Inorganica Chimica Acta, *168* (1990) 255–264

Preparation and Structural Characterization of Rhodium and Palladium Complexes of Mixed Phosphine/Amine Ligands with Methylene Spacers between Donor Atoms

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(Received July 24, 1989; revised September 26, 1989)

Abstract

The condensation of paraformaldehyde with diphenylphosphine and diphenylamine yields $Ph_2PCH_2NPh_2$ (**1**), with diphenylphosphine and aniline yields $Ph_2PCH_2N(Ph)CH_2PPh_2$ (**3**), with phenylphosphine and diphenyl amine yields $Ph_2NCH_2P(Ph)NPh_2$ (**2**) and with diphenylphosphine and ethylenediamine yields $(Ph_2PCH_2)_2N(CH_2)_2N(CH_2PPh_2)_2$ (**4**). Reactions of **1** and **2** with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ yield yellow $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ (**5**) and $Rh\{(Ph_2NCH_2)_2PPh\}_2(CO)Cl$ (**6**), respectively. X-ray diffraction studies show that these have planar $RhP_2(CO)Cl$ cores with the nitrogen atoms uncoordinated. Reactions of **3** and **4** with $(PhCN)_2PdCl_2$ yields complexes with bidentate P,P chelate rings. The X-ray crystal structures of $Pd\{(Ph_2PCH_2)_2NPh\}Cl_2$ and $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ are reported. In the latter the two planar PdP_2I_4 coordination units are widely separated (Pd···Pd, 10.197(1) Å).

Introduction

Polydentate phosphine ligands with methylene spacers between the donor atoms are useful backbones for the construction of polynuclear transition metal complexes [1]. The methylene group provides the proper separation and flexibility between the donor centers so that metal–metal distances in such complexes can span the range involved in metal–metal bonding and metal–ligand–metal bridged bonding. Bis(diphenylphosphino)methane has been widely exploited in this fashion [2] while (diphenylarsino)(diphenylphosphino)methane has been used in the rational synthesis of heterobinuclear complexes [3]. Bis(diphenylphosphinomethyl)phenylphosphine has been shown to form a rich array of trinuclear rhodium complexes [4]. Bis(diphenylphosphinomethyl)phenylarsine has been developed as a backbone for the formation of metallomacrocycles which can be converted into heterotrinuclear complexes involving both arrays of transition metal ions and arrays of transition metal and main group ions [5].

The preparation of new polydentate phosphine ligands with methylene spacers presents something of a synthetic challenge since one of the frequently used methods in the construction of other polydentate phosphine ligands, the addition of a P–H bond to an olefin [6], is clearly not applicable to this class of ligands.

Here we report the preparation and structural characterization of rhodium and palladium complexes of some polydentate ligands involving alternating phosphorus and nitrogen donors separated by methylene groups. These are obtained by condensation of an N–H and a P–H group with paraformaldehyde. Several examples of this version of the Mannich reaction have been used to form mixed amine/phosphine compounds [7–11] but the mode of the metal ion coordination of such ligands has not been explored.

Results

Heating a mixture of diphenylamine, diphenylphosphine and paraformaldehyde in toluene in a manner similar to that devised by Maier [7] for the corresponding reaction involving diethylamine, yields a colorless solution from which $Ph_2PCH_2NPh_2$ (**1**) is obtained as colorless crystals after evaporation and crystallization from dichloromethane/ethanol. Similar reactions of diphenylamine and phenylphosphine and of diphenylphosphine and aniline with paraformaldehyde yield $Ph_2NCH_2P(Ph)CH_2NPh_2$ (**2**) and $Ph_2PCH_2N(Ph)CH_2PPh_2$ (**3**), respectively. The hexadentate $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ (**4**) was obtained by the same procedure, which is similar to that used by Grim and Matienzo [8] to obtain this ligand. The ^{31}P NMR spectrum of each ligand consists of a single sharp resonance. The ^1H NMR spectra show complex multiplets in the phenyl region, but more informative and characteristic resonances for the methylene protons (see 'Experimental').

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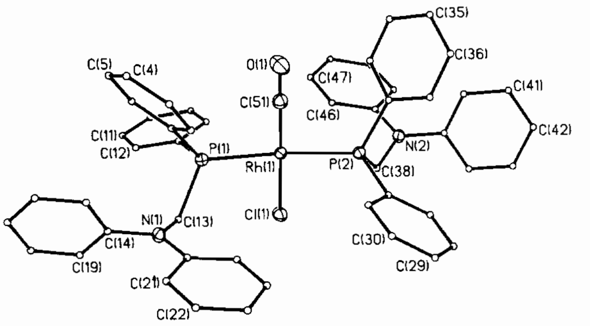

Fig. 1. A perspective view of $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ (5).

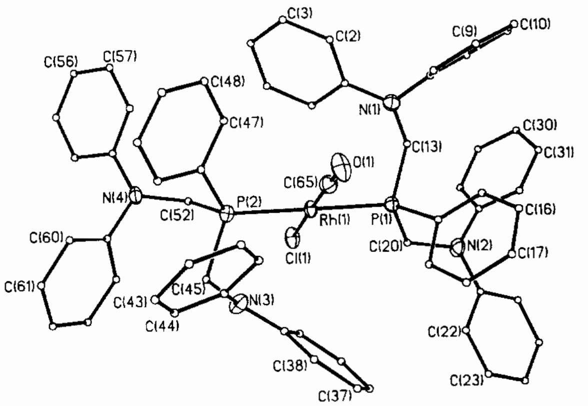

Fig. 2. A perspective view of $Rh(Ph_2NCH_2P(Ph)CH_2NPh_2)_2$-(CO)Cl (6).

