Rhodium complexes of the water-soluble phosphine Ph2PCH2CH2NMe3+. Their complexes with hydride, olefin, and carbon monoxide ligands. Their use as olefin hydrogenation and hydroformylation catalysts in aqueous solution and in aqueous/organic solvent two-phase systems, and adsorbed on a cation-exchange resin

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It is interesting to compare and contrast our attempts to synthesize compounds of the type $M(CO)_5[PPh_2AlR_2]$ with a study in which compounds of the type $M(CO)_5[PPh_2B(NR_2)_2]$ were reported.[37] The boron–phosphorus compounds were obtained by the reaction of $M(CO)_5PPh_2^-$ and $B(NR_2)_2Br$ in THF and the ligand displacement reactions of $M(CO)_5L$ (L = CO, THF, CH_3CN) by $B(NR_2)_2PR_2$. The analogous reactions to produce the aluminum compounds have yielded compounds in which the Al–P bond is cleaved and the Al and P atoms are bound to first-row elements instead. The only successful route to compounds of the type $M(CO)_5[PPh_2AlR_2]$ has involved displacement of the relatively unreactive ligand NMe_3 of $Cr(CO)_5NMe_3$ by $(Me_3SiCH_2)_2AlPPh_2$.

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Registry No. $Cr(CO)_5PPh_2K\cdot2$(dioxane), 85883-53-0; $Mo(CO)_5PPh_2K\cdot$dioxane, 85883-56-3; $W(CO)_5PPh_2K\cdot2$(dioxane), 85883-58-5; $Cr(CO)_5PPh_2H$, 18399-60-5; $W(CO)_5PPh_2H$, 18399-62-7; $Mo(CO)_5PPh_2H$, 18399-61-6; KH, 7693-26-7; NaH, 7646-69-7; $Cr(CO)_5PPh_2Li$, 85883-59-6; $KPPh_2$, 15475-27-1; THF, 109-99-9; $Cr(CO)_5[PPh_2(CH_2)_4OAlBr_2]$, 85883-60-9; $AlBr_3$, 7727-15-3; $Cr(CO)_5[PPh_2(CH_2)_4OAlMe_2]$, 85883-61-0; $Cr(CO)_5[PPh_2(CH_2)_4OAlEt_2]$, 85883-62-1; $[Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]]_2$, 85883-63-2; $BrAlMe_2$, 3017-85-4; $BrAlEt_2$, 760-19-0; $BrAl(CH_2SiMe_3)_2$, 85004-93-9; $Mo(CO)_5[PPh_2(CH_2)_4OAlBr_2]$, 85883-64-3; $Mo(CO)_5[PPh_2(CH_2)_4OAlEt_2]$, 85883-65-4; $W(CO)_5[PPh_2(CH_2)_4OAlBr_2]$, 85883-66-5; $W(CO)_5[PPh_2(CH_2)_4OAlEt_2]$, 85883-67-6; $Cr(CO)_5[PPh_2AlEt_2\cdot OEt_2]$, 85883-68-7; $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2\cdot OEt_2]$, 85883-69-8; $AlMe_3$, 75-24-1; $AlMe_2H$, 865-37-2; dimethoxyethane, 110-71-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, calculated hydrogen atom parameters (Table I-S), and anisotropic thermal parameters (Table II-S) (15 pages). Ordering information is given on any current masthead page.

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Rhodium Complexes of the Water-Soluble Phosphine $Ph_2PCH_2CH_2NMe_3^+$. Their Complexes with Hydride, Olefin, and Carbon Monoxide Ligands. Their Use as Olefin Hydrogenation and Hydroformylation Catalysts in Aqueous Solution and in Aqueous/Organic Solvent Two-Phase Systems and Adsorbed on a Cation-Exchange Resin

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Treatment of $[(\text{norbornadiene})RhCl]_2$ with $Ph_2PCH_2CH_2NMe_3^+NO_3^-$ (amphos nitrate) results in chloride bridge splitting to give $[NBDRhCl(\text{amphos})]^+NO_3^-$ (I). I reacts further with amphos to give $[NBDRh(\text{amphos})_2]^{3+}$ (II), which in turn reacts with hydrogen in methanol or water to give $[RhH_2(\text{amphos})_2(\text{solvent})_2]^{3+}$ or, if excess amphos is available, $[RhH_2(\text{amphos})_3(\text{solvent})]^{4+}$. While the latter complex is stable with respect to reductive elimination of hydrogen, the former readily loses hydrogen to give $[Rh(\text{amphos})_2(\text{solvent})_2]^{3+}$. Carbonylation of I and II appears to give $[cis\text{-}RhCl(CO)_2(\text{amphos})]^+$ and $[cis\text{-}Rh(CO)_2(\text{amphos})_2]^{3+}$, respectively. Aqueous solutions of II catalyze the hydrogenation of water-soluble olefins in single-phase systems, and the hydrogenation and hydroformylation of water-immiscible olefins dissolved in *n*-pentane, methylene chloride, and ethyl ether. Adsorption of II onto the sodium form of a strong acid, ion-exchange resin results in a novel supported catalyst system for the hydrogenation and hydroformylation of olefins in acetone solution. Virtually no leaching of rhodium into the olefin-containing phases occurs in the two-phase systems, although the rhodium can be readily recovered from the resin by elution with acid.

Introduction

The potential advantages of homogeneous over heterogeneous catalysis (relatively high selectivity, activity) are well recognized, but a major impediment to more general utilization of homogeneous systems revolves around the problem of separation of products from catalysts.[1] A common solution to this problem involves the attachment of a normally soluble catalyst to an insoluble support, in an attempt to combine the virtues of both homogeneous and heterogeneous catalysts.[2-4] Unfortunately, the anchoring of soluble metal catalyst precursors to, for instance, a variety of tertiary phosphine-functionalized supports has not in general led to useful catalysts; problems encountered

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include leaching of metal into the solvent, lowered activity or selectivity relative to purely homogeneous analogues, and supervenient oxidation of the phosphorus atoms.[4-9]

A quite different approach to the problem of separation of catalyst and product has involved the use of metal complexes of polar, water-soluble ligands such as sulfonated triarylphosphines.[10] While aqueous solutions of such complexes do catalyze reactions of water-immiscible substrates, possibly via a phase-transfer process, little has actually been done in this area.

