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Some Triphenylphosphinimine Complexes of Zinc, Cadmium, Mercury, Rhodium and Palladium

EDWARD W. ABEL and STUART A. MUCKLEJOHN
Department of Chemistry, University of Exeter, Exeter EX4 4QD, U.K.

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The in situ *alcoholysis of $Ph_3P{=}NSiMe_3$ in the presence of anhydrous halides of zinc, cadmium and mercury results in the formation of a range of co-ordination complexes of triphenylphosphinimine, $Ph_3P{=}NH$ (L). The complexes formed were of three types: i) the* trans *dimers $[(MX_2L)_2]$, ii) the cyclic dimers $[(MX_2L_2)_2]\cdot(CHCl_3)_2$ and iii) the polymeric $(M_2X_2L_3)_n$. Triphenylphosphinimine complexes of rhodium and palladium result from halogen bridge fission in $[\{PdCl(\eta\text{-}C_3H_5)\}_2]$ and $[\{Rh(CO)_2Cl\}_2]$.*

Introduction

The co-ordination properties of phosphinimines have not received extensive attention, but recent studies have shown them to be versatile ligands and capable of acting as formally one, two or four electron donors.

The triphenylphosphinimines $Ph_3P{=}NR$ behave as two electron donors by co-ordination of the nitrogen atom to a metal centre. Examples include the (albeit poorly characterized) complexes of $Ph_3P{=}NPh$ with CdI_2 and HgI_2 [1] and of $Ph_3P{=}NH$ with $CoCl_2$, $CuCl_2$ and NiI_2 [2]. The bidentate ligand $Ph_3P{=}NCH_2CH_2N{=}PPh_3$ forms complexes with Co, Ni, Cd and Hg [3], and palladium complexes of N-arylphosphinimines and N-silylphosphinimines are known [4].

Complexes of the formally one electron donors $R_3P{=}N{-}$ have been reported for ruthenium and osmium by the action of tertiary phosphines on nitrido complexes of the metals [5–8]. Another derivative of this type is $[MoCl_4(N{=}PPh_2n\text{-}Pr)(O{=}PPh_2n\text{-}Pr)]$ obtained from $[MoCl_4(PPh_2n\text{-}Pr)_2]$ and *p*-toluenesulphonyl azide [9, 10].

The reactions of phosphinimines with metal carbonyls has yielded a range of different types of complex. Triphenylphosphinimine and hexacarbonylvanadium form the ionic product $[V(Ph_3P{=}NH)_4]^{2+}$ $2[V(CO)_6]^-$ [11], but the carbonyl hydrides $[MH(CO)_3(\eta\text{-}C_5H_5)]$ (M = Cr, Mo and W) protonate the weakly basic trimethylphosphinimine to yield $[Me_3PNH_2]^+[M(CO)_3(\eta\text{-}C_5H_5)]^-$ [12].

Wittig type reactions of the triphenylphosphinimines have been reported with pentacarbonyliron [13], $PdCl_2/CO$ [14], and the Re=O bond in $[ReCl_3(O)(PPh_3)_2]$ [15].

High temperatures converted $[Mo(CO)_4(Ph_3P{=}NH)_2]$ [16] into $[Mo_2(CO)_6(\mu\text{-}Ph_3P{=}NH)_3]$ in which the phosphinimines each behave in a formally four electron donor role and bridge two molybdenum atoms [17].

As part of a wider investigation of the complexation properties of phosphinimines [18] and the related iso-electronic ylids [19], we have found that the easily prepared (eqn. 1) N-trimethylsilyltriphenylphosphinimine undergoes alcoholysis (eqn. 2), and subsequent formation of metal complexes of triphenylphosphinimine (eqn. 3).

