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Metal Carbonyl Derivatives of a Water Soluble Phosphine

R. T. SMITH and M. C. BAIRD*

Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6, Canada

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A new cationic, water soluble phosphine (2-diphenylphosphinoethyl)trimethylammonium iodide, $Ph_2PCH_2CH_2NMe_3^+I^-$, *(amphos iodide) has been synthesized and characterized. Its simple metal carbonyl substitution complexes* $[Fe(CO)_4amphos]^+$, $[Mo(CO)_5amphos]^+$, $[W(CO)_5amphos]^+$, *(as iodide salts) have been prepared and show greatly enhanced solubility in polar solvents. The properties of these complexes are compared with those of the corresponding complexes of neutral phosphines. Spectral data indicate that amphos acts as a typical tertiary phosphine, its electron donor properties being slightly lower than those of* $PMePh_2$ *and* PPh_3*.*

The new metal carbonyl complexes exhibit very low catalytic activity for the water gas shift reaction.

Introduction

The low water solubility of most organometallic compounds has confined the study of their chemistry to organic media. Water has a variety of properties that set it apart from most organic solvents, however, and hence it is possible that one might observe very different chemistry in aqueous solution. There has been increasing interest, therefore, in the water solubilization of organometallic compounds.

This is generally achieved via coordination of ligands, usually tertiary phosphines, which contain highly polar functional groups such as amino, carboxylic acid, hydroxide or sulphonate. A recent review article [1] describes a large number of compounds prepared from such phosphines, in some cases comparing catalytic activities of their complexes with those of the more typical, non-functionalized phosphines. Unfortunately hydroxyl containing ligands often do not exhibit greatly enhanced water solubility, while phosphines containing amino or carboxyl groups are soluble only in acidic or basic media respectively. Compounds containing sulphonated triphenylphosphine have also been extensively studied [2–4].

We are currently exploring a new approach to the water solubilization of phosphines, involving incorporation of a tetralkylammonium group, which should lead to properties independent of solution pH. We wish now to report the synthesis and characterization of a cationic phosphine, the (2-diphenylphosphinoethyl)trimethylammonium cation (amphos), as its iodide salt (amphos iodide). In order to gain an understanding of the electronic properties of amphos, we have also prepared several metal carbonyl derivatives, $[Fe(CO)_4amphos]^+$, $[Mo(CO)_5amphos]^+$ and $[W(CO)_5amphos]^+$. Comparison of the ^{13}C NMR, ^{31}P NMR and IR data for these complexes indicates that amphos has similar, although slightly lower, donor properties than do PPh_3 and $PMePh_2$. A preliminary report of some of this work has appeared [5]. A paper to follow will deal with a series of amphos–rhodium complexes and their catalytic properties.

Experimental

All operations were carried out under nitrogen using standard Schlenk tube techniques. Solvents were distilled from appropriate drying agents and stored over molecular sieves until used. Chemicals were purchased from Aldrich with the exception of the metal carbonyls and trichlorosilane (Alfa), and were used as received. Conductivities were run on a Philips PR9501 conductance meter and IR spectra were run on a Beckmann 4240 spectrophotometer. The 60 MHz ^1H NMR spectra were run on a Bruker HX-60 spectrometer, ^{31}P and ^{13}C NMR spectra on a Bruker CXP-200 spectrometer at 80.99 and 50.30 MHz respectively. Elemental analyses were performed by Canadian Microanalytical Services Ltd. Melting points are uncorrected.

Preparation of $Ph_2PCH_2CH_2NMe_2$

Lithium chips (2 g, 0.29 mol) were added to 50 ml of freshly distilled and degassed THF in a nitrogen-

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*Author to whom correspondence should be addressed.

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filled flask, and chlorodiphenylphosphine (16 g, 0.07 mol) in 50 ml dry THF was added dropwise via a pressure equalizing dropping funnel. After addition of the Ph_2PCl, the deep red solution of the diphenylphosphide anion was refluxed a further 2 hours, cooled and separated from the unreacted lithium [6]. An ether solution of 2-chloroethyldimethylamine (8.6 g, 0.08 mol) was then added dropwise to the solution of the anion. (The chloroamine must be prepared immediately before use from its hydrochloride salt by treatment with excess aqueous NaOH, extraction with ether followed by drying with $MgSO_4$ and filtering). After addition of the chloroamine was complete, the solution was refluxed for one hour. It was then carefully hydrolyzed with 50 ml degassed H_2O, and the organic layer was separated and dried. After removal of the solvent, the resulting oily residue was distilled *in vacuo* (150 °C, 0.1 mm) [7], giving the product. Yields varied between 50 and 75%.