We have earlier[11] reported the synthesis of the cationic, water-soluble phosphine (2-(diphenylphosphino)ethyl)trimethylammonium iodide ($Ph_2PCH_2CH_2NMe_3^+I^-$ = amphos iodide) and its metal carbonyl complexes [Fe(CO)$_4$amphos]I and [M(CO)$_5$amphos]I (M = Mo, W). As the carbonyl stretching frequencies of these compounds were found to be very similar to those of analogous complexes of neutral tertiary phosphines, it is clear that the effects of the positive charge are almost completely attenuated along the aliphatic chain of the ligand. However, the compounds did exhibit unusually high solubilities in polar solvents (water, methanol, acetonitrile), and it was anticipated that the coordination chemistry of amphos complexes of the platinum metals might prove interesting in such media. We now report details of the (amphos)rhodium(I) system, including some catalytic properties; a preliminary communication of this work has appeared.[12]

Experimental Section

Operations were normally carried out under nitrogen unless otherwise described. Solvents were distilled from appropriate drying agents and stored over molecular sieves until used. The 60-MHz ^{1}H NMR spectra were run on a Bruker HX-60 spectrometer and the ^{31}P spectra (all ^{1}H decoupled) and 200-MHz ^{1}H spectra on a Bruker CXP 200 spectrometer. IR spectra were run on a Beckman IR 4240 spectrophotometer and gas–liquid chromatography on a Hewlett Packard 5880A gas chromatograph with a flame ionization detector. Chemical analyses (except Rh) were carried out by Canadian Microanalytical Services Ltd.

Preparation of (2-(Diphenylphosphino)ethyl)trimethylammonium Nitrate (Amphos Nitrate). A column of anion-exchange resin (Biorad AG1-X8 or AG2-X8) was converted from the chloride to the nitrate form by elution with aqueous solutions of sodium or ammonium nitrate. The resin was then washed well with water (100 mL) and methanol (100 mL). Amphos iodide was converted to amphos nitrate by passing a deaerated methanol solution of the former through the column; the amount of resin was chosen so as to ensure that the capacity of the column exceeded the amount of iodide to be exchanged by a factor of 10. The resulting methanol solution of halide-free amphos nitrate could be reacted as such, or the solvent could be removed to give the compound as a gummy solid, shown to be pure by its ^{1}H and ^{31}P NMR spectra.[11]

Preparation of Chloro(norbornadiene)rhodium(I)–(2-(Diphenylphosphino)ethyltrimethylammonium Nitrate ([NBDRhCl(amphos)]NO$_3$ (I)). Amphos iodide (1.7 g, 4.4 mmol) was converted to the nitrate salt (see above). To this in 75 mL of methanol was added [NBDRhCl]$_2$[13] (NBD = norbornadiene) (1.0 g, 2.2 mmol), and the mixture was stirred until all of the rhodium compound had gone into solution. On concentration of the solution to about 20 mL (water aspirator), I began to precipitate; addition of 25 mL of ethyl completed the precipitation of yellow crystals, which were recrystallized from acetonitrile–ethyl ether: mp 175–177 °C; yield 90%. Anal. Calcd for $C_{24}H_{31}ClN_2O_3PRh$: C, 51.03; H, 5.53; N, 4.96; Cl, 6.28; P, 5.48. Found: C, 50.93; H, 5.73; N, 4.99; Cl, 6.55; P, 4.92. Conductivity measurements in acetonitrile showed that I is a 1:1 electrolyte (Λ_0 = 136 Ω^{-1} L$^{1/2}$, B = 650 Ω^{-1} L$^{1/2}$ equiv$^{-1/2}$).[14]

Table I. ^{31}P NMR Data

compd	δ_P^{a} (J(Rh–P))	Δ
amphos nitrate	−21.3	
[NBDRhCl(amphos)]$^+$ (I)	25.3 (176)	46.6
NBDRhCl(PPh$_3$)	31.6 (171)	37.0
[NBDRh(amphos)$_2$]$^{3+}$ (II)	15.7 (152)	36.7
[NBDRh(PPh$_3$)$_2$]$^+$	29.8 (157)	35.2
[NBDRh(PMePh$_2$)$_2$]$^+$	3.5 (140)	31.3
[RhH$_2$(amphos)$_2$(MeOH)$_2$]$^{3+}$ (III)	31.5 (122)	52.8
[RhH$_2$(PPh$_3$)$_2$(MeOH)$_2$]$^+$	41.8 (121)	47.2
[RhH$_2$(PMePh$_2$)$_2$(MeOH)$_2$]$^+$	23.8 (118)	51.6
[Rh(amphos)$_2$(MeOH)$_2$]$^{3+}$ (IV)	46.4 (205)	67.7
[Rh(PPh$_3$)$_2$(MeOH)$_2$]$^+$	57.2 (207)	62.6
[RhH$_2$(amphos)$_3$X]$^{3+\text{ or }4+}$ (V)	11.9 (95), 31.2 (117)	33.2, 52.5
RhH$_2$Cl(PPh$_3$)$_3$	20.7 (90), 40.3 (114)	26.1, 45.7

[a] In ppm relative to external H$_3$PO$_4$; downfield shifts positive. Coupling constants in hertz.

Reactions of I. A variety of reactions of I with excess amphos nitrate, hydrogen, and carbon monoxide in water, methanol, and acetonitrile were carried out and will be described below. Attempts to isolate pure samples of the cationic products by the addition of sodium tetrafluoroborate, tetraphenylborate, and hexafluorophosphate, however, were invariably unsuccessful. Only amphos salts or rhodium-containing gummy materials could ever be obtained on cooling and/or concentration of reaction solutions.