As expected, soft metal ions coordinate preferentially to the phosphorus atoms of these ligands while the nitrogen atoms are left uncoordinated. Treatment of $Rh_2(CO)_4(\mu\text{-}Cl)_2$ with four equivalents of $Ph_2PCH_2NPh_2$ yields yellow $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ (5) whose structure is shown in Fig. 1. The complex has the usual planar geometry associated with complexes containing a $RhP_2(CO)Cl$ core [14]. Essential interatomic distances and angles are presented in Table 1. The $Ph_2PCH_2NPh_2$ acts as a monodentate ligand binding solely through phosphorus. The Rh···N distances (4.480(3), 4.559(3) Å) are clearly non-bonding. Similarly, $Ph_2NCH_2P(Ph)CH_2NPh_2$ reacts with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ yielding yellow Rh-$\{(Ph_2NCH_2)_2PPh\}_2(CO)Cl$ (6) whose structure is shown in Fig. 2 with interatomic distances and angles given in Table 1. Again the structure consists of a planar $RhP_2(CO)Cl$ core with each of the phosphine ligands acting as a monodentate ligand. Despite the considerable bulk of these ligands, there is no distortion of the rhodium coordination geometry. The Rh···N separations (3.672(4) to 4.853(4) Å) are in the non-bonding range. Atomic coordinates for **5** and **6** are given in Tables 2 and 3 respectively.

The disposition of the phosphorus atoms in $Ph_2PCH_2N(Ph)CH_2PPh_2$ and in $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ allows these to form nearly strain-free, six-membered chelate rings in which the nitrogen atoms are uncoordinated. Addition of $(PhCN)_2PdCl_2$ to $(Ph_2PCH_2)_2NPh$ yields yellow $Pd\{(Ph_2PCH_2)_2NPh\}Cl_2$ (7). Its structure is shown in Fig. 3 and essential interatomic distances and angles are given in Table 4. Atomic coordinates for 7 are given in Table 5. The complex consists of a planar PdP_2Cl_2 core with the phosphine ligand adopting a flattened boat conformation that is similar to that seen in the related $Ph\{(Ph_2PCH_2)PPh\}Cl_2$ [12]. The dimensions of the complex are entirely normal. The long Pd···N separation of 3.740(2) Å precludes the existence of a bond between these atoms.

TABLE 1. Selected interatomic distances and angles in the rhodium complexes

	$Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ (5)	$Rh\{(Ph_2NCH_2)_2PPh\}_2(CO)Cl$ (6)
Distances (Å)		
Rh–P(1)	2.331(1)	2.299(2)
Rh–P(2)	2.325(2)	2.307(2)
Rh–Cl(1)	2.352(1)	2.377(2)
Rh–C	1.791(5)	1.809(8)
Rh···N(1)	4.480(3)	3.672(4)
Rh···N(2)	4.559(3)	4.853(4)
Rh···N(3)		3.699(4)
Rh···N(4)		4.829(4)
Angles (°)		
P(1)–Rh–P(2)	175.3(1)	180.0(2)
Cl(1)–Rh–C	175.5(1)	178.2(3)
P(1)–Rh–Cl(1)	87.0(1)	90.6(1)
P(1)–Rh–C	92.4(2)	87.6(3)
P(2)–Rh–Cl(1)	88.6(1)	89.5(1)
P(2)–Rh–C	92.1(2)	92.3(3)

TABLE 2. Atom coordinates (×10^4) and isotropic thermal parameters (Å^2 × 10^3) for $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ (5)

	x	*y*	*z*	U^a
Rh(1)	3630(1)	6724(1)	6102(1)	13(1)*
P(1)	4348(1)	6772(1)	5124(1)	14(1)*
P(2)	2886(1)	6563(1)	7044(1)	15(1)*
Cl(1)	3753(1)	5264(1)	6066(1)	24(1)*
N(1)	3465(3)	6252(2)	3467(2)	17(1)*
N(2)	3664(2)	59095(3)	8671(2)	17(1)*
O(1)	3638(3)	8561(2)	6258(2)	33(2)*
C(1)	4254(3)	7758(3)	4575(3)	18(1)
C(2)	3439(3)	8132(3)	4309(3)	18(1)
C(3)	3309(3)	8894(3)	3905(3)	23(1)
C(4)	3984(3)	9293(3)	3743(3)	30(1)
C(5)	4792(4)	8930(4)	4004(3)	35(1)
C(6)	4930(3)	8171(3)	4421(3)	25(1)
C(7)	5496(3)	6551(3)	5584(3)	14(1)
C(8)	5833(3)	6493(3)	6450(3)	26(1)
C(9)	6695(4)	6285(3)	6819(4)	34(1)
C(10)	7229(4)	6140(3)	6351(3)	28(1)
C(11)	6899(3)	6210(3)	5505(3)	24(1)
C(12)	6041(3)	6408(3)	5123(3)	19(1)
C(13)	4014(3)	5959(3)	4265(3)	17(1)
C(14)	3884(3)	6471(3)	2870(3)	17(1)
C(15)	3837(3)	7281(3)	2575(3)	23(1)
C(16)	4254(3)	7492(3)	2009(3)	24(1)
C(17)	4727(3)	6898(3)	1754(3)	27(1)
C(18)	4756(3)	6092(3)	2043(3)	29(1)
C(19)	4336(3)	5872(3)	2600(3)	24(1)
C(20)	2569(3)	6252(3)	3261(3)	14(1)
C(21)	2040(3)	6425(3)	2456(3)	20(1)
C(22)	1153(3)	6395(3)	2239(3)	24(1)
C(23)	762(4)	6191(3)	2821(3)	28(1)
C(24)	1279(3)	6027(3)	3626(3)	27(1)
C(25)	2175(3)	6062(3)	3853(3)	24(1)
C(26)	1751(3)	6309(3)	6529(3)	16(1)
C(27)	1247(3)	5866(3)	6904(3)	23(1)
C(28)	378(3)	5735(3)	6494(3)	26(1)
C(29)	−1(4)	6069(3)	5712(3)	32(1)
C(30)	482(3)	6535(3)	5338(3)	30(1)
C(31)	1361(3)	6635(3)	5742(3)	23(1)
C(32)	2839(3)	7475(3)	7678(3)	16(1)
C(33)	3592(3)	7925(3)	8031(3)	19(1)
C(34)	3581(3)	8646(3)	8482(3)	20(1)
C(35)	2822(3)	8915(3)	8590(3)	23(1)
C(36)	2070(3)	8461(3)	8246(3)	23(1)
C(37)	2078(3)	7743(3)	7794(3)	20(1)
C(38)	3311(3)	5682(3)	7807(3)	19(1)
C(39)	3107(3)	5956(3)	9164(3)	15(1)
C(40)	3132(3)	6641(3)	9663(3)	20(1)
C(41)	2623(3)	6668(3)	10174(3)	24(1)
C(42)	2060(3)	6017(3)	10165(3)	22(1)
C(43)	2019(3)	5345(3)	9643(3)	21(1)
C(44)	2540(3)	5315(3)	9149(3)	18(1)
C(45)	4544(3)	6091(3)	9004(3)	15(1)
C(46)	5033(3)	6302(3)	8497(3)	23(1)
C(47)	5913(3)	6466(3)	8841(3)	27(1)
C(48)	6319(4)	6412(3)	9688(3)	28(1)
C(49)	5835(3)	6198(3)	10191(3)	23(1)
C(50)	4961(3)	6037(3)	9859(3)	19(1)
C(51)	3621(3)	7838(3)	6184(3)	20(1)

