred in benzene (5 ml) for 1 h. The initial yellow solution deposited a yellow solid which was collected, washed with benzene (5 cm^3) and petroleum (5 ml), and then dried *in vacuo*; yield 0.15 g, 75%; $\nu_{max.}$ at 3 080w, 3 045w, 1 578w, 1 565m, 1 325m, 1 280s, 1 235w, 1 220w, 1 160m, 1 122m, 1 080w, 1 017w, 980m, 955m, 887w, 865m, 812w, 780s, 768s, 748m, 720m, 708m, 675w, 532s, 503s, 485w, 450w, 415w, and 340w.

(8) *(Cyclo-octa-1,5-diene)bis[tris(2-pyridyl)phosphine]-rhodium*(I) *Hexafluorophosphate*.—$[Rh(C_8H_{12})Cl]_2$ (0.14 g, 0.28 mmol) and $AgPF_6$ (0.14 g, 0.56 mmol) were stirred in ethanol (15 ml) for 15 min. The orange solution was filtered through Celite to remove AgCl, $P(py)_3$ (0.3 g, 1.13 mmol) was added, and the solution stirred (0.5 g). The solid which precipitated was collected, washed with Et_2O (10 ml), and dried *in vacuo*; yield 0.17 g, 68%; $\nu_{max.}$ at 1 585vw, 1 570vs, 1 557s (sh), 1 419vs, 1 330w, 1 281s, 1 154s, 986s, 896w, 873m, 845vs, 780w, 760s, 755m, 742m, 723w, 550vs, 512vs, 505s (sh), 495m, 485m, 443w, and 418m.

(9) *Carbonyltris(diphenyl-2-pyridylphosphine)hydrido-rhodium*(I).—$RhH(CO)(PPh_3)_3$ (0.2 g, 0.22 mmol) and $PPh_2(py)$ (0.34 g, 1.3 mmol) were stirred in tetrahydrofuran (5 ml) for 0.5 h at ambient temperature. Petroleum (20 ml) was added and the yellow precipitate collected, washed with petroleum (10 ml), and dried *in vacuo*; yield *ca.* 90%; $\nu_{max.}$ at 3 040w, 2 006vs, 1 925s, 1 576vs, 1 305w, 1 274w, 1 178m, 1 080m, 1 025m, 998m, 984m, 750s, 690vs, 619m, 530m, 505vs, 498vs, 416m, and 410m.

The interaction of $Rh(acac)(CO)_2$ (acac = acetylacetonate) with an excess of $P(py)_3$ in benzene at 60 °C under a slow stream of H_2 gave a red-brown powder. Spectroscopic data suggest that it is $Rh(acac)(CO)[P(py)_3]$ but analytical data, although close to calculated values, are not accurately reproducible.

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