All compounds were therefore identified by comparisons of their IR, their ^{1}H NMR, and, more particularly, their ^{31}P NMR spectral parameters with data for known compounds of other phosphines. As has been shown previously,[15] the coordination shift, Δ,[16] and ^1J(Rh–P) are generally very reliable criteria for the identification of solution species, being especially sensitive to the nature of the ligand trans to the phosphine. We therefore present all relevant ^{31}P NMR data for the complexes formed in solution in Table I, where they are compared with the corresponding data for the analogous, well-characterized triphenylphosphine and methyldiphenylphosphine systems.

Catalysis Studies. In general, solutions of amphos nitrate were generated in methanol as described above, and an appropriate weight of [NBDRhCl]$_2$ (about 0.05 mmol) was added to make solutions of the desired phosphine:rhodium ratio. (Henceforth the compositions of mixtures will often be denoted by this ratio, i.e., 1:1, 2:1, etc.) The methanol solution could then be used, or the methanol could be removed at reduced pressure to give a residue which could then be redissolved in some other solvent.

(a) Homogeneous hydrogenations of the water-soluble olefins, crotonic and maleic acids, were carried out in D$_2$O. Thus mixtures of a 2:1 or 3:1 catalyst (0.05 mmol, 10^{-2} M) were treated with maleic acid (0.4 g, 3.5 mmol) or crotonic acid (0.4 g, 4.6 mmol) in 5 mL of D$_2$O. The solutions were stirred under 1 atm of hydrogen at room temperature, samples being withdrawn periodically so that their ^{1}H NMR spectra could be recorded. The extent of hydrogenation could readily be obtained by integration of the spectra. The same olefins were also hydrogenated in methanol, aliquots being analyzed in the same way after removal of the methanol at reduced pressure. For comparison purposes, similar experi-

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(16) The difference in ^{31}P chemical shifts between free and coordinated ligands.

ments were conducted by using $[NBDRh(PPh_3)_2]PF_6$[17] as catalyst (0.05 mmol, 10^{-2} M).

Styrene (2 mL, 17 mmol) was hydrogenated in 20 mL of 1:1 ethanol–benzene by 2:1 and 3:1 catalysts (0.05 mmol, 2.5×10^{-3} M) and by $RhCl(PPh_3)_3$[18] (0.05 mmol, 2.5×10^{-3} M). The reactions were monitored by gas chromatography using a Carbowax on Chromosorb W column.

(b) Two-phase hydrogenations were performed typically by mixing a solution of a 2:1 or 3:1 catalyst (0.05 mmol, 2.5×10^{-3} M) in 20 mL doubly distilled, deaerated water with the water-immiscible olefins styrene (6 mL, 52 mmol) and 1-hexene (6 mL, 48 mmol). The olefins were either added neat or dissolved in 20 mL of an organic solvent (ethyl ether, methylene chloride, or *n*-pentane). The two-phase liquid mixtures were transferred by syringe to a nitrogen-filled pressure bottle of a Parr Hydrogenation Apparatus, the bottle was flushed several times with hydrogen, brought to 3 atm of hydrogen, and shaken for 6 h.

The organic phases were separated, and the reaction products were analyzed by gas chromatography; the styrene system was analyzed as described above, and the 1-hexene system was analyzed by using an *n*-octane on Poracil C column. The organic phases were also analyzed by rhodium by using a Perkin-Elmer 603 atomic absorption spectrophotometer. A typical procedure[19] involved evaporating a sample to near dryness, treating it with 10 mL of 12 M hydrochloric acid and 5 mL of 15 M nitric acid, and heating the mixture for several hours. The acid treatment was then repeated once, 1 mL of 18 M sulfuric acid was added, and the sample was heated until SO_3 fumes were clearly evident. The sample was cooled and brought to a known volume with distilled water. The sample and standards were run at 343.5 nm (3-mm slit width) by using a lean blue/air acetylene flame. Calibration curves showed that the detection limit was approximately 0.1 ppm or 1 μg for a 10-mL sample. Since most catalytic runs contained about 10 mg of rhodium, leaching of amounts as low as 0.01% of the total was detectable.

(c) Supported olefin hydrogenation catalysts were prepared by mixing a 2:1 or 3:1 catalyst (0.05 mmol, 10^{-3} M) in 50 mL of distilled water with 10 g of a macroreticular cation resin, Rexyn 101, the sodium form of a 200–400 mesh sulfonated polystyrene copolymer (Fisher Scientific). The resin had previously been pumped on at 0.1 mm for about 1 h. Adsorption of the catalyst onto the resin was generally complete within 1 h or less, as judged by the disappearance of the yellow color. The water was then filtered off under nitrogen, and the resin was washed successively with 50-mL portions of distilled water, methanol, and either acetone or ethyl ether. The resin was transferred immediately to a 300-mL Parr Mini Reactor, 2 mL of either 1-hexene or cyclohexene in 20 mL of either ethyl ether or acetone was added, and the reactor was sealed, flushed with hydrogen, and pressured to 5–12 atm with hydrogen. The reaction mixture was normally stirred 17 h, when the reactor was opened and the liquid layer was analyzed as above for organic products and rhodium.

(d) Two-phase hydroformylation reactions were carried out by using aqueous solutions of 2:1 and 3:1 catalysts (0.1 mmol, 5×10^{-3} M), buffered to pH 5–7 using NaH_2PO_4/Na_2HPO_4 mixtures, and 1-hexene (3 mL, 24 mmol), either neat or dissolved in a water-immiscible solvent (methylene chloride, ethyl ether, or *n*-pentane). The reactions were carried out in a Parr Mini Reactor at 90 °C and a pressure of 40 atm (H_2:CO = 1). After the mixture was stirred 24 h, the reactor was cooled to −78 °C and opened. The organic phases were then separated and analyzed as above.