^{a}Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Atom coordinates (×10^4) and isotropic thermal parameters (Å^2 × 10^3) for $Rh\{(Ph_2NCH_2)_2PPh\}_2(CO)Cl$ (6)

	x	*y*	*z*	U^a
Rh(1)	2454(1)	7110(1)	6426(1)	17(1)*
P(1)	1419(1)	5870(2)	6715(1)	18(1)*
P(2)	3495(1)	8350(2)	6136(1)	19(1)*
N(1)	341(4)	5358(6)	6050(2)	23(2)*
N(2)	544(4)	5624(6)	7379(2)	25(2)*
N(3)	5079(4)	7496(6)	6580(2)	23(2)*
N(4)	3591(4)	10704(6)	5807(2)	24(2)*
O(1)	3027(4)	4857(5)	6043(2)	34(2)*
Cl(1)	1942(1)	8878(2)	6744(1)	25(1)*
C(1)	439(5)	6267(7)	5782(2)	25(2)
C(2)	472(5)	5958(8)	5412(2)	29(2)
C(3)	551(6)	6861(8)	5146(2)	36(2)
C(4)	625(6)	8108(8)	5241(2)	38(2)
C(5)	610(6)	8413(8)	5611(2)	35(2)
C(6)	519(5)	7518(7)	5880(2)	27(2)
C(7)	98(5)	4115(7)	5946(2)	21(2)
C(8)	768(6)	3319(7)	5823(2)	27(2)
C(9)	530(6)	2100(8)	5745(2)	30(2)
C(10)	−379(6)	1654(8)	5793(2)	36(2)
C(11)	−1036(7)	2455(8)	5918(2)	43(2)
C(12)	−823(6)	3694(8)	5991(2)	31(2)
C(13)	250(5)	5678(7)	6434(2)	20(2)
C(14)	1861(5)	4330(7)	6832(2)	20(2)
C(15)	1355(5)	3240(7)	6774(2)	21(2)
C(16)	1755(5)	2110(8)	6879(2)	30(2)
C(17)	2671(5)	2057(8)	7049(2)	30(2)
C(18)	3196(6)	3110(7)	7108(2)	32(2)
C(19)	2811(5)	4265(7)	6997(2)	25(2)
C(20)	1046(5)	6493(7)	7154(2)	20(2)
C(21)	930(5)	5263(7)	7727(2)	18(2)
C(22)	1922(5)	5263(7)	7832(2)	25(2)
C(23)	2263(6)	4972(8)	8186(2)	37(2)
C(24)	1657(6)	4654(8)	8454(2)	38(2)
C(25)	694(6)	4600(7)	8346(2)	32(2)
C(26)	327(6)	4896(7)	7995(2)	27(2)
C(27)	−405(5)	5304(7)	7248(2)	22(2)
C(28)	−1092(6)	6193(8)	7154(2)	31(2)
C(29)	−2002(6)	5895(8)	6996(2)	39(2)
C(30)	−2217(7)	4656(8)	6938(2)	40(2)
C(31)	−1557(6)	3741(8)	7042(2)	37(2)
C(32)	−650(5)	4065(7)	7198(2)	23(2)
C(33)	4857(5)	6982(7)	6917(2)	20(2)
C(34)	4179(5)	7524(7)	7119(2)	22(2)
C(35)	4005(5)	7037(8)	7463(2)	29(2)
C(36)	4505(6)	6033(8)	7604(2)	30(2)
C(37)	5180(5)	5480(8)	7406(2)	28(2)

(continued)

TABLE 3. *(continued)*

	x	y	z	U^a
C(38)	5356(6)	5954(7)	7067(2)	27(2)
C(39)	5695(5)	6816(7)	6342(2)	23(2)
C(40)	5389(6)	5685(8)	6197(2)	39(2)
C(41)	5944(7)	5128(10)	5946(3)	54(3)
C(42)	6754(8)	5678(10)	5857(3)	61(3)
C(43)	7071(8)	6784(9)	6008(3)	59(3)
C(44)	6518(6)	7372(8)	6254(2)	41(2)
C(45)	4647(5)	8643(7)	6429(2)	24(2)
C(46)	3813(5)	7834(7)	5688(2)	22(2)
C(47)	3109(6)	7206(8)	5462(2)	32(2)
C(48)	3305(7)	6819(9)	5112(3)	48(3)
C(49)	4195(7)	7012(9)	4998(3)	53(3)
C(50)	4894(7)	7635(8)	5212(2)	46(3)
C(51)	4691(6)	8069(7)	5558(2)	30(2)
C(52)	3040(5)	9942(7)	6043(2)	22(2)
C(53)	3107(5)	11277(7)	5492(2)	24(2)
C(54)	3169(5)	12536(7)	5436(2)	26(2)
C(55)	2641(6)	13078(8)	5133(2)	37(2)
C(56)	2055(6)	12380(8)	4894(2)	39(2)
C(57)	2035(7)	11113(9)	4940(3)	43(2)
C(58)	2561(6)	10562(8)	5241(2)	35(2)
C(59)	4447(5)	11258(7)	5972(2)	23(2)
C(60)	5256(6)	11195(8)	5778(2)	33(2)
C(61)	6130(7)	11652(9)	5937(3)	50(3)
C(62)	6195(7)	12140(10)	6283(3)	57(3)
C(63)	5406(7)	12261(9)	6467(3)	50(3)
C(64)	4506(7)	11801(8)	6320(2)	43(2)
C(65)	2816(5)	5735(7)	6191(2)	23(2)

