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Coordination chemistry of 2,2-bis(diphenylphosphinomethyl) propionic acid

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Dedicated to Professor Bob Angelici in recognition of his distinguished contributions to inorganic chemistry.

Abstract

The coordination chemistry of the diphosphine ligands 2,2-bis(diphenylphosphinomethyl)propionic acid, **1**, and 2,2-bis(diphenylphosphinomethyl)propionate, **2**, with copper(I), silver(I), gold(I), palladium(II) and platinum(II) is described. Structure determinations show that the carboxylic acid group in **1** can hydrogen bond to solvent molecules, to anions or to the carboxylic acid group of a neighboring complex, as in the complexes $[MCl_2(\mathbf{1})]\cdot 2DMSO$ (M = Pd or Pt), $[Pt(\mathbf{1})_2](OTf)_2$ or $[Pd(NCMe)_2(\mathbf{1})](OTf)_2$, respectively. The tridentate diphosphine–carboxylate ligand **2** forms oligomeric or polymeric complexes, such as $[\{Ag(\mathbf{2})\}_n]$, $[\{PdCl(\mathbf{2})\}_n]$ or $[\{PtMe(\mathbf{2})\}_n]$.

Keywords: Diphosphine; Carboxylic acid; Palladium; Platinum; Copper; Silver; Gold

1. Introduction

Tertiary phosphines, R_3P, are strongly basic and are excellent ligands for late transition metals [1–5], so many derivatives have been prepared for use in transition metal catalysts or metal extraction and associated processes [6,7]. Bidentate phosphine ligands have been used in the self-assembly of complex structures in coordination chemistry, either by acting as anchoring chelate ligands [8,9] or as bridging ligands [10], and there is increasing interest in the use of hybrid ligands containing both a phosphine and a more weakly binding hard donor ligand in the synthesis of macrocycles, polymers or network materials [11–22]. In this regard, ligands containing both a tertiary phosphine and a carboxylic acid group have great potential for building complex structures[13–15,17–21]. Thus the phosphine can form a strong, more inert coordinate bond while the carboxylic acid group can participate in self-assembly through hydrogen bonding or it may be deprotonated to form a hard, more labile carboxylate ligand which can participate in self-assembly through dynamic coordination chemistry [13–26]. The early research on mixed phosphine–carboxylic acid complexes used the simple derivatives of diphenylphosphinobenzoic acid, diphenylphosphinoacetic acid or similar compounds, but there has been recent interest in the design of more complex derivatives, including carboxylic acid derivatives of diphosphine ligands (Chart 1) [13–15]. This paper reports the coordination chemistry of the new ligand 2,2-bis(diphenylphosphinomethyl)propionic acid (**1**, Chart 1) with some Group 10 and 11 transition metal ions.

2. Experimental

2.1. Synthesis and characterization by spectroscopic methods

NMR spectra were recorded using a Varian Mercury 400 or Inova 400 MHz NMR spectrometer. ESI-MS were recorded using a Micromass LCT spectrometer in MeCN solution.

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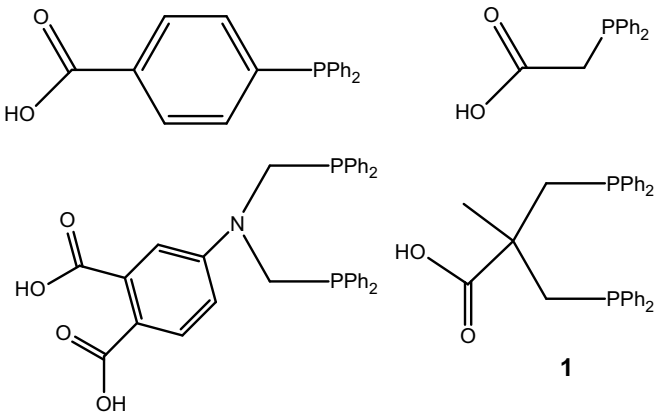


Chart 1. Some phosphine and diphosphine ligands with carboxylic acid substituents.

2.2. Bis(diphenylphosphinomethyl)propionic acid, *1*

To an ice-cooled solution of diphenylphosphine (4.6 mL, 26.5 mmol) in dry THF (50 ml), was added dropwise a solution of *n*-BuLi (2.0 M solution in cyclohexane, 17.1 mL, 25.6 mmol). The red solution was stirred at 0 °C for 1 h. To this solution, was added dropwise methyl 2,2-bis(chloromethyl)propionate (2.45 g, 13.24 mmol) was added dropwise. The mixture was stirred at 0 °C for 8 h, then warmed to room temperature. Water (20 mL) was added to the mixture, then the solvent THF was removed in vacuo. The mixture was extracted with dichloromethane (3×20 mL), the organic solution was washed with water (3×20 mL), and dried over $MgSO_4$. Evaporation of the solvent yielded a yellow oil, which was added to a solution of NaOH (4 g), EtOH (30 mL) and water (30 mL), and the mixture was heated under reflux for 2 h. After cooling, the mixture was acidified with aqueous HCl (2 M) until pH 6. The mixture was then extracted with CH_2Cl_2, and the extracts were washed with water, and dried over MgSO4. The solvent was removed under vacuum, and the residue was recrystallized from CH_2Cl_2–MeOH to afford the product as white crystals. Yield 51%. *Anal.* Calc. for $C_{29}H_{28}O_2P_2$: C, 74.03; H, 6.00. Found: C, 73.68; H, 5.57%. ^{1}H NMR ($CDCl_3$): $\delta(^1H) = 1.16$ [s, 3H, Me]; 2.58 [m, 2H, $^2J(HH) = 14$ Hz, $^2J(PH) = 2$ Hz, CH_2]; 2.63 [m, 2H, $^2J(HH) = 14$ Hz, $^2J(PH) = 2$ Hz, CH_2]; 7.2–7.5 [m, 20H, Ph]; δ (^{31}P) = −22.17 [s, P].