$$Me_3SiN_3 + Ph_3P \rightarrow Ph_3P{=}NSiMe_3 + N_2 \qquad (1)$$

$$Ph_3P{=}NSiMe_3 + EtOH \rightarrow Ph_3P{=}NH + Me_3SiOEt \qquad (2)$$

$$nPh_3P{=}NH + MX_m \rightarrow [MX_m(Ph_3P{=}NH)_n]. \qquad (3)$$

Results and Discussion

N-Trimethylsilyltriphenylphosphinimine underwent reaction with the anhydrous dihalides of zinc, cadmium and mercury in ethanol solution to produce triphenylphosphinimine metal complexes. All of these complexes were soluble in and recrystallized from chloroform, and were moisture sensitive. The products were all well formed crystals as examined by optical microscopy and by electron micrographs. The characterizations of these complexes are reported in Table I, and interesting differences in stoichiometry are noted. The presence of chloroform was initially detected from the elemental analysis data. Its presence or absence in the formulations in Table I was, however, very positively confirmed by the g.l.c. of these complexes.

TABLE I. Characterization of Triphenylphosphinimine Complexes of Zinc, Cadmium and Mercury.

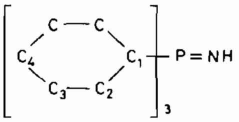
Complex	Yield/%	M.p./°C	ν(P=N)^a/cm^{-1}	Analysis					
				Calc./%			Found/%		
				C	H	N	C	H	N
$[ZnCl_2(HN{=}PPh_3)]_2$	66	89–91	1112	52.23	3.89	3.39	51.84	3.68	3.12
$[ZnBr_2(HN{=}PPh_3)]_2$	21	90–92	1112	43.03	3.21	2.79	43.44	3.30	2.60
$[ZnI_2(HN{=}PPh_3)]_2$	45	188–190	1118	36.24	2.70	2.35	37.56	2.78	2.34
$[CdCl_2(HN{=}PPh_3)]_2$	40	216–218	1114	46.94	3.50	3.04	47.09	3.32	2.99
$[Cd_2Br_4(HN{=}PPh_3)_3]$	18	138–140	1116	47.13	3.49	3.05	47.01	3.62	2.89
$[CdI_2(HN{=}PPh_3)_2]_2{\cdot}2CHCl_3$	27	200–202	1116	42.72	3.19	2.69	42.12	3.13	2.78
$[HgCl_2(HN{=}PPh_3)]_2{\cdot}CHCl_3$	42	99–100	1106	36.52	2.73	2.30	36.67	2.71	2.16
$[HgBr_2(HN{=}PPh_3)]_2{\cdot}CHCl_3$	21	84–86	1110	31.86	2.38	2.01	31.11	2.32	2.04
$[Hg_2I_4(HN{=}PPh_3)_3]$	65	114–116	1110	37.26	2.78	2.41	37.10	2.84	2.12

^{a}Spectrum recorded in KBr disc.

TABLE II. ^{13}C N.m.r. Data for *cis*[$Rh(CO)_2Cl(Ph_3P{=}NH)$].

	δ^a/ppm	J(^{13}C–^{31}P)	J(^{13}C–^{103}Rh)
		Hz	Hz
$C_1{}^b$	128.31	100.58	
$C_2{}^b$	132.85	10.26	
$C_3{}^b$	129.08	12.45	
$C_4{}^b$	133.27	2.45	
CO^c	185.24	3.3	68.4
	182.50	unresolved	
	179.53	3.8	76.6

^{a}In $CDCl_3$ solution (30 °C), chemical shifts relative to TMS. ^{b}Resolution 0.24 Hz. ^{c}Resolution 0.6 Hz.



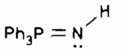
All of the zinc halides formed compounds of stoichiometry ZnX_2L ($L = Ph_3P{=}NH$) as also did cadmium chloride. Whilst mercury(II) chloride and bromide gave the analogous 1:1 halide to ligand ratio, these both had chloroform in their crystals. Cadmium iodide was unique with the stoichiometry CdI_2L_2 (with chloroform present), and cadmium bromide and mercury(II) iodide gave complexes $[M_2X_4L_3]$. Changing the molar ratio of the reagents did not alter the stoichiometry of the eventual chloroform recrystallized product in any of the above cases.