An attempt was also made to hydroformylate neat 1-hexene by using a 3:1 catalyst (0.1 mmol, 5×10^{-3} M, pH 5.8) in an absence of added hydrogen (P_{CO} = 40 atm), hoping to utilize the water gas shift reaction, i.e.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (1)$$

The extent of (1) in the absence of olefin was determined by measuring carbon monoxide, hydrogen, and carbon dioxide by gas chromatography (TC detector, Poropak N column).

Hydroformylation of ethyl ether solutions of 1-hexene (3 mL) using the types of 2:1 and 3:1 supported catalysts described in (c) above were attempted. The reactions were generally stirred for 24 h in a Parr Mini reactor under 40 atm of 1:1 hydrogen–carbon monoxide.

Results and Discussion

The potential of iodide ion to act as a ligand to rhodium necessitated the conversion of the previously reported amphos iodide[11] to the nitrate salt. This was easily effected by using an anion-exchange column. Attempts to prepare amphos complexes of rhodium by reacting amphos nitrate with $RhCl_3 \cdot 3H_2O$ and $[(C_2H_4)_2RhCl]_2$ gave solutions containing, as judged by their ^{31}P NMR spectra, mixtures of products. Reaction with $[NBDRhCl]_2$ in methanol in the appropriate ratio, however, proceeded smoothly at room temperature to give within 15 min a near quantitative yield of $[NBDRhCl(amphos)]NO_3$ (I). This compound, a 1:1 electrolyte in acetonitrile, has been characterized by elemental analyses and is the product expected from chloride bridge splitting, i.e.

$$[NBDRhCl]_2 + 2\,amphos^+NO_3^- \rightarrow \underset{I}{2[NBDRhCl(amphos)]NO_3} \qquad (2)$$

The reaction also occurs in water, although more slowly because of the insolubility of the norbornadiene complex. A variety of other tertiary phosphines is known to react similarly,[20] and the ^{31}P NMR spectral parameters (Δ, J(Rh–P)) compare well with those of $NBDRhClPPh_3$ (Table I). As well, the Rh–Cl stretching frequency of I (283 cm^{-1}) matches that of the triphenylphosphine analogue (286 cm^{-1}).[21] In contrast, however, to $NBDRhClPPh_3$, which is inert to hydrogen,[22] I decomposes rapidly in the presence of hydrogen in methanol or water to give rhodium metal and norbornane, i.e.

$$I + H_2 \rightarrow Rh\ metal + norbornane \qquad (3)$$

Reaction of I in water or methanol with another equivalent of amphos nitrate gave a new species which exhibited a single resonance in its ^{31}P NMR spectrum at room temperature, broadened because of rapid phosphine exchange. Cooling a methanol solution containing a slight excess of amphos nitrate to −70 °C gave two ^{31}P resonances, a singlet at δ −21.3 for free amphos and a doublet at δ 15.7 (J(Rh–P) = 152 Hz). The new species appears to be a bis(amphos) complex, II, i.e.

$$I + amphos \rightarrow \underset{II}{[NBDRh(amphos)_2]^{3+}} \qquad (4)$$

While there are precedents for five-coordination in such cases,[23] II was shown not to contain coordinated chloride ion by carrying out its formation in the absence of halide. Thus treatment of $[NBDRhCl]_2$ with 2 equiv of silver nitrate in ethanol gave insoluble silver chloride and, presumably, $[NBDRh(EtOH)_2]^+$. Addition to the solution of 2 equiv of amphos nitrate gave rise to a species with a ^{31}P NMR spectrum identical with that of II. Further addition of 10 equiv of tetraethylammonium chloride did not change the spectrum, nor did the addition of excess amphos nitrate, as mentioned above. Thus the tris(amphos) species $[NBDRh(amphos)_3]^{4+}$ also does not form, in contrast to the behavior of other phosphines.[17a,20]

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Although, as mentioned in the Experimental Section, II could not be obtained sufficiently pure for elemental analyses, the ^{31}P NMR spectral parameters compare well with those of the well-known triphenylphosphine and methyldiphenylphosphine[24] analogues (Table I). Thus there can be little doubt but that the structure of II is as formulated.

Bubbling hydrogen through a chloride-free, methanol solution of II for 5 min gave a pale yellow solution with quantitative formation of norbornane. The ^{31}P NMR spectrum at −70 °C showed a doublet at δ 31.5, with coordination shift and J(Rh–P) very similar to those of $[RhH_2(PR_3)_2(MeOH)_2]^+$ ($PR_3 = PPh_3$, $PMePh_2$[24]) (Table I), which are prepared similarly via the hydrogenation of $[NBDRh(PR_3)_2]^+$.[24] The ^1H NMR spectrum of a CD_3OD solution at −70 °C exhibited a broad resonance with some fine structure at δ −20.11, similar to that of $[RhH_2(PPh_3)_2(EtOH)_2]^+$ in methylene chloride (δ −22.31),[17b] and thus the hydrogenation reaction is as

$$\underset{\mathrm{II}}{[\mathrm{NBDRh(amphos)_2}]^{3+}} + 3\mathrm{H_2} \xrightarrow{\mathrm{MeOH}} \underset{\mathrm{III}}{[\mathrm{RhH_2(amphos)_2(MeOH)_2}]^{3+}} + \text{norbornane} \quad (5)$$

Interestingly, when the reaction was done in the presence of 1 equiv of chloride per rhodium, a species in addition to III was formed. Although the room-temperature ^{31}P NMR spectrum of the reaction mixture exhibited only a single broad doublet, the low-temperature (−70 °C) spectrum exhibited two doublet resonances, that attributed to III, and another to slightly lower field (δ 35.0) but with the same coupling constant. Since III and the new species are clearly exchanging at room temperature, it is concluded that the latter is $[RhH_2(amphos)_2Cl(MeOH)]^{2+}$, with a coordinated chloride. The solvent molecules in complexes similar to III are known to be very substitution labile.[25]