2.3. Lithium 2,2-bis(diphenylphosphinomethyl)propionate, Li(*2*)

To a solution of **1** (1.175 g, 2.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise a solution of $LiOH \cdot H_2O$ (104.9 mg, 2.5 mmol) in MeOH (5 mL). The solution was stirred overnight, then the solvent was evaporated to give the product as a white solid, which was washed with ether and dried under vacuum. Yield 99%. *Anal.* Calc. for $C_{29}H_{27}LiO_2P_2$: C, 73.11; H, 5.71. Found: C, 73.23; H, 5.54%. NMR ($CDCl_3$), $\delta(^1H) = 0.86$ [s, 3H, Me]; 2.39 [m, 2H, $^2J(HH) = 14$ Hz, $^2J(PH) = 5$ Hz, CH_2]; 2.47 [m, 2H, $^2J(HH) = 14$ Hz, $^2J(PH) = 3$ Hz, CH_2]; 6.8–7.4 [m, 20H, Ph]; $\delta(^{31}P) = -20.63$ [s, P].

2.3.1. [CuI(*1*)] (*3*)

The ligand **1** (47 mg, 0.1 mmol) was added to CuI (19 mg, 0.1 mmol) in MeCN (20 mL). A colorless clear solution formed initially, then the product precipitated from solution as a pale yellow solid, which was filtered, washed with MeCN and ether, and dried under vacuum. Yield: 94%. *Anal.* Calc. for $C_{29}H_{28}CuIO_2P_2$: C, 52.70; H, 4.27. Found: C, 52.26; H, 4.03%. Crystals were obtained from hot MeOH/MeCN solution but were not suitable for X-ray structure determination.

2.3.2. [AuCl(*1*)] (*4*)

The ligand **1** (47 mg, 0.1 mmol) was added to a solution of [AuCl(SMe_2)] (29.5 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) to give a colorless solution. The solution was stirred for 1 h., then ether (10 mL) was added to precipitate the product as a white solid, which was separated by filtration, washed with ether, and dried under vacuum. Yield: 88%. *Anal.* Calc. for $C_{29}H_{28}AuClO_2P_2$: C, 49.55; H, 4.01. Found: C, 49.54; H, 3.89%. NMR ($CDCl_3$), $\delta(^1H) = 0.95$ [br s, 3H, Me]; 2.3–2.5 [br m, 4H, CH_2]; 6.5–7.3 [m, 20H, Ph]; $\delta(^{31}P) = 26.4$ [br s, P].

2.3.3. [{Ag(*2*)}$_n$] (*5*)

A mixture of ligand **1** (47 mg, 0.1 mmol) and Ag_2O (14 mg, 0.06 mmol) in MeCN (5 mL) and MeOH (3 mL) was stirred for 15 h. The solution was filtered to remove insoluble material, the volume of solvent was reduced to ca. 1 mL under vacuum, and ether (10 mL) was added to precipitate the product as a white solid. Yield: 83%. *Anal.* Calc. for $C_{29}H_{27}AgO_2P_2$: C, 60.33; H, 4.71. Found: C, 59.84; H, 4.32%. NMR ($CDCl_3$): $\delta(^1H) = 0.9$ [br s, 3H, Me]; 2.2–2.5 [br m, 4H, CH_2]; 6.6–7.4 [m, 20H, Ph]; $\delta(^{31}P) = 25$ [br, P].

2.3.4. [{Au(*2*)}$_n$] (*6*)

The salt Li(**2**) (47.7 mg, 0.1 mmol) was added to a solution of [AuCl(SMe_2)] (29.5 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) to give a colorless solution. The solution was stirred for 1 h, then filtered and ether (10 mL) was added to the filtrate to precipitate the product as a white solid, which was filtered, washed with water, alcohol and ether and dried under vacuum. Yield: 96 %. *Anal.* Calc. for $C_{29}H_{27}AuO_2P_2$: C, 52.27; H, 4.08. Found: C, 51.96; H, 4.11%. NMR ($CDCl_3$), $\delta(^1H) = 0.88$ [br s, 3H, Me]; 2.3–2.5 [br m, 4H, CH_2]; 6.5–7.5 [m, 20H, Ph]; $\delta(^{31}P) = 36.7$ [br s, P].

2.3.5. [$PdCl_2$(*1*)] (*7*)

A solution of [$PdCl_2$(COD)] (28.5 mg, 0.1 mmol) CH_2Cl_2 (3 mL) was added to a solution of ligand **1** (47 mg, 0.1 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred for 2 h, then the yellow solid precipitate was separated

by filtration, washed with CH_2Cl_2 and ether, and dried under vacuum. Yield: 63 %. *Anal.* Calc. for $C_{29}H_{28}Cl_2O_2P_2Pd$: C, 53.77; H, 4.36. Found: C, 53.36; H, 4.18%. NMR (DMSO-d_6–$CDCl_3$): $\delta(^1H) = 0.87$ [s, 3H, Me]; 3.21 [m, 4H, CH_2]; 7.8–8.6 [m, 20H, Ph]; $\delta(^{31}P) = 25.2$ [s, PdP]. Crystals suitable for X-ray diffraction were obtained by recrystallization from DMSO/MeCN/Et_2O.