All of the complexes in Table I were shown to be non-conducting in dichloromethane solution at 10^{-5} mol dm^{-3}, whereas 1:1 electrolytes in the same solvent would have conductivities of about 20 ohm^{-1} cm^3 mol^{-1} [20].

Only fragments from the triphenylphosphinimine were observed in the mass spectra of these compounds, as has also been noted for other metal complexes of this ligand [17].

^{1}H n.m.r. spectra were not especially informative showing, as expected, only phenyl protons as a multiplet at δ 7.5–7.7 (15H) and a broad NH peak at δ 1.04–1.64 (1H).

All of the complexes had an intense (P=N) absorption in the region 1106–1118 cm^{-1} of the infrared spectrum. This confirms [16] the behaviour of the ligand as a two electron nitrogen donor as in (I), and not as the dipolar form (II) where the P–N frequency drops to around 930 cm^{-1} [17].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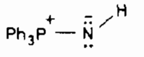
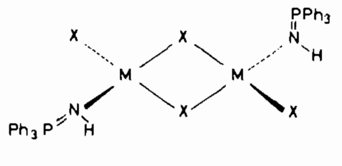

II

The formation of 1:1 complexes of the zinc halides is analogous to their reaction with the bulky tertiary phosphines [21], whereas less bulky phosphines have given 1:2 complexes [22–24]. We have determined the molecular weights of the zinc complexes in chloroform solution by vapour pressure osmometry, and they are all dimeric. By analogy



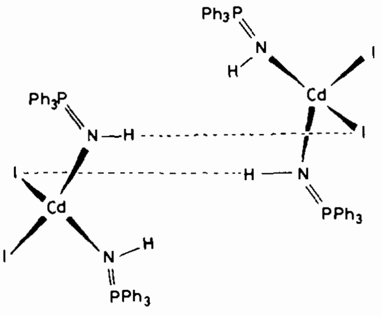
III

Proposed Structure of the Complexes [*trans*-$(MX_2L)_2$] where M = Zn, X = Cl, Br and I; M = Cd, X = Cl and M = Hg, X = Cl and Br.

with the known structures of analogous zinc [21], cadmium [25] and mercury [26] complexes, we propose the *trans* bridging structure illustrated in (III), with each metal atom in a tetrahedral configuration.

Only in the mercury(II) complexes was chloroform present, and there is a possibility that this could be weakly hydrogen bonded in the crystals of these compounds.

Of the complexes reported herein cadmium iodide was unique in forming a 2:1 ligand to metal halide complex, and here also chloroform is present in the crystal. Not unexpectedly for a 2:1 complex the stereochemistry around the cadmium atom is a tetrahedral array of two phosphinimine and two iodide ligands. However, the infrared spectrum showed two very different N–H stretching frequencies at 3338 cm^{-1} and 3259 cm^{-1}, suggesting different roles for the two phosphinimine ligands. This was confirmed by the remarkable features of structure revealed by the X-ray analysis [18]. The molecule contains two $\{CdI_2(Ph_3P{=}NH)_2\}$ units joined by a N–H---I hydrogen bond as illustrated in (IV), the hydrogen-bonded and non-hydrogen-bonded phosphinimines accounting for the very different N–H infrared frequencies.

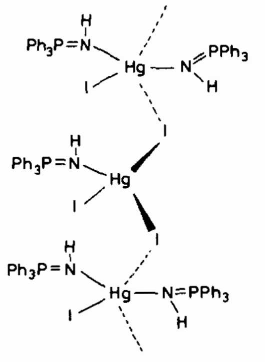


IV

The Structure of $[\{CdI_2(Ph_3P{=}NH)_2\}_2]$.

In the eight membered ring formed, the Cd–I distances (2.773 Å) are somewhat different from the non-ring Cd–I distances (2.735 Å), but both the ring and non-ring Cd–N distances (2.18 Å) are equivalent. The P–N bond distances average 1.57 Å by comparison with the P–N distance of 1.60 Å in $[Mo_2(CO)_6(\mu\text{-}Ph_3P{=}NH)_3]$ [17], and of 1.58 Å in the one electron phosphinimidate ligand [8].