[a]Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

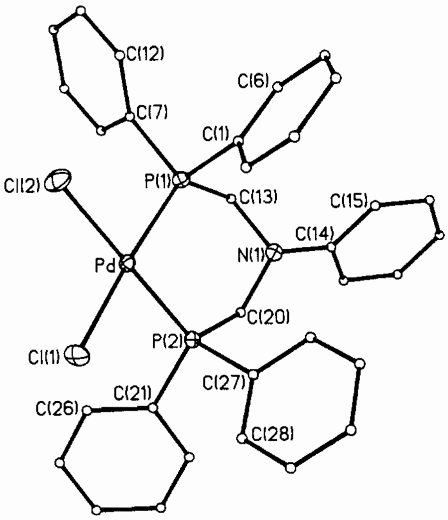

Fig. 3. A perspective view of Pd$\{(Ph_2PCH_2)_2NPh\}Cl_2$ (7).

The reaction between $(PhCN)_2PdCl_2$ and $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ yields yellow $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2Cl_4$. Treatment of this with sodium iodide converts it into orange $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ (8) whose structure is shown in Fig. 4. Atomic coordinates are given in Table 6. It is a centrosymmetric dimer with two chelating NC_2P_2Pd rings. Again the nitrogen atoms are uncoordinated. Interatomic dimensions are collected in Table 4. The chelate rings adopt a flattened boat conformation with only the nitrogen atom substantially out of the plane formed by the C_2P_2Pd unit. The coordination about palladium in 8 is somewhat distorted from planarity, much more so than that seen in 7. Thus the *trans* P–Pd–I angles (165.5(1), 172.2(1)°) are significantly bent. This may be caused by the larger size of the iodide ligands, but the I–Pd–I angle is only slghtly wider than 90°.

The two palladium centers are relatively removed from one another and are non-interacting except for the ligand bridge. The relationship between these two units is best appreciated by turning to the stereoscopic view shown in Fig. 5. The Pd···Pd

TABLE 4. Selected interatomic distances and angles in the palladium complexes

	Pd$\{(Ph_2PCH_2)_2NPh\}Cl_2$ (7)	$Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ (8)
Distances (Å)		
Pd–P(1)	2.243(2)	2.285(2)
Pd–P(2)	2.239(2)	2.268(2)
Pd–hal(1)	2.340(2)	2.655(1)
Pd–hal(2)	2.362(2)	2.650(1)
Pd···N	3.740(2)	3.626(2)
Pd···Pd′		10.197(1)
Angles (°)		
P(1)–Pd–hal(1)	171.9(1)	165.5(1)
P(2)--Pd–hal(2)	175.9(1)	172.2(1)
P(1)–Pd–P(2)	94.0(1)	94.9(1)
P(1)–Pd–hal(2)	87.4(1)	88.7(1)
P(2)–Pd–hal(1)	86.9(1)	86.8(1)
hal(1)–Pd–hal(2)	91.2(1)	91.5(1)

TABLE 5. Atom coordinates (×10^4) and isotropic thermal parameters ($Å^2$ × 10^3) for $Pd\{(Ph_2PCH_2)_2NPh\}Cl_2$ (7)

	x	y	z	U^a
Pd	2711(1)	4847(1)	3630(1)	11(1)*
P(1)	2810(1)	4583(1)	1398(2)	12(1)*
P(2)	3465(1)	4043(1)	4341(2)	11(1)*
Cl(1)	2661(1)	5349(1)	5915(2)	21(1)*
Cl(2)	1945(1)	5808(1)	2931(2)	24(1)*
Cl(3)	4487(1)	858(2)	4405(2)	42(1)*
Cl(4)	4674(1)	−426(2)	2051(3)	69(1)*
N(1)	3793(2)	3688(4)	1753(5)	13(1)
C(1)	3056(2)	5763(5)	680(6)	13(1)
C(2)	3167(3)	6597(5)	1520(7)	22(2)
C(3)	3360(3)	7494(6)	998(7)	26(2)
C(4)	3450(3)	7562(6)	−399(7)	24(2)
C(5)	3344(3)	6708(5)	−1237(7)	21(1)
C(6)	3152(3)	5819(5)	−706(7)	20(1)
C(7)	2213(3)	4195(5)	366(7)	17(1)
C(8)	2042(3)	3175(5)	461(6)	15(1)
C(9)	1593(3)	2831(5)	−274(7)	21(1)
C(10)	1302(3)	3503(5)	−1139(7)	23(2)
C(11)	1466(3)	4515(6)	−1271(7)	24(2)
C(12)	1922(3)	4861(6)	−494(7)	23(2)
C(13)	3276(2)	3589(5)	927(6)	14(1)
C(14)	4237(3)	3392(5)	1010(7)	16(1)
C(15)	4387(3)	4070(5)	13(7)	18(1)
C(16)	4820(3)	3838(5)	−720(7)	20(1)
C(17)	5111(3)	2970(5)	−445(7)	23(2)
C(18)	4965(3)	2294(6)	531(7)	24(2)
C(19)	4522(3)	2488(5)	1248(7)	22(2)
C(20)	3774(3)	3210(5)	3112(6)	13(1)
C(21)	3445(2)	3190(5)	5793(6)	13(1)
C(22)	3916(3)	2781(5)	6414(7)	17(1)
C(23)	3913(3)	2143(5)	7540(7)	19(1)
C(24)	3431(3)	1906(6)	8064(7)	23(2)
C(25)	2968(3)	2302(5)	7474(7)	19(1)
C(26)	2968(3)	2926(5)	6316(7)	17(1)
C(27)	3967(2)	5009(5)	4842(6)	14(1)
C(28)	4079(3)	5266(5)	6222(6)	18(1)
C(29)	4446(3)	6023(5)	6593(7)	20(1)
C(30)	4699(3)	6543(5)	5604(7)	22(2)
C(31)	4585(3)	6296(6)	4230(7)	23(2)
C(32)	4222(3)	5524(5)	3843(7)	19(1)
C(33)	4293(4)	−238(7)	3444(9)	43(2)