2.3.6. [$PtCl_2$(**1**)] (**8**)

To a solution of [$PtCl_2$(COD)] (32.4 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) was added a solution of ligand **1** (47 mg, 0.1 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred overnight, then the white solid precipitate was collected by filtration, washed with CH_2Cl_2 and ether, and dried under vacuum. Yield: 73%. *Anal.* Calc. for $C_{29}H_{28}Cl_2O_2P_2Pt$: C, 47.29; H, 3.83. Found: C, 47.60; H, 4.02%. NMR (DMSO-d_6–$CDCl_3$): δ ($^1H) = 0.86$ [s, 3H, Me]; 3.2–3.3 [m, 4H, CH_2]; 7.8–8.6 [m, 20H, Ph]; $\delta(^{31}P) = 0.1$ [s, ^1J(PtP) = 4210 Hz, PtP].

2.3.7. [$Pd(NCMe)_2$(**1**)]$(OTf)_2$ (**9**)

To a suspension of [$PdCl_2$(**1**)], **7** (129 mg, 0.2 mmol) in acetonitrile (10 mL) was added AgOTf (110 mg, 0.42 mmol). The mixture was stirred for 15 h, the insoluble solid (AgCl) was removed by filtration, volume of the filtrate was reduced to ca. 1 mL, and ether (10 mL) was added to precipitate the product as a white solid, which was separated, washed with ether and dried under vacuum. Yield: 76 %. *Anal.* Calc. for $C_{35}H_{34}F_6N_2O_8P_2PdS_2$: C, 43.92; H, 3.58; N, 2.93. Found: C, 43.39; H, 3.78; N, 3.01%. NMR (CD_3CN–$CDCl_3$): $\delta(^1H) = 1.18$ [s, 3H, Me]; 1.95 [s, 6H, MeCN]; 2.83 [dd, 2H, ^2J(HH) = 15 Hz, ^2J(PH) = 8 Hz, CH_2]; 2.93 [dd, 2H, ^2J(HH) = 15 Hz, ^2J(PH) = 8 Hz, CH_2]; 7.5–8.0 [m, 20H, Ph]; $\delta(^{31}P) = 31.1$ [s, PdP].

2.3.8. [Pt(**1**)$_2$]$(OTf)_2$ (**10**)

A mixture of [$Pt(EtCN)_4$]$(OTf)_2$ (35.7 mg, 0.05 mmol) and ligand **1** (47 mg, 0.10 mmol) in acetonitrile (4 mL) was warmed at 50 °C for 10 min. The volume of the colorless solution which formed was reduced to ca. 1 mL, and ether (10 mL) was added to precipitate the product as a white solid. Yield: 63%.

2.3.9. [$PtMe_2$(**1**)] (**11**)

To a solution of [Pt_2Me_4(μ-SMe_2)$_2$] (0.05 mmol) in CH_2Cl_2, (1 mL) was added a solution of ligand **1** (47 mg, 0.1 mmol) in CH_2Cl_2 (1 mL). The solution was stirred for 30 min., then concentrated to 0.5 mL and ether (10 mL) was added to precipitate the product as a white solid, which was separated, washed with ether and dried under vacuum. Yield: 96%. *Anal.* Calc. for $C_{31}H_{34}O_2P_2Pt$: C, 53.52; H, 4.93. Found: C, 53.12; H, 4.66%. NMR (CD_3CN–$CDCl_3$): $\delta(^1H) = 0.22$ [m, 6H, J(PtH) = 69 Hz, MePt]; 1.17 [s, 3H, Me]; 2.3 [m, 4H, CH_2]; 7.5–8.0 [m, 20H, Ph]; $\delta(^{31}P) = 4.83$ [s, J(PtP) = 2264 Hz, PtP].

2.3.10. [$PtMe(OH_2)$(**1**)](OTf) (**12**)

A solution of CF_3SO_3H (20 mg) in water (0.5 mL) was added to a solution of [$PtMe_2$(**1**)] (10 mg) in MeCN (1 mL). The mixture was stirred for 15 min, then the solvent was evaporated to give the product as a white solid, which was washed with water, MeOH and ether and dried under vacuum. Yield: 73%. *Anal.* Calc. for $C_{31}H_{33}F_3O_6P_2PtS$: C, 43.92; H, 3.92. Found: C, 43.72; H, 4.06%. NMR (CD_3CN): $\delta(^1H) = 0.08$ [m, 3H, J(PH) = 4, 7 Hz, J(PtH) = 53 Hz, MePt]; 0.91 [s, 3H, Me]; 2.66 [dd, 2H, ^2J(HH) = 14 Hz, ^2J(PH) = 9 Hz, CH_2]; 2.68 [dd, 2H, ^2J(HH) = 14 Hz, ^2J(PH) = 8 Hz, CH_2]; 2.78 [dd, 2H, ^2J(HH) = 14 Hz, ^2J(PH) = 6 Hz, CH_2]; 2.80 [dd, 2H, ^2J(HH) = 14 Hz, ^2J(PH) = 6 Hz, CH_2]; 7.3–7.8 [m, 20H, Ph]; $\delta(^{31}P) = 3.86$ [m, ^2J(PP) = 61 Hz, ^1J(PtP) = 5255 Hz, PtP trans to O]; 5.48 [m, ^2J(PP) = 61 Hz, ^1J(PtP) = 2044 Hz, PtP trans to Me].