Preparation of $Ph_2P(O)CH_2CH_2NMe_2$

10 g of $Ph_2PCH_2CH_2NMe_2$ (0.039 mol) were dissolved in 30 ml degassed acetone in a nitrogen-filled flask. An equimolar amount of 10% H_2O_2 (12 ml) was added dropwise via a dropping funnel, and the mixture was refluxed for one hour. The solvents were then removed under reduced pressure, and the crude product was recrystallized from CH_3CN/petroleum ether (b.p. 30–60). (Yield 90%; m.p. 111–112 °C). (Found: C, 70.07; H, 7.39. $C_{16}H_{20}NOP$ requires C, 70.31; H, 7.38).

Preparation of $Ph_2P(O)CH_2CH_2NMe_3^+I^-$

10 g of $Ph_2P(O)CH_2CH_2NMe_2$ (0.037 mol) were dissolved in 50 ml acetone and a five fold excess of CH_3I (26 g, 11.5 ml) was added. The solution was stirred for four hours, after which the crude, air stable solid was filtered off and recrystallized from CH_3CN. (Yield 95%; m.p. 240–242 °C; Λ_M 115 ohm^{-1} cm^{-1} in H_2O) (Found: C, 49.31; H, 5.40. $C_{17}H_{23}INOP$ requires C, 49.17; H, 5.58).

Preparation of $Ph_2PCH_2CH_2NMe_3^+I^-$ *(amphos iodide)*

To 7 g (17 mmol) of $Ph_2P(O)CH_2CH_2NMe_3^+I^-$, suspended in 50 ml degassed CH_3CN under N_2, was added a five fold excess of $HSiCl_3$ (11.4 g, 85 mmol). The mixture was refluxed for 24 hours. Most of the excess $HSiCl_3$ was then blown off by a strong stream of N_2, and the remaining silicon compounds were carefully hydrolyzed with 10 ml of degassed H_2O. The mixture was filtered and the solvents were removed *in vacuo*. The last traces of water were removed by azeotropic distillation with CH_3CN. The crude phosphine was generally pure enough for most purposes, but it can be recrystallized from CH_3CN/Et_2O. (Yield 90%; m.p. 194–196 °C; Λ_M 97 ohm^{-1} cm^{-1} in methanol). The iodide could not be obtained analytically pure, but metathesis in methanol with sodium tetraphenylborate gave the tetraphenylborate salt, which could be recrystallized from CH_3CN/Et_2O. (Found: C, 83.20; H, 7.33; N, 2.42. $C_{41}H_{43}BNP$ requires C, 83.24; H, 7.32; N, 2.37). The complexes $[Fe(CO)_4amphos]^+I^-$, $[Mo(CO)_5amphos]^+I^-$ and $[W(CO)_5amphos]^+I^-$ could be prepared by the thermal reaction of amphos with the parent metal carbonyl. Unfortunately yields were low and large amounts of the bisphosphine complex formed; as well, iodide coordination occurred. Reaction of amphos and the parent metal carbonyl with $(CH_3)_3NO$ in polar solvents failed because of competitive solvent coordination. Hence the best route to these amphos complexes appears to be via coordination of the neutral amino phosphine, followed by alkylation (*vide infra*).

Preparation of $[Fe(CO)_4amphos]^+I^-$ *(*IV*) and* $[W(CO)_5amphos]^+I^-$ *(*V*)*