$[Cd_2Br_4(Ph_3P{=}NH)_3]$ and $[Hg_2I_4(Ph_3P{=}NH)_3]$ are believed to have the polymeric structure illustrated in (V). Such a stoichiometry has been reported [25] for some tertiary phosphine and arsine complexes of mercury(II) iodide and cadmium bromide and iodide, and very interestingly the only zinc complex of this stoichiometry, $[Zn_2Br_4(C_4H_5N_2)_3]$, was reported as unstable [23]. One possible explanation of this 2:3 stoichiometry is the presence of a 1:1 molecular lattice of MX_2L_2 and MX_2L units. Goldstein *et al.* [27] have recently shown, however, that these MX_2L_2 and MX_2L units in $[Hg_2X_4(PEtMe_2)]$ are joined in a polymeric structure by halogen bridges. By analogy we assign such a structure to the corresponding phosphinimine complexes, in which the mercury atoms of the chain are alternatively tetra- and penta-co-ordinate.



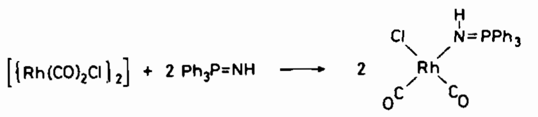
V

Proposed Structure of $[M_2X_4(Ph_3P{=}NH)_3]_n$ (M = Cd, X = Br and M = Hg, X = I).

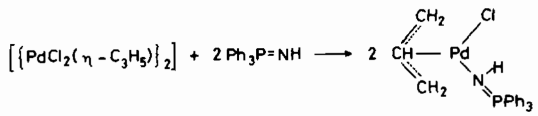
The two phosphinimines $Me_3SiN{=}PPh_2Me$ and $Me_3SiN{=}PPhMe_2$ after alcoholysis underwent reaction with the anhydrous dihalides of zinc, cadmium and mercury, but the white solid products were unstable upon recrystallization.

It would appear that the stoichiometries of the isolated crystalline species reported above are dependent upon a not easily rationalized variation of metal, halide, solvent and crystal packing.

In an effort to obtain well characterized phosphinimine complexes of the heavier transition metals, we treated the halogen-bridged complexes $[\{Rh(CO)_2Cl\}_2]$ and $[\{PdCl_2(\eta^3\text{-}C_3H_5)\}_2]$ with N-trimethylsilyltriphenylphosphinimine in the presence of ethanol (Eqs. 4 and 5).



(4)



(5)

In the rhodium complex, *cis*-$[Rh(CO)_2Cl(Ph_3P{=}NH)]$, the presence of two metal carbonyl bands of approximately equal intensity in the infrared spectrum indicates the formation of the *cis* square planar product. Data from the ^{13}C n.m.r. spectrum of this compound is reported in Table II.

There are two doublets due to the metal carbonyl carbon atoms, but two of the signals overlap to form a broad unresolved central peak. All ^{13}C signals show splitting due to phosphorus coupling, but only the metal carbonyl carbon atoms show ^{103}Rh coupling. Further the non-equivalence of these two carbonyls causes substantially different chemical shifts (δ 183.87 and δ 181.01) and different carbon–rhodium coupling constants (68.4 and 76.6 Hz); a trend already noted for the analogous amine complexes [28]. The action of triphenylphosphine and triphenylarsine upon *cis*-[Rh(CO)$_2$Cl(Ph$_3$P=NH)] is to displace the phosphinimine ligand and a further carbonyl group (Eq. 6).

$$\mathrm{Rh(CO)_2Cl(Ph_3P{=}NH)]} + 2\mathrm{L} \rightarrow$$
$$[\mathrm{Rh(CO)ClL_2}] + \mathrm{CO} + \mathrm{Ph_3P{=}NH} \qquad (6)$$

(L = PPh$_3$ and AsPh$_3$)

The complex [PdCl(η^3-C$_3$H$_5$)(Ph$_3$P=NH)] was thermally unstable with extensive decomposition at 5 °C after four days. Although characterization by elemental analysis was good, it did not prove possible to obtain very well resolved ^1H n.m.r. spectra.