2.3.11. [{$PtMe$(**2**)}$_n$] (**14**)

A solution of complex **11** (25 mg) in CD_2Cl_2 (0.6 mL) was allowed to react over a period of 15 days, while the course of the reaction was monitored by ^{31}P NMR. After 1 day, peaks assigned to [PtMe(**1**)(μ-**2**)$PtMe_2$], **13**, were observed. NMR: $\delta(^{31}P) = 2.86$ [m, ^2J(PP) = 46 Hz, ^1J(PtP) = 5152 Hz, PtP trans to O]; 4.89 [m, ^2J(PP) = 46 Hz, ^1J(PtP) = 2244 Hz, PtP trans to Me]; 5.12 [m, ^1J(PtP) = 2250 Hz, 2PtP trans to Me]. After 15 days, the product appeared to be a mixture of oligomers [{PtMe(**2**)}$_n$] (**14**). The product was precipitated by addition of ether (2 mL). Yield: 35%. *Anal.* Calc. for $C_{30}H_{30}O_2P_2Pt$: C, 53.02; H, 4.45. Found: C, 53.24; H, 4.33%. NMR: $\delta(^{31}P) = 2.83$ [m, ^2J(PP) = 50 Hz, ^1J(PtP) = 5160 Hz, PtP trans to O]; 4.86 [m, ^2J(PP) = 50 Hz, ^1J(PtP) = 2250 Hz, PtP trans to Me].

2.3.12. [{$PdCl$(**2**)}$_n$]

To a solution of Li(**2**) (48 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added a solution of [$PdCl_2$(COD)] (28.5 mg, 0.1 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 2 h. The yellow solid which formed, was separated, washed with water, methanol and ether and dried under vacuum. Yield: 78%. *Anal.* Calc. for $C_{29}H_{27}ClO_2P_2Pd$: C, 56.98; H, 4.45. Found: C, 56.35; H, 4.09%. NMR ($CDCl_3$): $\delta(^{31}P) = 18.8$ [br]; 21.3 [br].

2.3.13. [{$PtCl$(**2**)}$_n$]

This was prepared in a similar way from [$PtCl_2$(COD)]. Yield 82%. *Anal.* Calc. for $C_{29}H_{27}ClO_2P_2Pt$: C, 49.76; H, 3.89. Found: C, 49.38; H, 3.70%. NMR ($CDCl_3$): $\delta(^{31}P) = 4.1$ [br]; 5.8 [br].

2.4. X-ray structure determinations

Data were collected at 150 K using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data

Table 1
Crystal data and structure refinement for complexes **7** and **8** as DMSO solvates

Complex	**7** · 2DMSO	**8** · 2DMSO
Formula	$C_{33}H_{40}Cl_2O_4P_2PdS_2$	$C_{33}H_{40}Cl_2O_4P_2PtS_2$
Formula weight	804.01	892.70
Temperature (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.1153(2)	10.1892(2)
b (Å)	10.3271(2)	10.3810(2)
c (Å)	17.5809(5)	17.7404(4)
α (°)	103.697(1)	102.759(1)
β (°)	96.259(1)	96.590(1)
γ (°)	90.546(1)	90.311(1)
V (Å^3)	1772.48(7)	1817.13(6)
Z	2	2
D_{calc} (Mg/m^3)	1.506	1.632
μ (mm^{-1})	0.918	4.246
Data/restraints/parameter	8135/0/349	8246/0/349
R_1 [$I > 2\sigma(I)$]	0.0497	0.0484
wR_2 [$I > 2\sigma(I)$]	0.1207	0.1190

reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The SHELXTL-NT V6.1 suite of programs was used to solve the structures by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details of the crystal data and refinements are in Tables 1 and 2.

Crystals of **7** · 2DMSO and **8** · 2DMSO were grown from a solution in DMSO/MeCN by slow diffusion of ether. Crystals of **9** · $CHCl_3$ were grown from a solution in MeCN/$CHCl_3$ by slow diffusion of ether. Crystals of **10** were grown from a solution in MeCN/$CHCl_3$ by slow diffusion of ether.

Table 2
Crystal data and structure refinement for complexes **9** and **10**

Complex	**9** · $CHCl_3$	**10**
Formula	$C_{36}H_{35}Cl_3F_6N_2O_8P_2PdS_2$	$C_{60}H_{56}F_6O_{10}P_4PtS_2$
Formula weight	1076.47	717.07
Temperature (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	tetragonal
Space group	$P\bar{1}$	$P4(3)2(1)2$
a (Å)	13.7413(2)	14.3375(1)
b (Å)	13.7647(3)	14.3375(1)
c (Å)	14.0753(3)	29.3277(3)
α (°)	73.850(1)	90
β (°)	71.906(1)	90
γ (°)	62.029(1)	90
V (Å^3)	2207.00(7)	6028.72(9)
Z	2	4
D_{calc} (Mg/m^3)	1.620	1.580
μ (mm^{-1})	0.845	2.579
Data/restraints/parameter	12,666/0/493	5301/0/327
R_1 [$I > 2\sigma(I)$]	0.0448	0.0587
wR_2 [$I > 2\sigma(I)$]	0.0999	0.0779