Even under 1 atm of hydrogen, III and its chloro derivative both lose hydrogen over a period of 1 h to give a new species, IV. The ^1H NMR spectrum of a reaction mixture clearly demonstrated this conversion, as the hydride resonance gradually disappeared. As well, in the ^{31}P NMR spectrum, the resonances of the hydrides were replaced by a new doublet at much lower field, δ 46.4. The coordination shift and J(Rh–P) are very similar to those[24] of $[Rh(PPh_3)_2(MeOH)_2]^+$ and $[Rh(PMePh_2)_2(MeOH)_2]^+$ (Table I), and the observed reaction clearly involves reductive elimination of hydrogen, i.e.

$$\underset{\mathrm{III}}{[\mathrm{RhH_2(amphos)_2(MeOH)_2}]^{3+}} \rightarrow \underset{\mathrm{IV}}{[\mathrm{Rh(amphos)_2(MeOH)_2}]^{3+}} + \mathrm{H_2} \quad (6)$$

Solvent effects are very important in this reaction, as hydrogenation of II in water yields the aqua analogue of IV quantitatively within 2 min, no dihydride being detected. The amphos system is thus strikingly different from the methyldiphenylphosphine system, in which the reductive elimination step does not occur.[24] The solvent effect observed here also appears to be unprecedented.

While II does not react further with amphos, hydrogenation of either a mixture of $[NBDRhCl]_2$ and 6 equiv of amphos or of a solution of II plus 1 equiv of amphos in methanol gave a new species, V, formulated as $[RhH_2(amphos)_3Cl]^{3+}$ or $[RhH_2(amphos)_3(MeOH)]^{4+}$.

$$[\mathrm{NBDRhCl}]_2 + 6\,\mathrm{amphos} \rightarrow \underset{\mathrm{V}}{[\mathrm{RhH_2(amphos)_3X}]^{3+\ \text{or}\ 4+}} \quad (7)$$

$$X = Cl^-, \mathrm{MeOH}$$

The ^1H NMR spectrum of V at −70 °C (CD_3OD) exhibited a doublet at δ −10.4 (J(P–H) = 168 Hz) and a singlet at δ −17.8 (relative intensities 1:1), while the ^{31}P NMR spectrum at −70 °C consisted of a doublet of doublets centered at δ 31.2 and a broad doublet at δ 11.9 (relative intensities 2:1) (Table I). These spectral parameters compare very well with those of $RhH_2Cl(PPh_3)_3$,[26] strengthening the formulation of V (the data do not suggest a possible distinction between chloride and methanol as the sixth ligand).

In the analogous complexes of triphenyl- and tri-*p*-tolylphosphines, the phosphines trans to hydrogen are known to be labile and to exchange rapidly on the NMR time scale at room temperature.[26] The NMR spectrum of V showed a similar exchange phenomenon at room temperature, even the hydride resonances becoming exceedingly broadened. However, there was no exchange evident between free amphos and V at −70 °C, and V is much more stable with respect to loss of hydrogen at room temperature than is III. No changes in the ^{31}P spectrum were observed after several hours under an atmosphere of hydrogen.

Reactions of I and II with carbon monoxide were examined briefly, although literature precedents were not as useful in determining structures of products in these cases. Treatment of a yellow solution of I in acetonitrile with CO gave a colourless solution within seconds. Analysis of the solution showed that norbornadiene had been released quantitatively, while the IR spectrum of the solution exhibited two bands of equal intensity at 2070 and 1995 cm^{-1}, indicating a cis-dicarbonyl arrangement. The well-characterized compounds *cis*-$RhCl(CO)_2$(amine) (amine = pyridine, *p*-toluidine, hexylamine, allylamine)[27] exhibit ν(CO) at ~2090 and ~2020 cm^{-1}, and the somewhat less well-characterized triphenylphosphine analogue[28] exhibits ν(CO) at 2088 and 2002 cm^{-1}. The ^{31}P NMR spectrum indicated the presence of a single species (δ 24.6 (J(Rh–P) = 127 Hz)), and thus the carbonylation reaction probably proceeds as

$$\underset{\mathrm{I}}{[\mathrm{NBDRhCl(amphos)}]^+} + 2\mathrm{CO} \rightarrow \underset{\mathrm{VI}}{[cis\text{-}\mathrm{RhCl(CO)_2(amphos)}]^+} + \mathrm{NBD} \quad (8)$$

Similar chemistry occurred in water and methanol, as judged by ^{31}P NMR spectroscopy. Reaction of II with CO in acetonitrile also resulted in displacement of the norbornadiene, forming a single product (VII) with ν(CO) at 2068 and 1991 cm^{-1} and a ^{31}P resonance at δ 23.5 (J(Rh–P = 124 Hz). Although $[NBDRh(PPh_3)_2]^+$ is reported to be inert to CO,[17a] $[(1,5\text{-cyclooctadiene})Rh(PPh_3)_2]^+$ reacts with CO with displacement of the diene to yield the tricarbonyl complex $[Rh(CO)_3(PPh_3)_2]^+$, with ν(CO) at 2037 and 2023 cm^{-1}. These frequencies are sufficiently different from those observed in the amphos system that it seems likely that the carbonylation of II proceeds as

The similarities in chemical shift and J(Rh–P) between VI and VII are consistent with the amphos being trans to

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$$\underset{\text{II}}{[\text{NBDRh(amphos)}_2]^{3+}} + 2\text{CO} \rightarrow \underset{\text{VII}}{[\text{Rh(CO)}_2(\text{amphos})_2]^{3+}} + \text{NBD} \quad (9)$$

the same ligand in both cases.

Catalyst Studies

As shown above, II is capable of activating hydrogen by oxidative addition to form the compounds III and IV, both of which are of types widely recognized as being key intermediates in many homogeneous, rhodium olefin hydrogenation catalyst systems.[29] We were prompted, therefore, to make an investigation of the catalyst activities of the new compounds.