Equimolar amounts of $Ph_2PCH_2CH_2NMe_2$ (2.0 g, 7.7 mmol) and the parent carbonyl ($Fe(CO)_5$ 1.5 g, or $W(CO)_6$, 2.7 g) were dissolved in degassed CH_2Cl_2 under N_2. The temperature was lowered to −78 °C in a dry ice/acetone bath, and one equivalent of $(CH_3)_3N^+O^-$ (trimethylamine oxide) (0.58 g) was added. The reaction mixture was allowed to come to room temperature over a period of several hours, and the solvent was removed *in vacuo* to give precipitates of $Fe(CO)_4(Ph_2PCH_2CH_2NMe_2)$ (*I*) or $W(CO)_5(Ph_2PCH_2CH_2NMe_2)$ (*II*). These were extracted into Et_2O, and a five fold excess of CH_3I (5.5 g, 38 mmol) in Et_2O was added dropwise. The solution was stirred for 12 hours, yielding a precipitate of crude $[Fe(CO)_4amphos]I$ (*IV*) or $[W(CO)_5amphos]I$ (*V*). These could not, however, be obtained analytically pure, and were both converted (metathesis with sodium tetraphenylborate in methanol) to the corresponding tetraphenylborate salts. $[Fe(CO)_4amphos]BPh_4$: yield 74%; m.p. 202–205 °C; Λ_M 87 ohm^{-1} cm^{-1} (CH_3OH). (Found: C, 70.20; H, 5.61. $C_{45}H_{43}BFeNO_4P$ requires C, 71.17; H, 5.71). $[W(CO)_5amphos]BPh_4$: yield 50%; m.p. 189–191 °C; Λ_M 90 ohm^{-1} cm^{-1} (CH_3OH). (Found: C, 59.89; H, 4.90. $C_{46}H_{43}BNO_5PW$ requires C, 60.35; H, 4.73).

Preparation of $[Mo(CO)_5amphos]^+I^-$ *(*VI*)*

This compound can be prepared in a similar fashion to the above compounds, but the yields tend to be low because of formation of the disubstituted chelate complex, $Mo(CO)_4(\overline{Ph_2PCH_2CH_2N}Me_2)$. Better yields were obtained by combining $Mo(CO)_5N(CH_3)_3$ [8] (2.3 g, 7.8 mmol) and the aminophosphine (2.0 g, 7.8 mmol) in degassed CH_2Cl_2 under N_2. The mixture was stirred at room temperature for 4 hours, the solvent was removed *in vacuo*, and the residue was extracted twice with 50 ml

TABLE I. ^1H and ^{31}P NMR Data.

Compound	$\delta(NMe_{2,3})$	$\delta(P)$[a]	Coordination Shift[b]
$Ph_2PCH_2CH_2NMe_2$	2.10 ($CDCl_3$)	−20.8 (CH_3OD)	–
$Ph_2PCH_2CH_2NMe_3^+I^-$	3.10 (D_2O)	−20.3 (D_2O)	–
I	2.28 ($CDCl_3$)	–	–
II	2.34 ($CDCl_3$)	–	–
III	2.35 ($CDCl_3$)	–	–
IV	3.21 (CD_3CN)	64.1 (CD_3CN)	84.4
V	3.08 (CD_3CN)	6.9 (CD_3CN)	27.2[c]
VI	3.13 (CD_3CN)	26.6 (CD_3CN)	46.9
$Fe(CO)_4(PMePh_2)$	–	56.2 ($CDCl_3$)	84.2
$W(CO)_5(PMePh_2)$	–	3.8[d]	24.2[e]
$Mo(CO)_5(PMePh_2)$	–	15.0[d]	43.0

[a] ppm. Relative to ext. H_3PO_4. [b] δP(complex) − δP (free ligand) (ppm). [c] J_{WP} = 244 Hz. [d] Reference 25. [e] J_{WP} = 245 Hz.

Note: The ^1H resonances of the two CH_2 groups in the above compounds are very broad because of coupling to each other and to ^{31}P, as well as having similar chemical shifts. Resonances spread over 0.75 ppm are typical. Hence no assignments are made.

TABLE II. IR Data.

Complex Type	L	ν_{CO}	(in CH_2Cl_2)	(cm^{-1})
$Fe(CO)_4L$	amphos	2054 (m)	1983 (wk)	1945 (vs) 1932 (vs)
	$Ph_2PCH_2CH_2NMe_2$	2049 (m)	1976 (wk)	1942 (vs)
	$PMePh_2$	2048 (m)	1974 (wk)	1934 (vs)
	PPh_3	2049 (m)	1975 (wk)	1935 (vs)
$W(CO)_5L$	amphos	2073 (wk)	1938 (vs)	
	$Ph_2PCH_2CH_2NMe_2$	2070 (wk)	1928 (vs)	
	$PMePh_2$	2069 (wk)	1930 (vs)	
	PPh_3	2070 (wk)	1935 (vs)	
$MO(CO)_5L$	amphos	2074 (wk)	1944 (vs)	
	$Ph_2PCH_2CH_2NMe_2$	2070 (wk)	1940 (vs)	
	$PMePh_2$	2069 (wk)	1940 (vs)	
	PPh_3	2070 (wk)	1940 (vs)	