3. Results and discussion

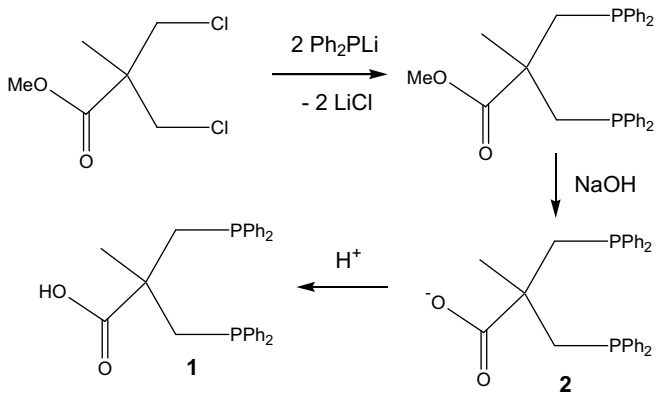
3.1. Synthesis and characterization of ligand 1 and its lithium salt 2

The ligand **1** was prepared by reaction of the methyl ester of 2,2-bis(chloromethyl)propionic acid with lithium diphenylphosphide, followed by hydrolysis of the initial product which is presumed to be the methyl ester, methyl 2,2-bis(diphenylphosphinomethyl)propionate, with sodium hydroxide and acidification to give the desired ligand **1** (Scheme 1). The pure product 2,2-bis(diphenylphosphinomethyl)propionic acid, **1**, was obtained as a colorless solid in 51% yield overall, without isolation or purification of the intermediates (Scheme 1). In the ^{31}P NMR spectrum, ligand **1** gave a singlet resonance at $\delta = -22.17$(s), and in the ^{1}H NMR spectrum the methyl group gave a singlet at $\delta = 1.16$. The ^{1}H NMR resonances of the diastereotopic CH_2 groups were more complex, appearing as an [AB] multiplet, with geminal coupling ^2J(HH) = 14 Hz, and with further coupling to phosphorus.

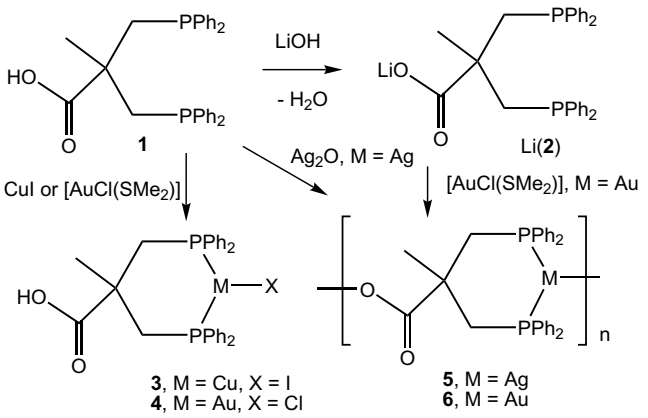
The reaction of ligand **1** with butyllithium gave the corresponding lithium salt, lithium 2,2-bis(diphenylphosphinomethyl)propionate, Li(**2**) (Scheme 2). The lithium salt Li(**2**) was isolated as a white solid which was soluble in chloroform. Its NMR spectra were similar to those of **1**, with minor differences in chemical shift values. For example, the ^{31}P NMR spectrum of Li(**2**) gave a singlet resonance at $\delta = -20.63$.

3.2. Synthesis and characterization of complexes with copper(I), silver(I) and gold(I)

The ligand **1** reacted with copper(I) iodide in acetonitrile solution to give the complex [CuI(**1**)] (**3**), and with [AuCl(SMe_2)] to give [AuCl(**1**)] (**4**), with displacement of SMe_2 (Scheme 2). We were unable to isolate a corresponding silver halide complex in pure form, but reaction of



Scheme 1. Synthesis of ligand **1**.



Scheme 2. Synthesis of Li(**2**) and coinage metal complexes **3**–**6**.

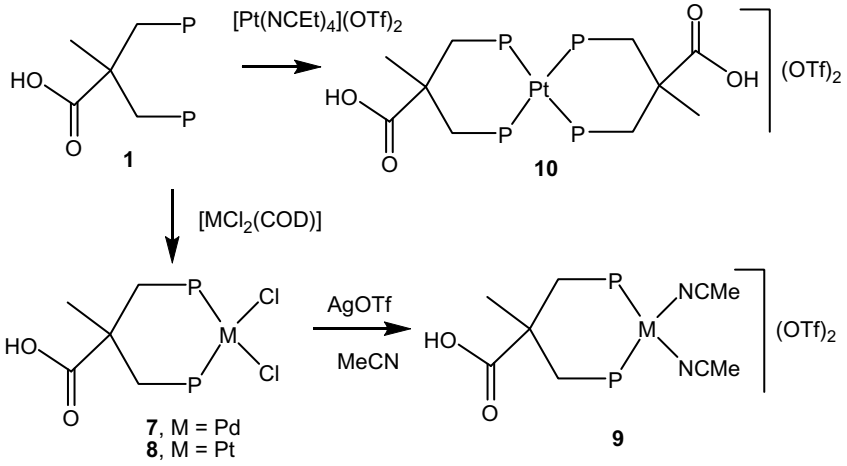
ligand **1** with silver(I) oxide gave the carboxylate complex [Ag(**2**)] (**5**). The related carboxylate complex of gold(I), [Au(**2**)] (**6**), was prepared by reaction of Li(**2**) with [AuCl(SMe_2)], with elimination of lithium chloride and dimethylsulfide (Scheme 2). We were not able to prepare the copper(I) analog of **5** and **6** in pure form, nor were we able to prepare complexes with different ratios of diphosphine ligand **1** or **2** to M (M = Cu, Ag or Au).