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 6. Atom coordinates (×10^4) and isotropic thermal parameters ($Å^2$ × 10^3) for $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ (8)

	x	y	z	U^a
Pd	4158(1)	2205(1)	869(1)	12(1)*
I(1)	2866(1)	1313(1)	466(1)	23(1)*
I(2)	4058(1)	1549(1)	2009(1)	19(1)*
P(1)	5008(1)	3203(1)	1277(1)	13(1)*
P(2)	4331(1)	2604(1)	−147(1)	14(1)*
N(1)	5268(4)	3893(3)	130(3)	16(2)*
C(1)	5734(4)	2943(4)	1903(3)	14(1)
C(2)	6462(4)	2491(4)	1762(3)	20(2)
C(3)	7002(5)	2266(4)	2241(3)	21(2)
C(4)	6842(5)	2481(4)	2856(3)	20(2)
C(5)	6131(5)	2918(4)	3003(3)	22(2)
C(6)	5568(5)	3148(4)	2532(3)	22(2)
C(7)	4320(4)	4003(4)	1583(3)	13(1)
C(8)	4648(5)	4741(4)	1811(3)	18(2)
C(9)	4113(5)	5368(4)	2000(3)	20(2)
C(10)	3247(5)	5270(5)	1954(3)	25(2)
C(11)	2907(5)	4538(5)	1744(4)	27(2)
C(12)	3448(5)	3917(4)	1560(3)	21(2)
C(13)	5704(4)	3761(4)	724(3)	16(1)
C(14)	5338(4)	4719(4)	−136(3)	15(1)
C(15)	5294(4)	3193(4)	−282(3)	14(1)
C(16)	3551(4)	3299(4)	−466(3)	16(1)
C(17)	2871(5)	3543(4)	−90(4)	21(2)
C(18)	2327(5)	4153(5)	−308(4)	31(2)
C(19)	2455(6)	4511(6)	−896(4)	39(2)
C(20)	3105(5)	4243(5)	−1273(4)	30(2)
C(21)	3658(5)	3651(4)	−1065(3)	23(2)
C(22)	4427(4)	1736(4)	−662(3)	17(1)
C(23)	3922(4)	1613(4)	−1204(3)	17(1)
C(24)	4032(5)	912(4)	−1566(4)	23(2)
C(25)	4629(5)	333(4)	−1413(3)	23(2)
C(26)	5124(5)	443(5)	−883(4)	28(2)
C(27)	5024(5)	1141(4)	−517(3)	20(2)

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

separation is 10.197(1) Å which appears to be close to the maximal separation that this chelate geometry can allow. This orientation allows ample space for the phenyl substituents. It is clear that phenyl–phenyl contacts will increase if the two metal centers were to be brought closer together.

The uncoordinated nitrogen atoms of all four of these structures have the potential for coordinating other, hard metal centers, but they clearly avoid binding to the relatively soft metal ions used here. Attempts to obtain polynuclear species using these complexes are planned.

Experimental

Preparation of Compounds

All reactions were carried out under dry nitrogen. Toluene was deoxygenated by freeze–pump–thawing, and all other solvents were used as purchased. Diphenylphosphine, phenylphosphine, paraformaldehyde, ethylenediamine, and diphenylamine were purchased from Aldrich and used with no further purification. Aniline (Mallinkroft) was distilled to eliminate oxide that had formed. All ^{31}P NMR spectra were recorded on either a Nicolet NT-200 spectrometer operating at a frequency of 80.98 MHz or a GE QE-300 spectrometer operating at a frequency of 121 MHz, in $CDCl_3$ as a solvent and phosphoric acid as an external reference. All proton spectra were recorded on a GE QE-300 spectrometer in $CDCl_3$ using TMS as an internal reference.

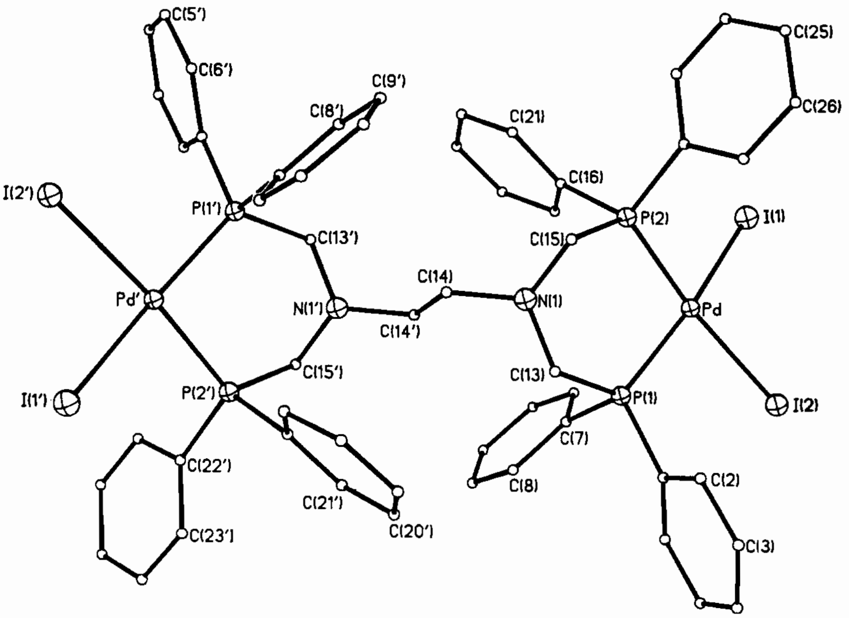

Fig. 4. A perspective view of $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ (8).