portions of petroleum ether (b.p. 30–60). The solvent was removed *in vacuo*, the residue of $Mo(CO)_5(Ph_2PCH_2CH_2NMe_2)$ (*III*) was dissolved in Et_2O and excess CH_3I (2.7 g, 19 mmol) was added to give *VI*. The work-up procedures were then the same as above. (Yield 65%, m.p. of the tetraphenylborate salt 154–156 °C; Λ_M 84 ohm^{-1} cm^{-1} in CH_3OH). (Found: C, 66.27; H, 5.40. $C_{46}H_{43}BMoNO_5P$ requires C, 66.76; H, 5.24).

Spectroscopic data for all the new compounds are shown in Tables I–III.

Results and Discussion

Amphos iodide is synthesized easily in high yield from 2-dimethylaminethyldiphenylphosphine [7] ($Ph_2PCH_2CH_2NMe_2$) by oxidation to the phosphine oxide [9, 10] with hydrogen peroxide, alkylation at nitrogen with CH_3I, followed by reduction with $HSiCl_3$ [11, 12] to give the air stable phosphine. The oxidation step is necessary to protect phosphorus during alkylation. All attempts to alkylate the

TABLE III. ^{13}C NMR Data.

Compound	δ ^{13}C^a, (J$_{PC}$)^b			
	PCH$_2$	NCH$_2$	NMe$_{2,3}$	Solvent
$Ph_2PCH_2CH_2NMe_2$	26.85 (11)	56.91 (21)	45.45	CD_3CN
$Ph_2PCH_2CH_2N^+Me_3I^-$	21.86 (15)	64.92 (30)	53.58	CD_3CN
IV	24.15 (26)	60.27	51.29	DMSO-d$_6$
V	27.50 (24)	63.91	54.00	CD_3CN
VI	23.77 (23)	60.48	51.21	DMSO-d$_6$

^{a}Ppm relative to TMS. ^{b}Hz; if no value given J$_{PC}$ was less than the resolvable limit ≈2 Hz).

free aminophosphine resulted in P-methylation as shown by the appearance of resonances typical of phosphonium salts in the ^{31}P NMR spectrum [13], concurrently with the characteristic methyl doublet in the ^{1}H NMR spectrum due to coupling with phosphorus. Attempts to alkylate at nitrogen after coordination of the aminophosphine to cobalt(II) halides [7] also failed.

As is seen in Table I, the N-methyl protons of amphos are deshielded with respect to those of its precursor, $Ph_2PCH_2CH_2NMe_2$, while the ^{31}P chemical shifts remain essentially identical. Thus the electronic effect of the quaternary ammonium functionality on the ^{31}P chemical shift is negligible. This is not unexpected, since electronic effects generally contribute only slightly to the chemical shifts in similar compounds [14], and the quaternized nitrogen is well removed from the phosphorus atom. As can be seen, the ^{31}P chemical shift of amphos is similar to that of $PEtPh_2$ (−12.3 ppm) [14] and almost identical to that of $Ph_2PCH_2CMe_3$ (−23.9 ppm) [15].

In order to examine the donor properties of amphos, we have prepared several simple monosubstituted metal carbonyl complexes. These complexes can be prepared by the thermal reaction of amphos salts with the parent metal carbonyl, but this route leads to disappointingly low yields and significant amounts of disubstituted products.

Instead, a much superior route involving the mild decarbonylating agent trimethylamine oxide, $(CH_3)_3N^+O^-$ [16], was developed. Reaction of the metal carbonyl at −78 °C with one equivalent of amine oxide in the presence of $Ph_2PCH_2CH_2NMe_2$ leads to relatively high yields of monosubstituted products *I–III*. The IR spectra in the carbonyl region of the reaction solutions (Table II) clearly showed that monosubstitution had occurred. Subsequent treatment with CH_3I yielded the desired amphos complexes *IV–VI*, all shown to be 1:1 electrolytes. While chelation is well known for aminoalkylphosphines [17], it did not present a problem with the iron and tungsten complexes. Only in the reaction of $Mo(CO)_6$ with the trimethylamine oxide and aminophosphine was chelation observed in significant amounts (~20% of crude product). Complexes *IV–VI* showed N-methyl proton chemical shifts essentially the same as that of free amphos, while the ^{31}P resonances were shifted downfield considerably, indicating coordination through phosphorus. The IR spectra in the carbonyl region were typical of these types of complexes [18].