The complexes **3**–**6** were sparingly soluble in common organic solvents. The NMR spectra showed the expected resonances but they were much broader than in the precursor compounds **1** or Li(**2**), perhaps as a result of reversible association in solution. The IR spectra of **3** and **4** contained peaks due to ν(OH) in the range 2610–2690 cm^{-1} and ν(C=O) in the range 1675–1680 cm^{-1}, indicating the presence of hydrogen bonding associated with the carboxylic acid groups [13–21]. The copper(I) complex **3** is less soluble than the gold(I) complex **4**, which could indicate higher association of complex **3** through formation of $Cu_2(\mu\text{-}I)_2$ units [27]. In the absence of an X-ray structure determination, the nature of supramolecular association of these complexes remains uncertain.

3.3. Synthesis and characterization of complexes with palladium(II) and platinum(II)

Reaction of ligand **1** with [MCl_2(COD)], M = Pd or Pt, COD = 1,5-cyclooctadiene, occurred by displacement of COD to give the corresponding complexes [MCl_2(**1**)], (**7**, M = Pd; **8**, M = Pt) as shown in Scheme 3. The reaction of **7** with silver triflate in acetonitrile solution gave the complex [Pd($NCMe)_2$(**1**)]$(OTf)_2$, **9** (Scheme 3), with elimination of insoluble silver chloride. The reaction of ligand **1** with [Pt($NCEt)_4$]$(OTf)_2$ occurred with displacement of the propionitrile ligands to give the complex [Pt($\mathbf{1}$)$_2$]$(OTf)_2$, **10** (Scheme 3). These complexes were sparingly soluble, but most were sufficiently soluble to be characterized in solution by ^{1}H and ^{31}P NMR spectroscopy. For example, complex **8** gave a broad singlet in the ^{31}P NMR spectrum, with satellites due to coupling to ^{195}Pt, with ^1J(PtP) = 4210 Hz, typical of complexes with *cis*-[$PtCl_2P_2$] coordination. The broadness of the resonances for complexes **7**, **8** and **10** is tentatively attributed to reversible supramolecular oligomerization in solution, but the compounds were not sufficiently soluble to allow a detailed study by variable temperature NMR. The structures of complexes **7**–**10** (Scheme 3) were confirmed by X-ray structure determinations.

The complexes **7** and **8** were crystallized as the DMSO solvates, and they were isomorphous and isostructural. The structures are shown in Fig. 1 and a comparison of key structural parameters is given in Table 3. In each case, the metal has the expected *cis*-MCl_2P_2 coordination, M = Pd or Pt, and the 6-membered MP_2C_3 chelate ring has the chair conformation (Fig. 1). The M–P distances are slightly shorter and the angle P–M–P is correspondingly slightly greater for M = Pt than for M = Pd (Table 3). There is a hydrogen bond between the carboxylic acid group and a DMSO solvate molecule, with O(7)···O(24A) = 2.599(4) and 2.616(7) Å in **7** and **8**, respectively (Fig. 1, Table 3).



Scheme 3. Synthesis of complexes **7**–**10** (P = PPh_2).

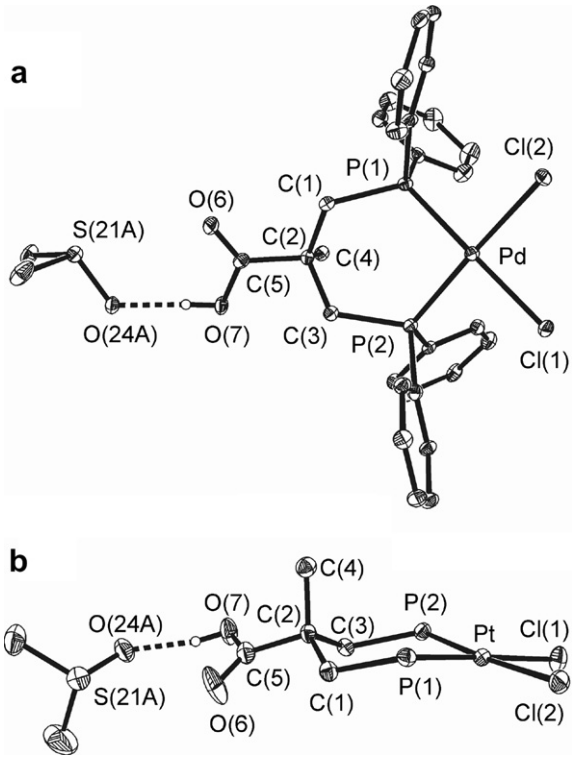


Fig. 1. Structures of (a) complex **7** · DMSO, and (b) complex **8** · DMSO.

Individual cations in complex **9** have a similar structure as in **7**, with palladium(II) centers having the *cis*-PdN2P2 coordination, and with the 6-membered chelate ring in the chair conformation (Fig. 2). However, in complex **9** each carboxylic acid group forms a pairwise hydrogen bond with a neighboring molecule, thus creating a supramolecular dimer (Fig. 2), with distances O(7)···O(6A) = O(7A)···O(6) = 2.653(3) Å.