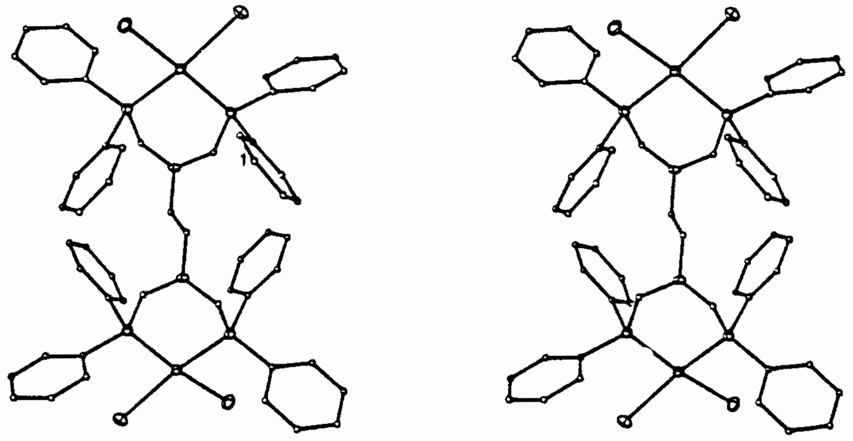

Fig. 5. A stereoscopic view of $Pd_2\{(Ph_2PCH_2)_2NCH_2\}_2I_4$ (8).

(Diphenylamino)(diphenylphosphino)methane, $(C_6H_5)_2NCH_2P(C_6H_5)_2$ (1)

Diphenylphosphine, 1.1 g (5.92 mmol), was added to mixture of 1 g (5.92 mmol) of diphenylamine and 0.5 g of paraformaldehyde in 30 ml of toluene at 65 °C. This mixture was stirred until all the solid paraformaldehyde disappeared (about 4–5 h). This solution was allowed to cool and then filtered through celite. The solvent was removed by rotary evaporation, leaving a clear oil or a colorless solid. This was dissolved in *c.* 10 ml of methylene chloride. Ethanol (*c.* 30 ml) was added to this solution and it was mixed thoroughly. The flask containing this solution was then evacuated and filled with nitrogen. At this point a white crystalline solid formed and the flask was cooled to −20 °C overnight to allow for complete precipitation. The white crystalline product was collected on a glass frit, washed with small portions of ethanol and vacuum dried; yield 1.45 g (67%). Melting point (m.p.) 92–94 °C, NMR $^{31}P\{^1H\}$, δ, −23.4 ppm; ^1H (CH_2) d 4.53 ppm (J(P–H) = 4.93 Hz).

Bis(diphenylphosphinomethyl)phenylamine, $([C_6H_5)_2PCH_2]_2NC_6H_5)$ (2)

Aniline, 1.07 g (10.9 mmol), and 4.06 g (21.8 mmol) of diphenylphosphine were added by syringe into a Schlenk flask containing 40 ml of toluene and 0.5 g of paraformaldehyde at 65 °C. This mixture was stirred at 65 °C until the solid paraformaldehyde completely disappeared (about 4–5 h). The product was obtained from this mixture using the procedure described for **1**; yield 3.5 g (67%). m.p. 109–112 °C (dec.), NMR $^{31}P\{^1H\}$ δ, −27 ppm; $^1H(CH_2)$ d 3.94 ppm. (J(P–H) 4.40 Hz).

Bis(diphenylaminomethyl)phenylphosphine, $([(C_6H_5)_2NCH_2]_2PC_6H_5)$ *(3)*

Phenylphosphine, 1 g (9.1 mmol), in 10 ml of toluene was added to a Schlenk flask containing 3.07 g (18.2 mmol) of diphenylamine and 0.5 g of paraformaldehyde in 30 ml of toluene at 65 °C. This solution was stirred at 65 °C for 4–5 h, at which time the solid paraformaldehyde had disappeared. The product was obtained as described above; yield 2.97 g g (71.6%). m.p. 99–102 °C (dec.), NMR $^{31}P\{^1H\}$ δ, −34.7 ppm; $^1H(CH_2)$ mult. 4.17 ppm. (J(P–H) = 3.07 Hz) (J(H–H) 2.44 Hz).

N,N,N′,N′-Tetrakis(diphenylphosphinomethyl)-ethylenediamine, $[((C_6H_5)_2PCH_2)_2NCH_2]_2$ *(4)*

Ethylenediamine, 0.49 g (8.2 mmol), was added to a stirred slurry of 0.75 g of paraformaldehyde in 60 ml toluene. This mixture was heated to 65 °C and 6.1 g (32.7 mmol) of diphenylphosphine was added. The resulting mixture was stirred at 65 °C for 6 h, and the product isolated as described for **1**; yield 6.7 g (93%). m.p. 77–79 °C (lit. [8] 77–78), NMR $^{31}P\{^1H\}$ δ, −27.9 ppm; $^1H(CH_2)$ d 3.50 ppm J(P–H) 3.23 Hz; s 2.87 ppm.

$Rh[(C_6H_5)_2NCH_2P(C_6H_5)_2]_2(CO)Cl$ *(5)*

A solution containing 26 mg (0.067 mmol) of $[Rh(CO)_2Cl]_2$ in 5 ml of toluene was added dropwise over 10 min to a solution containing 100 mg (0.27 mmol) of **1** in 10 ml of toluene. The resulting yellow solution was stirred for 30 min, and then filtered through celite. Ethyl ether (30 ml) was added, mixed, and a yellow crystalline solid began to slowly form. The mixture was collected, washed with ether and vacuum dried; yield 74 mg (67%). $^{31}P\{H\}$ NMR, δ = 25.0 ppm, J(P, Rh) = 83.5 Hz. IR, ν(CO) = 1968 cm^{-1}.