Experimental

All reactions were performed under an atmosphere of dry nitrogen, and solvents were distilled from appropriate drying agents prior to use. Infrared spectra were recorded on Perkin Elmer 257 or 357 spectrometers. ^1H and ^{13}C n.m.r. spectra were recorded on Jeol MH100 and PS100 spectrometers respectively; and mass spectra were recorded on a Hitachi-Perkin Elmer RMU 6 instrument. Microanalyses were performed at the Department of Chemistry, University of Exeter, or The Butterworth Consultancy. All products were either oxygen and/or moisture sensitive.

Preparation of N-Trimethylsilyltriphenylphosphinimine [29]

Trimethylsilylazide (7.9 cm^3 {6.9 g} 60 mmol) was added to triphenylphosphine (14.5 g, 55 mmol) at 110 °C, and the temperature raised to 140 °C over 1 hr, and this temperature maintained until no further gas was evolved (~4½ hr), After cooling, the slight excess of the azide was removed under vacuum, and the white residue recrystallized from acetonitrile to yield pure product (18.2 g, 95%) m.p. 75–77 °C (lit. [29] 76–77 °C).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Zinc Chloride

Anhydrous zinc chloride (0.277 g, 2.0 mmol) was dissolved in ethanol (20 cm^3) and the N-trimethylsilyltriphenylphosphinimine (1.42 g, 4.0 mmol) added and stirred for 2 hr. Volatiles were removed under vacuum to leave a white oily residue. This was recrystallized twice from chloroform/hexane to yield bis(dichlorotriphenylphosphiniminezinc) (Table I). In substantially the same way were prepared the corresponding bromo and iodo complexes, (Table I).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Cadmium Chloride

Anhydrous cadmium chloride (0.426 g, 2.3 mmol) was dissolved in hot ethanol (20 cm^3) and the N-trimethylsilylphosphinime (1.62 g, 4.6 mmol) was added, and the mixture maintained at 60–70 °C for 2 hr. Upon cooling a white precipitate settled and was isolated by decantation. Recrystallization from chloroform/hexane gave white crystals of bis(dichlorotriphenylphosphiniminecadmium) (Table I).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Cadmium Bromide

The addition of a solution of anhydrous cadmium bromide (0.315 g, 1.2 mmol) in ethanol (20 cm^3) to a solution of N-trimethylsilyltriphenylphosphinimine (0.407 g, 1.2 mmol) in ethanol (10 cm^3) produced a white precipitate in 10 minutes at room temperature. This was separated by decantation and recrystallized from chloroform to yield tetrabromotris(triphenylphosphinimine)dicadmium (Table I).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Cadmium Iodide

Anhydrous cadmium iodide (0.874 g, 2.4 mmol) and N-trimethylsilyltriphenylphosphinimine (1.63 g, 4.7 mmol) were dissolved in hot ethanol (35 cm^3). The reaction mixture was stirred at 30 °C for 1 hr, during which time a white precipitate was deposited. This product was recrystallized twice from chloroform/hexane to yield white crystals of bis{di-iodobis(triphenylphosphinimine)cadmium}dichloroform (Table I).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Mercury(II) Bromide

Addition of a solution of anhydrous mercury(II) bromide (0.216 g, 0.60 mmol) in ethanol (10 cm^3) to a solution of N-trimethylsilyltriphenylphosphinimine (0.236 g, 0.67 mmol) in ethanol (10 cm^3) produced a flaky white precipitate after a few minutes stirring at room temperature. After one hour the precipitate was removed and recrystallized twice from chloroform to give bis(dibromotriphenylphosphiniminemercury) chloroform (Table I).

In an exactly analogous manner we isolated the corresponding bis(dichlorotriphenylphosphiniminemercury) chloroform (Table I).