The platinum center in complex **10** is more distorted from square planar stereochemistry and the 6-membered chelate rings are considerably more twisted, when compared to complex **8** (Fig. 3). These effects appear to arise because of steric congestion between phenyl substituents of the two diphosphine ligands in complex **10**. The carboxylic acid groups on the two diphosphine ligands are mutu-

Table 3
Bond lengths [Å] and angles [°] for complexes **7** · 2DMSO and **8** · 2DMSO

	7 · 2DMSO, M = Pd	**8** · 2DMSO, M = Pt
M–P(1)	2.244(1)	2.230(1)
M–P(2)	2.234(1)	2.220(2)
M–Cl(1)	2.358(1)	2.353(2)
M–Cl(2)	2.337(1)	2.342(2)
P(2)–M–P(1)	93.67(4)	94.72(6)
Cl(2)–M–Cl(1)	91.39(4)	88.67(7)
P(1)–M–Cl(2)	87.72(4)	88.69(6)
P(2)–M–Cl(1)	87.21(4)	87.94(6)
O(7)···O(24A)	2.599(4)	2.616(7)

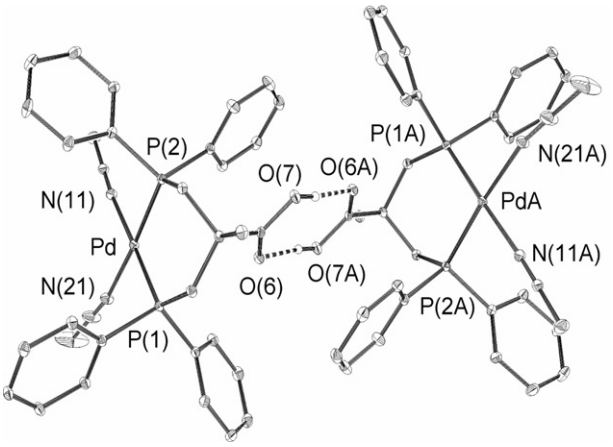


Fig. 2. Structure of the dimer of cations $[Pd(NCMe)_2(\mathbf{1})]^{2+}$ in complex **9**. Selected bond parameters: Pd–N(11) 2.091(2); Pd–N(21) 2.103(2); Pd–P(2) 2.2414(6); Pd–P(1) 2.2534(7) Å; N(11)–Pd–N(21) 85.88(9); N(11)–Pd–P(2) 88.80(6); N(21)–Pd–P(1) 92.19(7); P(2)–Pd–P(1) 93.14(2)°; O(7)···O(6A) 2.653(3) Å.

ally *anti* and there is a 2-fold symmetry axis containing the platinum atom which makes the diphosphine ligands crystallographically equivalent (Fig. 3a). In complex **10**, each carboxylic acid group forms a hydrogen bond to a triflate anion, with O(16)···O(32) = O(16A)···O(32A) = 2.748 (8) Å (Fig. 3b).

The reaction of ligand **1** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gave the dimethylplatinum(II) complex $[PtMe_2(\mathbf{1})]$, **11** (Scheme 4). One methylplatinum group was easily cleaved from

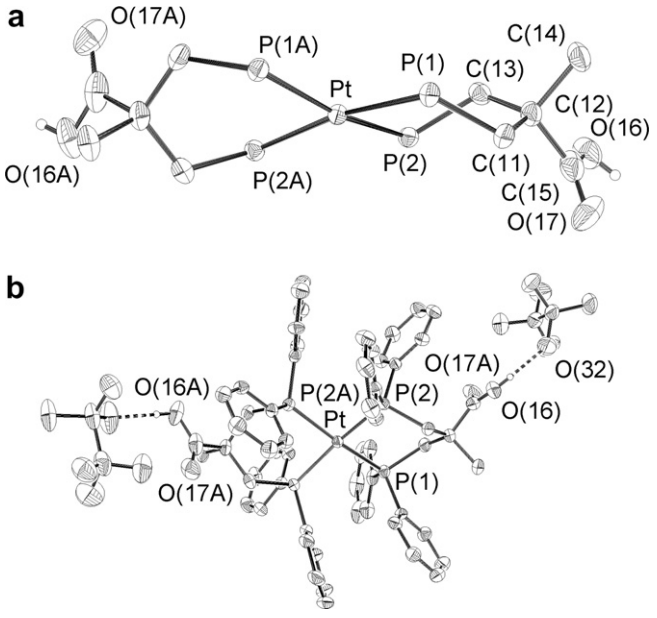
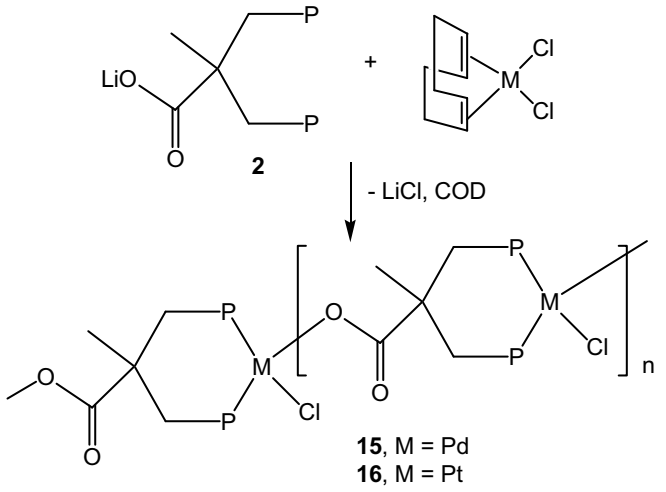


Fig. 3. The structure of complex **10**: (a) an individual cation, with phenyl groups omitted for clarity; (b) the complete structure with phenyl groups and hydrogen bonded triflate groups included. Selected bond parameters: Pt–P(2) 2.347(1); Pt–P(1) 2.360(1) Å; P(2)–Pt–P(2A) 93.26(8)°; P(2)–Pt–P(1) 87.60(5)°; P(1)–Pt–P(1A) 93.38(7)°; O(16)···O(32) 2.748(8) Å. Symmetry transformations used to generate equivalent atoms: A, $y+1$, $x-1$, $-z$.

complex **11** by triflic acid to give methane and the aqua complex [PtMe(OH_2)(**1**)], **12** (Scheme 4). The carboxylic acid group in **11** was less reactive than triflic acid, but it did react slowly over a period of several days to cleave a methylplatinum group. The initial product is proposed to be the binuclear complex **13** and then further reaction occurred to give oligomeric complexes **14** (Scheme 4).