For comparison purposes the analogous $PMePh_2$ and PPh_3 complexes were prepared [19]; their spectral characteristics are listed in Tables I and II. The coordination shifts of the ^{31}P resonances (δP(complex) − δP(free ligand)) for the amphos and $PMePh_2$ complexes are quite similar, indicating that despite the quaternary ammonium functionality, amphos may have donor properties not greatly different from those of $PMePh_2$. Consideration of the IR data (Table II), however, suggests that amphos is a somewhat poorer donor than either $PMePh_2$ or PPh_3. Thus for all three amphos complexes, the carbonyl stretching frequencies are somewhat higher than are the corresponding bands of the complexes of the neutral phosphine or of either $PMePh_2$ and PPh_3. The differences, however, although significant, are generally slight.

Problems arose in assigning the ^{13}C NMR spectra, listed in Table III. The presence of the phosphorus atom has very little effect on the chemical shift of C_1 of the R group in the ^{13}C NMR spectra of tertiary phosphines of the type $PRPh_2$ [14]. In addition, carbon-phosporus coupling constants (~15 Hz) are not generally attenuated when R is a long chain alkyl group, and hence are not very useful in assigning carbon chemical shifts [14].

The nitrogen atom of $Ph_2PCH_2CH_2NMe_2$, however, is expected to cause significant deshielding of the N–CH_2 resonance [20], leading to the assignment in Table III. The ^{13}C NMR spectral parameters of amphos are similar, except that the N-CH_2 resonance is deshielded even more because of the quaternization of the nitrogen. In this case $^2J_{PC}$ is, in fact, larger than $^1J_{PC}$.

On coordination of amphos, the P-CH_2 resonance is deshielded and $^1J_{PC}$ increases slightly. The N-CH_2 chemical shift changes less, but $^2J_{PC}$ is reduced below the resolvable limit (~2 Hz). A similar effect has been noted with phosphine oxides [20]. While very little is known about the effects of coordination on the carbon resonances of phosphines, $^1J_{PC}$ values of about 35 Hz and very small $^2J_{PC}$ values have been observed for complexes of palladium(II) and platinum(II) [21, 22].

Amphos is quite water soluble in neutral, acidic or basic conditions, although the addition of 2% methanol facilitates wetting. The metal carbonyl complexes, while not readily soluble in pure water, show greatly enhanced solubility in polar solvents relative to those of the $PMePh_2$ and PPh_3 analogues. Thus the amphos complexes are freely soluble in both methanol and acetonitrile, and remain in solution when water is added to bring the solutions to 1:1 V/V and 3:1 V/V respectively. The iron complex (*IV*) is the most soluble. For example 0.20 g dissolved in 10 ml methanol will not give a turbid solution on the addition of 100 ml H_2O. In contrast, the $PMePh_2$ complexes are virtually insoluble in methanol and precipitate from CH_3CN solution on the addition of even one tenth the volume of water.

It had been originally anticipated that the amphos complexes might be very good homogeneous catalysts for the water gas shift reaction, *i.e.*

$$CO + H_2O \rightarrow CO_2 + H_2$$

It was hoped that the overall cationic nature of the complexes would facilitate nucleophilic attack by water or hydroxide on coordinated CO [23]. Employing basic conditions under which $Fe(CO)_5$ is a very active catalyst [24], (140°, pCO = 480 psi, 1 mmol catalyst, aq. MeOH) the iron amphos complex showed much less activity (turnover ≈ 5 mol H_2O/mol catalyst/day) than does $Fe(CO)_5$ (≈1000 mol H_2/mol catalyst/day). The molybdenum and tungsten complexes showed no activity, and none of the complexes was active under neutral conditions.

We are continuing our investigations into transition metal complexes of amphos, particularly with respect to their uses as homogeneous catalysts in aqueous and polar media.

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