(a) Olefin Hydrogenations in Single-Phase Systems. Solutions of II in water and methanol were normally generated from the reaction of $[\text{NBDRhCl}]_2$ with 4 equiv of freshly ion-exchanged amphos nitrate. The solutions in water and methanol were found to catalyze the hydrogenation of the water soluble olefins maleic and crotonic acids, and typical experimental results are shown in Figure 1, which also compares favorably the activity of the 2:1 amphos complex with that of the triphenylphosphine complex $[\text{NBDRh(PPh}_3)_2]^+$.[17]

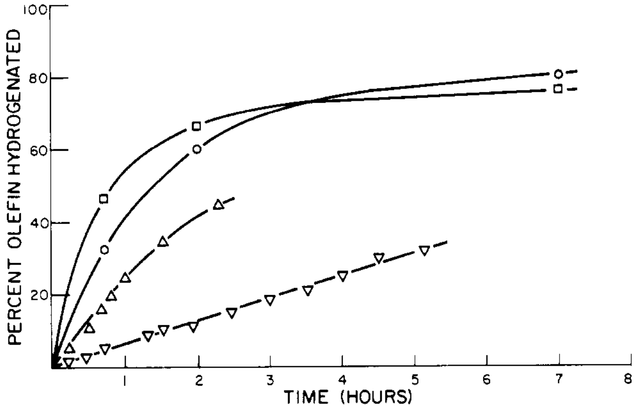

Figure 1. The catalytic hydrogenation of (a) 12.9 mmol of maleic acid in 30 mL of methanol at 1 atm of H_2 by 0.056 mmol of $[\text{NBDRh(amphos)}_2]^{3+}$ (□) or $[\text{NBDRh(PPh}_3)_2]^+$ (○) and (b) 17 mmol of styrene in 20 mL of 1:1 ethanol–benzene at 1 atm of H_2 by 0.05 mmol of $[\text{NBDRh(amphos)}_2]^{3+}$ + amphos (▽) or $\text{RhCl(PPh}_3)_3$ (△).

Rates were significantly higher in methanol than in water, possibly either because of the much higher solubility of hydrogen in the former solvent[30] or because of the relatively low stability of the aquated dihydride $[\text{RhH}_2(\text{amphos})_2(\text{H}_2\text{O})_2]^{3+}$ (see above). Addition of a third equivalent of amophos per rhodium also resulted in a decrease in activity, presumably because of blocking of the site at which the olefin would coordinate.[31] Solutions of a 3:1 catalyst in 1:1 ethanol–benzene were found to exhibit activities about one-fourth that of $\text{RhCl(PPh}_3)_2$[18,29,31] for the hydrogenation of styrene (Figure 1).

To summarize, the amphos–rhodium system provides olefin hydrogenation catalysts which are roughly comparable in activities with the well-known triphenylphosphine system.[29,31] The new catalysts have the advantage of considerable air stability and are much more active in pure water than are the corresponding rhodium catalysts containing sodium (*m*-sulfonylphenyl)diphenylphosphine.[32] However, there is little basis for comparison with work recently published on hydrogenations of water-soluble olefins by rhodium complexes of chelating diphosphines of the types $\text{RN(CH}_2\text{CH}_2\text{PPh}_2)_2$ (R = polar functional groups).[33]

(b) Two-Phase "Homogeneous" Hydrogenations. Of great interest was the discovery that aqueous solutions of II would catalyze the hydrogenations of water-immiscible olefins, either neat or dissolved in a water-immiscible solvent. Rates were inconveniently low under 1 atm of hydrogen in these cases, and the reactions were therefore carried out under 3 atm of hydrogen in a Parr hydrogenation apparatus. Repeated monitoring during the course of the reactions was therefore not facile, and the reactions were routinely run for 6 h after which the solutions were analyzed; results are shown in Table II.

As can be seen, the 2:1 catalysts were again more active than the 3:1 systems, and 1-hexene was hydrogenated faster than styrene, as has been found elsewhere for other rhodium homogeneous catalysts.[31] The 1-hexene reaction was also accompanied by partial (10–20%) isomerization of the olefin to internal olefins, as occurs when $[\text{NBDRh(PPh}_3)_2]^+$ is used as a catalyst precursor.[17b] In the latter case, a monohydride species of the type $\text{RhH(PPh}_3)_2(\text{solvent})_x$ is a key intermediate, but such a species was not identified in the amphos system.

Variation of the organic cosolvent produced some interesting results, the activities for hydrogenation of styrene decreasing in the order ethyl ether ≫ neat olefin > *n*-pentane > methylene chloride. Halogenated solvents are known to inhibit hydrogenation in single-phase homogeneous catalysis,[18,34] and it is possible that two-phase hydrogenations are affected similarly. That *n*-pentane should be a much poorer solvent than ethyl ether is not as easily rationalized, though it may be of consequence that ethyl ether is much more soluble in water than is *n*-pentane.[35] The hydrogenation of 1-hexene followed a similar pattern, with the greatest activity being observed in ethyl ether, the lowest in methylene chloride solution.

It was necessary to ensure that deionized water was used for all experiments as it was found that the distilled water on tap in the laboratory contained low levels of some impurity, possibly chloride ion, which inhibited hydrogenation. In agreement with this hypothesis, added chloride did poison the catalyst. (This was not a problem in the single phase reactions already discussed, as these were carried out in D_2O.)

The utility of the two-phase hydrogenations lies in the great ease of separation of product from catalyst by simple decantation. The colorless organic phases separated easily with little emulsification and were analyzed for rhodium content in order to determine the extent of catalyst leaching from the aqueous phase. In all cases the organic phases contained virtually no rhodium, amounts found being less than 0.25 ppm and corresponding to less than 0.1% of the total catalyst used.