The complexes **11**–**14** were characterized by their spectroscopic properties. For example, complex **11** gave a single methylplatinum resonance in the ^{1}H NMR, and a single resonance in the ^{31}P NMR at $\delta(^{31}P) = 4.83$, with characteristic coupling $^1J(PtP) = 2264$ Hz, in the range expected for a phosphorus atom *trans* to a methyl group [12,28]. The less symmetrical complex **12** gave two resonances in the ^{31}P NMR, one with a low value of the coupling constant $^1J(PtP) = 2044$ Hz, for the phosphorus *trans* to methyl, and the other with a much higher value of $^1J(PtP) = 5255$ Hz, for the phosphorus *trans* to the oxygen atom of the aqua ligand. The oligomeric complex **14** appears to form by stepwise intermolecular elimination of methane as shown in Scheme 4. In the ^{31}P NMR, there are a series of overlapping resonances with $^1J(PtP)$ ca. 2250 Hz and another series with $^1J(PtP)$ ca. 5160 Hz, which are assigned to phosphorus atoms *trans* to methyl and oxygen, respectively [12,28,29].

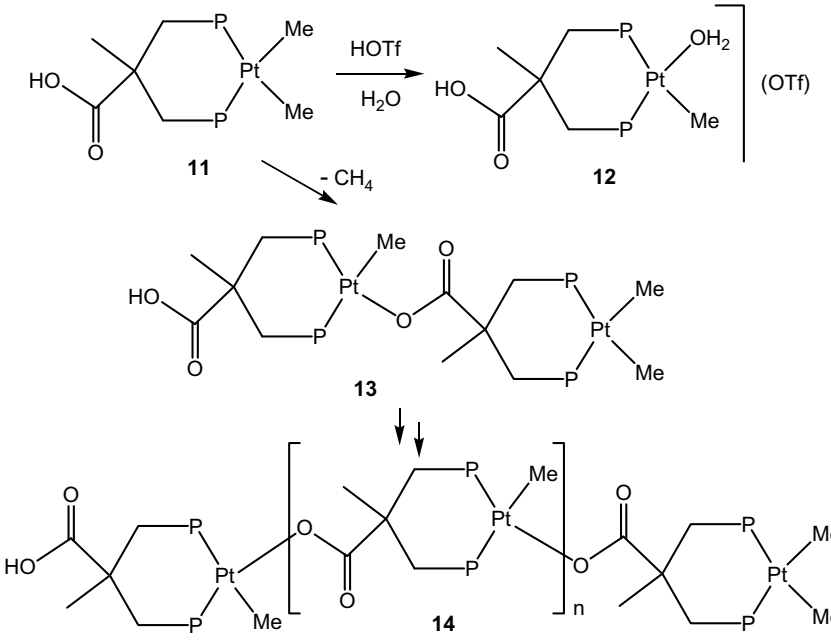
Very sparingly soluble oligomeric complexes [{MCl(**2**)}$_n$], **15**, M = Pd; **16**, M = Pt, were prepared by reaction of the salt Li(**2**) with the complexes [MCl_2(COD)], with elimination of LiCl and 1,5-cyclooctadiene, as shown in Scheme 5. The complexes were isolated in analytically pure form but they were insufficiently soluble to give good NMR spectra, so the proposed structures are tentative.



Scheme 5. P = PPh_2. Oligomeric chloro derivatives of palladium and platinum.

4. Conclusions

The ligand 2,2-bis(diphenylphosphinomethyl)propionic acid, **1**, acts primarily as a chelating diphosphine ligand in neutral solution. An indication of the low tendency of the carboxylic acid group to coordinate (with deprotonation) is illustrated by the reaction of [$PdCl_2$(**1**)] with silver triflate in acetonitrile solution to give the cationic complex [Pd($NCMe)_2$(**1**)]$^{2+}$, in which the ligand **1** did not undergo deprotonation. The carboxylic acid group in complexes of **1** took part in hydrogen bonding. However, the familiar dimerization by self-association between pairs of carboxylic acid units was observed only in the complex



Scheme 4. Methylplatinum complexes.

$[Pd(NCMe)_2(\mathbf{1})]^{2+}$. In other cases, the carboxylic acid group in **1** formed a hydrogen bond to a solvent molecule or to a triflate anion. Thus, as seen also in related studies, there is a fine balance between the different possible modes of hydrogen bonding, and so it is difficult to predict the nature of the supramolecular association [15].

The ligand **1** can be deprotonated by base to give the corresponding carboxylate anion **2**, which appears to act as a bridging tridentate diphosphine–carboxylate ligand in all cases studied. The complexes formed are oligomeric or polymeric in nature and so definitive structural characterization of these complexes of **2** proved to be difficult. An interesting case was discovered in the case of the complex $[PtMe_2(\mathbf{1})]$, which underwent slow intermolecular elimination of methane to give the oligomeric complex $[\{PtMe(\mathbf{2})\}_n]$ (Scheme 4).

Acknowledgements

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Appendix A. Supplementary material

CCDC 654076, 654077, 654078 and 654079 contain the supplementary crystallographic data for **7**, **8**, **9** and **10**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.08.032.

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