$Rh\{[(C_6H_5)_2NCH_2]_2PC_6H_5\}_2(CO)Cl$ *(6)*

A solution containing 21 mg (0.054 mmol) $[Rh(CO)_2Cl]_2$ in 5 ml of toluene was added dropwise to a solution containing 100 mg (0.22 mmol) of **2** in 10 ml of toluene over the course of 5 min. The resulting brownish-yellow solution was stirred for 10 min, then it was filtered through celite. Ethyl ether (30 ml) was added and as the solution was stirred yellow crystals began to form. The mixture was cooled to −20 °C for 10 h. The resulting yellow solid was collected on a glass frit and washed with ethyl ether; yield 105 mg (88%). $^{31}P\{H\}$ NMR, δ = 26.8 ppm, J(P, Rh) = 70.2 Hz; IR, ν(CO) = 1972 cm^{-1}.

$Pd([(C_6H_5)_2PCH_2]_2NC_6H_5)Cl_2\cdot CH_2Cl_2$ *(7)*

A solution of 78 mg (0.20 mmol) of $Pd(PhCN)_2Cl_2$ in 7 ml of methylene chloride was added dropwise to a solution containing 100 mg of **3** in 8 ml of methylene chloride over 5 min. The resulting pale yellow solution was filtered through celite. Ethyl ether was slowly added until precipitation of the crystalline solid was complete (*c.* 15 ml). The solid was collected on a glass frit. Recrystallization was achieved by dissolving the compound in a minimum of methylene chloride and precipitating it with ether; yield 110 mg (79%). $^{31}P\{H\}$ NMR, δ = 10.4 ppm.

$Pd_2[((C_6H_5)_2PCH_2)_2NCH_2]_2I_4$ *(8)*

A solution containing 103 mg (0.26 mmol) $Pd(PhCN)_2Cl_2$ in 10 ml of methylene chloride was added dropwise to a solution containing 100 mg (0.13 mmol) of **4** in methylene chloride over the course of 5 min. Potassium iodide (100 mg) in 5 ml of methanol was added to this yellow solution at which time it turned a deep orange. This solution was filtered through celite and then the solvent was removed by rotary evaporation. The resulting solid was dissolved in a minimum amount of methylene chloride and ethyl ether was added slowly until precipitation was complete. The orange, crystalline solid was collected on a glass frit, washed with ether and dried under vacuum; yield 134 mg (69%). $^{31}P\{H\}$ NMR, δ = −9.8 ppm.

X-ray Data Collection

$Rh[(C_6H_5)_2NCH_2P(C_6H_5)_2]_2(CO)Cl$ *(5)*

Large yellow blocks were formed by slow diffusion of ethyl ether into a solution of **5** in methylene chloride. The crystals were rapidly coated with a light hydrocarbon oil to reduce solvent loss. A suitably sized crystal was cut and mounted on a glass fiber and placed in the cold stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 apparatus. Unit cell parameters were obtained by least-squares refinement of 10 reflections with 13° $< 2\theta <$ 24°. The space group $P2_1/n$ (an alternate of $P2_1/c$ (no. 14)) was uniquely determined by the observed conditions; $h0l$, $h + l = 2n$ and $0k0$, $k = 2n$. No decay in the intensities of two check reflections was observed. Data collection parameters are summarized in Table 7. The data were corrected for Lorentz and polarization effects.

$Rh\{[(C_6H_5)_2NCH_2]_2PC_6H_5\}_2(CO)Cl$ *(6)*

Yellow–green needles were formed by diffusion of ethyl ether into a solution of **6** in methylene chloride. Unit cell parameters were obtained by least-squares refinement of 10 reflections with 12° $< 2\theta <$ 17°. The space group $P2_1/c$ (no. 14) was uniquely determined by the observed conditions:

TABLE 7. Crystal data and data collection parameters for 5–8

	5	6	7	8
Formula	$C_{51}H_{44}ClN_2OP_2Rh$	$C_{65}H_{58}ClN_4OP_2Rh$	$C_{33}H_{31}NP_2PdCl_4$[b]	$C_{54}H_{52}I_4N_2P_4Pd_2$
Formula weight	901.24	1111.52	751.78	1573.36
Color and habit	yellow blocs	yellow needles	yellow needles	orange blocks
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$Pbca$
a (Å)	16.392(4)	14.036(6)	25.319(7)	15.848(4)
b (Å)	16.026(3)	10.783(2)	13.045(3)	16.325(7)
c (Å)	17.058(3)	36.422(8)	9.773(2)	21.219(12)
β (°)	108.82(2)	95.34(3)	94.72(1)	
V (Å^3)	4241(1)	5488(2)	3217(1)	5490(4)
T (K)	130	130	130	130
Z	4	4	4	4
Crystal dimensions (mm)	13 × 35 × 35	13 × 25 × 56	13 × 12 × 39	15 × 35 × 40
D_{calc} (g cm^{-3})	1.41	1.35	1.55	1.81
Radiation (Å)	Mo Kα (λ = 0.71069)			
μ(Mo Kα (cm^{-1})	5.65	4.51	8.49	30.11
Range of absorption factors	1.62–3.20	1.09–1.60	1.18–1.80	2.05–12.02
Diffractometer	$P2_1$, graphite monochromator			
Scan method	ω	ω	ω	ω
Scan range (°)	1.0	1.0	0.9	1.0
Offset for background (°)	1.0	1.0	0.9	1.0
Scan speed (° min^{-1})	20	25	20	30
2θ range, (°)	0–45	0–50	0–50	0–50
Octants collected	$h, k, \pm l$	$h, k, \pm l$	$\pm h, k, l$	h, k, l
No. data collected	6081	10754	6359	5418
No. unique data	5832	10184	5668	4822
	[R(merge) = 0.005]	[R(merge) = 0.010]	[R(merge) = 0.007]	[R(merge) = 0.005]
No. data used in refinement	4334[$I > 2\sigma(I)$]	5791[$I > 2\sigma(I)$]	4064[$I > 2\sigma(I)$]	3865[$I > 2\sigma(I)$]
No. parameters refined	268	342	200	163
R[a]	0.042	0.074	0.050	0.040
R_w[a]	0.041[$w = 1/\sigma^2(F_o)$]	0.067[$w = 1/\sigma^2(F_o)$]	0.050[$w = 1/\sigma^2(F_o)$]	0.042[$w = 1/\sigma^2(F_o)$]

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$ and $R_w = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o w^{1/2}|$. [b] Includes one molecule of CH_2Cl_2.