While we have not attempted to ascertain a maximum turnover number in any case, it was found that an aqueous catalyst system could be reused with little or no loss of activity, even after exposure to air. Indeed, hydrogenations could even be run under 4 atm of a 3:1 hydrogen–air

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Table II. Two-Phase "Homogeneous" Hydrogenation Reactions[a]

amphos:Rh	10^3[catalyst], M	olefin	solvent(s)	activity[b]
3	2.5	styrene	H_2O	84
3	3.0	styrene	H_2O/CH_2Cl_2	42
3	3.0	styrene	$H_2O/n\text{-}C_5H_{12}$	48
3	3.0	styrene	H_2O/Et_2O	228
2	3.0	styrene	H_2O/Et_2O	426
2	2.5[c]	styrene	H_2O/Et_2O	90
3	2.5	1-hexene	H_2O	120
3	2.5	1-hexene	H_2O/Et_2O	342
2	3.0	1-hexene	H_2O/Et_2O	504

[a] P_{H_2} = 3 atm, T = 25 °C; 20 mol of H_2O + 20 mL of cosolvent (if any). [b] Turnover number = number of moles of olefin reduced per mole of catalyst in 6 h. [c] $+5.0 \times 10^{-3}$ M $Et_4N^+Cl^-$.

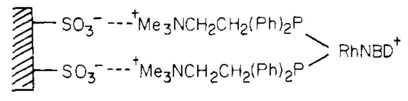
mixture, although activity did eventually decrease because of slow oxidation of amphos to the oxide, as shown by ^{31}P NMR spectroscopy. Aged catalyst systems often exhibited the amphos oxide resonance at δ 35.9.

The only similar two-phase catalytic hydrogenation systems which appear to have been reported utilize rhodium and ruthenium complexes of Na[(*m*-$SO_3C_6H_4PPh_2$)].[36] While relative activities are difficult to compare, these systems were in fact virtually inactive unless a water-soluble organic co-solvent was added. They were also found to be exceedingly air-sensitive, in contrast to the amphos system, and in some cases catalysis was retarded by sulfonate coordination, a type of inhibition which cannot occur with amphos complexes.

(c) Supported Olefin Hydrogenation Catalysts. The cationic nature of the ligand amphos led to the possibility of supporting its coordination compounds via ionic attachment to cation-exchange resins. Very few reports of ionically supported complexes capable of catalytic activity have appeared in the literature, and, of those that have, most involve metal complexes that are ionic in nature rather than having ligands which have ionic functional groups. For example, $[RhCl_6]^{3-}$, $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$, and $[RhI_2(CO)_2]^-$ have been supported on anion-exchange resins, the first three being utilized as hydrogenation catalysts,[37] the last as a methanol carbonylation catalyst.[38]

Addition of a strong acid, macroreticular cation-exchange resin in the sodium form to a stirred, aqueous solution of II resulted in essentially quantitative (by AA) adsorption of the rhodium within 1 h. Catalytic hydrogenation studies using the Parr hydrogenation apparatus were generally unsatisfactory, however, because the resin beads tended to collect at the top of the glass pressure vessel and thus were not in complete contact with the liquid in the flask. All reactions were therefore run in a 300-mL stirred Parr mini reactor equipped with a glass liner. Solutions of olefin (1-hexene, cyclohexene) were hydrogenated (5–12 atm) for 17 h, and while the reaction conditions were somewhat variable as various attempts were made to achieve optimization, yields of hydrogenated product of 90–98% were normally achieved by using acetone solutions; little isomerization of 1-hexene to internal olefins was observed if the reactions were stopped short of completion. Acetone was much better as a solvent for the olefins than was ethyl ether, possibly because the latter did not solvate well the highly polar surfaces of the resin heads. Used catalyst was found to exhibit little or no loss of activity when reused, although no attempt was made to determine a maximum possible turnover number.

The mode of attachment of II to the resin is not known, but it is anticipated that it involves essentially ion-pairing between the tetraalkylammonium moieties of the coordinated amphos ligands and sulfonate groups on the surface of the resin, i.e.



VIII

Indirect evidence for the formation of VIII comes from finding that conversion of II to IV by treatment with hydrogen prior to adsorption on the resin gave a hydroformylation catalyst of reduced activity (see below). While the bulky NBD and two PPh_2 moieties of II may well inhibit direct ion pairing of the cationic metal center to a sulfonate group, the steric protection may be largely lost in IV, possibly leading to adsorption of both "ends" of the cationic molecule and hence to lowered activity. Sulfonate coordination has been cited by others as a possible reason for deactivation of homogeneous catalysts.[36]

The organic phases from reactions of supported II were catalytically inactive, and chemical analyses showed that the rhodium concentrations were in the range 0.10–0.25 ppm in both ether and acetone. Although metal leaching has been recognized as a major limitation to the technical use of supported platinum metal catalysts,[4] there are in fact few relevant analytical data in the literature. We note, however, that rhodium leaching from covalently bonded supports during hydroformylation experiments can be an order of magnitude higher[5,7] than that found here and still apparently be deemed to be "low".[4] We had rather expected that leaching into the relatively polar acetone, at least, would be significant, given the ionic nature of the catalyst binding. That the systems appeared to exhibit relatively low dispositions to leaching came as a pleasant surprise.

On the other hand, because of the ionic nature of the bonding, the rhodium could be quantitatively recovered from the resin after a reaction by elution with 6 M perchloric acid. We are unaware of attempts to recover rhodium covalently bonded to supports. Since in most cases recovery of the metal would require destruction of the support, it is probably a problem which has not been hitherto addressed.