Interaction of N-Trimethylsilyltriphenylphosphinimine and Anhydrous Mercury(II) Iodide

The addition of a solution of N-trimethylsilyltriphenylphosphinimine (0.357 g, 1.0 mmol) in ethanol (10 cm^3) to anhydrous mercury(II) iodide (0.251 g, 0.55 mmol) in ethanol (50 cm^3) produced an immediate pale yellow precipitate. After separation this was found to be sparingly soluble in chloroform from which recrystallization gave tetra-iodotris(triphenylphosphinimine)dimercury (Table I), as pale yellow crystals.

Interaction of N-Trimethylsilyltriphenylphosphinimine and Bis(chlorodicarbonylrhodium)

N-Trimethylsilyltriphenylphosphinimine (0.36 g, 1.04 mmol) was dissolved in ethanol (10 cm^3) and bis(chlorodicarbonylrhodium) (0.20 g, 0.52 mmol) was added. A little gas was evolved and a yellow solution was formed. After 20 minutes stirring at room temperature a fine yellow precipitate had formed, and was recrystallized from ethanol to give *cis*-chlorodicarbonyltriphenylphosphiniminerhodium, (80%), ν(P=N) 1120 cm^{-1}; ν(CO) 2066(9.3), 1986(10) cm^{-1}. Calcd. for $C_{20}H_{16}ClNO_2PRh$: C, 50.93; H, 3.42; N, 2.97%. Found: C, 49.92; H, 3.33; N, 2.83%.

Interaction of *cis*-Chlorodicarbonyltriphenylphosphiniminerhodium and Triphenylphosphine

cis-Chlorodicarbonyltriphenylphosphiniminerhodium (0.053 g, 0.11 mmol) was dissolved in warm ethanol (10 cm^3) and triphenylphosphine (0.036 g, 0.14 mmol) added. Carbon monoxide was evolved and a yellow crystalline precipitate had formed within five minutes. This was washed with a little cold ethanol, and dried under vacuum to yield chlorocarbonylbis(triphenylphosphine)rhodium (0.040 g) m.p. 192–193 °C. ν(CO) (KBr disc) 1982 cm^{-1}. Calcd. for $C_{37}H_{30}ClOP_2Rh$: C, 64.32; H, 4.38; N, 0.00%. Found: C, 63.82; H, 4.33; N, 0.00%.

In an exactly analogous reaction was formed chlorocarbonylbis(triphenylarsine)rhodium (56%) m.p. 230–232 °C (dec.). ν(CO) (KBr disc) 1985 cm^{-1}. Calcd. for $C_{37}H_{30}ClOAs_2Rh$: C, 57.06; H, 3.88; N, 0.00%. Found: C, 57.02; H, 3.80; N, 0.00%.

Interaction of Bis(μ-chloro-η^3-allylpalladium) and N-Trimethylsilyltriphenylphosphinimine

Bis(μ-chloro-η^3-allylpalladium) (0.27 g, 0.73 mmol) and N-trimethylsilyltriphenylphosphinimine (0.52 g, 1.46 mmol) were dissolved in hot ethanol (10 cm^3), and the solution was maintained at 65–70 °C for 3 hr. The resulting yellow solution was filtered hot, and solvent removed (25 °C/0.1 mm) from the filtrate. The resulting yellow solid was recrystallized from warm ethanol.

The resulting chloro-η^3-allyltriphenylphosphiniminepalladium (0.11 g, 16%) ν(P=N) 1116 cm^{-1}, m.p. 152–154 °C (dec.) (Calcd. for $C_{21}H_{21}ClNPPd$: C, 54.80; H, 4.60; N, 3.04%. Found: C, 53.95; H, 4.49; N, 2.93%), was very sensitive to air and to moisture, and showed signs of extensive decomposition after 4 days storage at 5–10 °C in a sealed ampoule. Solutions of the complex in $CDCl_3$ were not stable, and only poor quality ^{1}H n.m.r. spectra were obtainable. δ 7.7 (m) [C_6H_5]; δ 2.3 (s) [–NH]; δ 1.2 (d), δ 3.7 (d), δ 5.0 (m) [η^3-C_3H_5].

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