$h0l$, $l = 2n$ and $0k0$, $k = 2n$. No decay in the intensities of the two check reflections was observed. Data collection parameters are summarized in Table 7. All other data collection procedures were identical to those for 5.

Pd{[(C$_6$H$_5$)$_2$PCH$_2$]$_2$NC$_6$H$_5$}Cl$_2$·CH$_2$Cl$_2$ (7)

Yellow needles were formed by diffusion of ethyl ether into a solution of 7 in methylene chloride. Unit cell parameters were obtained by least-squares refinement of 10 reflections with 11° $< 2\theta <$ 24°. No decay in the intensities of the two check reflections was observed. Data collection parameters are summarized in Table 7. All other data collection procedures were identical to those for 5.

Pd$_2$[((C$_6$H$_5$)$_2$PCH$_2$)$_2$NCH$_2$]$_2$I$_4$ (8)

Orange blocks were formed by diffusion of methanol into a solution of 8 in methylene chloride. A suitable cyrstal was selected and mounted as previously described. Unit cell parameters were obtained by least-squares refinement of 16 reflections with 15° $< 2\theta <$ 30°. The space group *Pbca* (no. 61) was uniquely determined by the observed conditions: $h0l$, $l = 2n$, $hk0$, $h = 2n$, and $0kl$, $k = 2n$. No decay in the intensities of the two check reflections was observed. Data collection parameters are summarized in Table 7. All other data collection procedures were identical to those for 5.

Solution and Refinements of Structures

All calculations were carried out on a Data General MV/10000 computer using the SHELXTL version 5 software package. Scattering factors and corrections for anomalous dispersion were taken from a standard source [13].

Rh[(C$_6$H$_5$)$_2$NCH$_2$P(C$_6$H$_5$)$_2$]$_2$(CO)Cl (5)

The position of the rhodium atom was generated by FMAP8, the Patterson solving routine in the SHELXTL software package. Other atomic positions were located by successive difference Fourier maps.

Anisotropic thermal parameters were assigned to rhodium, phosphorus, nitrogen, chlorine and oxygen atoms, with all other atoms refined using isotropic thermal parameters. All hydrogen atom positions were fixed using a riding model with a fixed C–H vector of 0.96 Å and the isotropic thermal parameter set at 20% greater than that of the carbon to which the particular hydrogen is bound. An absorption correction was applied [14]*. The final R value of 0.042 was computed with a data to parameter ratio of 16.2. This yielded a goodness of fit of 1.265 and a maximum shift/e.s.d. of 0.007 for overall scale from the final refinement cycle. A value of 0.48 e/Å^3 was found to be the largest feature on the final difference map. This peak was 0.68 Å from C(28). The weighting scheme was $w = [\sigma^2(F_o)]^{-1}$.

$Rh\{[(C_6H_5)_2NCH_2]_2PC_6H_5\}_2(CO)Cl$ *(6)*

The position of the rhodium atom was generated by FMAP8. Other atomic positions were located by successive difference Fourier maps. Final stages of the refinement included treatment of the hydrogen atoms as with **5** and an absorption correction Anisotropic thermal parameters were used for Rh, P, N, Cl and O atoms. The final R value of 0.074 was computed with a data to parameter ratio of 16.9. This yielded a goodness of fit of 1.363 and a maximum shift/e.s.d. of 0.004 for overall scale from the final refinement cycle. A value of 1.06 e/Å^3 was found to be the largest feature on the final difference map. This peak was 0.69 Å from C(62). The weighting scheme was $w = [\sigma^2(F_o)]^{-1}$.

$Pd([(C_6H_5)_2PCH_2]_2NC_6H_5)Cl_2 \cdot CH_2Cl_2$ *(7)*

The position of the palladium atom was generated by FMAP8. Other atomic positions were located by successive difference Fourier maps. Final stages of the refinement included treatment of the hydrogen atoms as in **5** and an absorption correction. Anisotropic thermal parameters were assigned to Pd, P and Cl atoms. The final R value of 0.050 was computed with a data to parameter ratio of 20.32. This yielded a goodness of fit of 3.81 and a maximum shift/e.s.d. of 0.007 for overall scale from the final refinement cycle. A value of 1.82 e/Å^3 was found to be the largest feature on the final difference map. This peak was 0.64 Å from Cl(1). The weighting scheme was $w = [\sigma^2(F_o)]^{-1}$.

$Pd_2[((C_6H_5)_2PCH_2)_2NCH_2]_2I_4$ *(8)*

The structure was solved by direct methods, giving the position of the palladium and one of the iodine atoms. Other atomic positions were located by successive difference Fourier maps. Final stages of the refinement included treatment of the hydrogen atoms as in **5** and an absorption correction. Anisotropic thermal parameters were used in the refinement of Pd, I, P and N atoms. The final R value of 0.040 was computed with a data to parameter ratio of 22.60. This yielded a goodness of fit of 1.03 and a maximum shift/e.s.d. of 0.007 for overall scale from the final refinement cycle. A value of 1.22 e/Å^3 was found to be the largest feature on the final difference map. This peak was 0.60 Å from C(19). The weighting scheme was $w = [\sigma^2(F_o)]^{-1}$.

Supplementary Material

Listings of thermal parameters, hydrogen atom coordinates, bond distances and angles and observed and calculated structure factors are available from the authors on request.

Acknowledgement

We thank the U.S. National Science Foundation (CHE-8941209) for support.

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*The method obtains an empirical tensor form an expression relating F_o and F_c.

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