(d) Hydroformylation Reactions. Aqueous solutions containing the 3:1 catalyst were found to hydroformylate 1-hexene (either neat or in methylene chloride, ethyl ether, or n-pentane solutions) in two-phase reactions at 90 °C and 40 atm of 1:1 CO–H_2; the results are shown in Table III. The reactions, which were allowed to go to completion, gave heptanals in high yields, generally ~90%, with *n*:iso ratios as high as 4 but surprisingly dependent on the solvent. Small amounts of hexane, 2-hexenes, and heptanol were also sometimes observed through side reactions. The

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Table III. Two-Phase "Homogeneous" Hydroformylation Reactions of 1-Hexene[a]

			product distributns, %			
amphos:Rh	pH	solvent(s)	heptanals (*n*:iso)	hexane	hexenes	heptanol
3	6.8	H_2O	86 (4.6)	3	5	1
4	6.8	H_2O	94 (3.4)	1	2	2
10	6.8	H_2O	89 (3.4)	2	7	2
3	5.8	H_2O	88 (4.0)	1	4	0
3	5.0	H_2O	76 (4.0)	16	3	0
3	5.8	H_2O/Et_2O	96 (1.7)	1	1	0
3	5.8	H_2O/CH_2Cl_2	90 (2.4)	1	6	0
3	5.8	$H_2O/n\text{-}C_5H_{12}$	90 (3.3)	1	6	0
3[b]	5.8	H_2O	5 (1.1)	2	93	0

[a] P = 40 atm; CO:H_2 = 1.1; temp = 90 °C; time = 24 h. [b] P_{CO} = 40 atm, P_{H_2} = 0.

organic phases were generally yellow in colour after reaction and thus were analyzed for rhodium after product analysis by gas chromatography. The concentrations of rhodium were, however, found to be quite small, usually less that 0.5 ppm, and corresponding to leaching of less than 0.1% of the total rhodium into the aqueous phase.

It was thought advisable to buffer the aqueous phase as the use of hydroformylation precursors containing chloride is known to liberate HCl.[39] Between pH 5.5 and 6.8, the hydroformylation of neat 1-hexene proceeded in 90% yield, but at pH 5.0 the yield of heptanals dropped to 76% and the undesirable hydrogenation of 1-hexene to hexane became important (16%). Increasing the phosphine to rhodium ratio, a variable known to increase product linearity in other rhodium systems,[40] had little effect in the two-phase system. At a phosphine to rhodium ratio of 10, the *n*:iso ratio, in fact, decreased slightly to 3.4 from the value of 4.6 observed with a 3:1 mixture.

Interestingly, in the absence of added hydrogen, 1-hexene could still be hydroformylated by the 3:1 amphos mixture, though yields were low (~5%). The explanation for this is likely to be related to the observation that the aqueous rhodium system can also catalyze the water gas shift reaction (eq 1), thus providing the hydrogen necessary for hydroformylation. Several other rhodium phosphine complexes have been reported to be active catalysts for the water gas shift reaction,[41,42] and indeed, when the reaction was done in absence of 1-hexene, hydrogen was formed in quantities comparable with those of the heptanals in the previous experiment. As well, the amount of carbon dioxide found corresponded to the amount of heptanals, and it would thus appear that any hydrogen produced in the presence of 1-hexene was consumed to form the heptanals. The *n*:iso ratio was low (1.1) because of the higher partial pressure of carbon monoxide (40 atm), a factor well understood to decrease product linearity in single phase hydroformylations with traditional rhodium catalysts.[43]

Preliminary hydroformylation experiments were also carried out with complexes adsorbed onto macroreticular cation exchange resins. Aqueous amphos–rhodium solutions were adsorbed onto the resins in a fashion similar to that described above, and solutions of 1-hexene in ethyl ether were reacted under the same conditions as in the previous hydroformylation experiments. In contrast to the two-phase homogeneous reactions, however, in which II proved to be a somewhat less active hydroformylation catalyst, supported II was catalytically active, as was the supported 3:1 mixture. Yields were much lower for the 3:1 complex (~30%), though a high *n*:iso ration of 6.8 was observed. Isomerization to 2-hexenes was the predominant reaction (65%) in this case. Hydroformylation with supported complex II, in contrast, gave a 90% yield of heptanals with an *n*:iso ratio of only 2.4.

In a second set of experiments, aqueous solutions of either II or the 3:1 mixture were treated with hydrogen (1 atm) for 5 min prior to being supported on resins. As shown previously, exposure to hydrogen quantitatively reduces NBD to norbornane, giving either complex IV (from II) or complex III (from the 3:1 mixture). Complexes adsorbed from these solutions hydroformylated 1-hexene to heptanals in 30% yield with *n*:iso ratios of about 2, the major reaction being isomerization of the substrate to 2-hexenes (65%).

These reactions do show promise, however, as the organic phases were easily separated from the resin and again contained less than 0.5 rpm rhodium.

The only two liquid-phase hydroformylation reactions reported in the literature are based on Na(*m*-$SO_3C_6H_4PPh_2$) complexes of rhodium and ruthenium. Wilkinson et al. have described the activity of $RuHCl_3$, where L = the above sulfonated triphenylphosphine, though few details were given.[36] Rhône-Poulenc Industries have patented the two phase hydroformylation of a number of olefins based on catalysts formed from rhodium precursors such as $(COD)RhCl_2$ and sulfonated triphenylphosphine.[44] They report high yields of heptanals (~90%) for the hydroformylation of 1-hexene, with *n*:iso ratios as high as 9. After reaction the organic phases were coloured, though no rhodium analyses were performed. Many supported rhodium hydroformylation catalysts are known,[2,43] of course, with better activities and n:iso ratios than found here. However, as noted above, leaching of rhodium is often significant.[5,7]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this research in the forms of an operating grant to M.C.B., a graduate scholarship to R.T.S., and a summer research award to L.J.S. The research was also facilitated by a loan of $RhCl_3 \cdot 3H_2O$ from Johnson Matthey Ltd. and a grant from Du Pont Canada, Inc., toward the purchase of the Bruker CXP 200.

Registry No. I, 83951-74-0; II, 83951-76-2; III, 83951-77-3; IV, 83951-78-4; V (X = Cl), 85735-66-6; V (X = MeOH), 85735-67-7; VI, 85735-69-9; VII, 85735-70-2; $[NBDRhCl]_2$, 12257-42-0; $[RhH_2(amphos)_2Cl(MeOH)]^{2+}$, 83951-75-1; $Ph_2PCH_2CH_2NMe_3^+I^-$, 79416-06-1; $Ph_2PCH_2CH_2NMe_3^+NO_3^-$, 85735-68-8; styrene, 100-42-5; 1-hexene, 592-41-6; crotonic acid, 3724-65-0; maleic acid, 110-16-7.

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