Formation of Metallamacrocycles from Palladium(II), Platinum(II) and Copper(I) Complexes and the Ditopic Ligands $[\{p\text{-}(Ph_2PO)C_6H_4\}_2CMe_2]$, $[\{2\text{-}Ph_2PO\text{-}3,5\text{-}(Me_3C)_2C_6H_2\}_2S]$, $[\{p\text{-}[(C_{10}H_6O)_2PO]C_6H_4\}_2CMe_2]$

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The new ligands bis(phosphinito) $[\{2\text{-}Ph_2PO\text{-}3,5\text{-}(Me_3C)_2C_6H_2\}_2S]$ (**4**) and chiral bis(phosphite) $[\{p\text{-}[(C_{10}H_6O)_2PO]C_6H_4\}_2CMe_2]$ (**5**) were synthesised and their reactions with palladium(II), platinum(II), copper(I) substrates were studied. The ligand **3** $[\{p\text{-}(Ph_2PO)C_6H_4\}_2CMe_2]$, previously reported by us, was also used in the same reactions. Ligands **3** and **5** formed 28-membered metallamacrocycles while ligand **4** afforded the analogous compound only in the reaction with the copper(I) substrate. In the reaction of **3** with $[Pd(PhCN)_2Cl_2]$ the metallamacrocycle $[PdCl_2(\mu\text{-}\mathbf{3})]_2$ (**6**) or the oligomer $[Pd_2Cl_4(\mu\text{-}\mathbf{3})]_n$ (**7**) were formed, depending on the molar ratio used. The reaction of **3** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ afforded compound $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2(\mu\text{-}\mathbf{3})\}$ (**8**). The allylpalladium macrocycle $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}\mathbf{3})]_2[OTf]_2$ (**9**) was obtained by treating a solution of **8** in THF with $AgCF_3SO_3$. The reactions of ligand **3** with $[Pt(COD)I_2]$ or $[Cu(NCCH_3)_4]BF_4$ led to the formation of metallamacrocycles $[PtI_2(\mu\text{-}\mathbf{3})]_2$ (**10**) and $[Cu_2(\mu\text{-}\mathbf{3})_2][BF_4]_2\cdot 2CH_3CN$ (**11**), respectively. The structure of **10** was also elucidated by X-ray analysis. Reactions of **4** with palladium(II) and platinum(II) complexes afforded a mixture of two very different compounds in almost an equimolar ratio. An X-ray analysis established that one is a mononuclear compound, formed by modification of the ligand **4**, containing a P,S-chelate, namely $\{PdCl_2\{[2\text{-}Ph_2PO\text{-}3,5(Me_3C)_2C_6H_2][3,5\text{-}(Me_3C)_2C_6H_2OH]S\}\}$ (**12**). The reaction between $[Cu(NCCH_3)_4]BF_4$ and **4** afforded the ionic metallamacrocycle $[Cu(\mu\text{-}\mathbf{4})][BF_4]_2\cdot 2CH_3CN$ (**14**). In compound **10**, the size of the central cavity formed by the bridging ligand **3** was determined.

Introduction

In the last twenty years a number of studies have indicated that hydrogen bond formation is not the unique mode through which the supramolecular self-assembly of molecules can occur and coordination bond formation was found to be a very useful tool to promote supramolecular self-assembly processes.[1a,2] In fact the preferred coordination numbers, the geometry of transition metal complexes and the shape of the bi- and polydentate ligands drives a spontaneous supramolecular self-assembly process to give metallamacrocycles with trigonal, square-planar, and tetrahedral coordinated metal ions.[2] In this context, a renewed interest in metallamacrocycles has recently been observed. Additionally, they can potentially act as host molecules in the generation of supramolecular architectures.[3] Several bi- or polydentate rigid aromatic nitrogen ligands have been used in reactions with transition metal complexes, generally in a square-planar configuration, to induce metallamacrocyclic structure formation.[1,4] Recently,[5] "flexible" non-chelating proligands HE-EH [HE-EH = $1,4\text{-}(HOCH_2)_2C_6H_4$, $1,3\text{-}(HOCH_2)_2C_6H_4$, $(4\text{-}HOC_6H_4)_2CH_2$] have been used in the reaction with $[Mo(NO)(tp^*)I_2]_2$ {tp* = $HB(3,5\text{-}Me_2C_3HN_2)_3$} in the presence of NEt_3, to afford the dinuclear metallacyclophanes $[Mo(NO)(tp^*)(E\text{-}E)]_2$ as the major product. In these reactions, kinetic control in the formation of the dinuclear metallamacrocycles was observed.

Lately,[6] we have synthesized the large valence angle bis(*p*-phosphinito) ligands $[p\text{-}(Ph_2PO)C_6H_4]_2X$ (X = O, **1**; S, **2**; CMe_2, **3**), designed to induce a bridging coordination in transition metal complexes. The reactions of **1−3** with $[Ru(p\text{-cymene})Cl_2]_2$, $[Rh(C_5Me_5)Cl_2]_2$, $[Rh(C_5H_5)(CO)_2]_2$ gave dinuclear complexes in which the two metal centres are bridged by only one phosphinito ligand.[6]

In this paper we report the synthesis of the new ligands bis(phosphinito) $[\{2\text{-}Ph_2PO\text{-}3,5\text{-}(Me_3C)_2C_6H_2\}_2S]$ (**4**) and chiral bis(phosphite) $[\{p\text{-}[(C_{10}H_6O)_2PO]C_6H_4\}_2CMe_2]$ (**5**), and the reactions of **3**, **4** and **5** with palladium(II), platinum(II), and copper(I) substrates. The crystal structures of the dichloromethane solvates of the macrocyclic dinuclear complex $[Pt\{[p\text{-}(Ph_2PO)C_6H_4]_2CMe_2\}I_2]_2$ (**10**) and of $[PdCl_2\{[2\text{-}Ph_2PO\text{-}3,5\text{-}(CMe_3)_2C_6H_2][3,5\text{-}(CMe_3)_2\text{-}C_6H_2OH]S\}]$ (**12**) are also reported.

Results and Discussion

Synthesis of Ligands 4 and 5

In order to synthesise a bis(phosphinito) ligand with a bigger steric requirement than ligands **1−3**, we prepared

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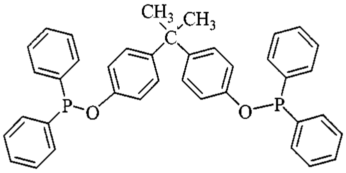
ligand **4** which has sulfur as the bridging atom, two phosphinito groups at the 2-position, and four *tert*-butyl groups as substituents in the aromatic moieties.



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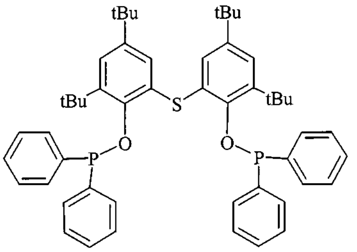

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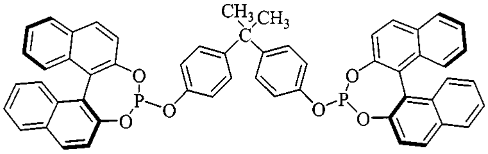

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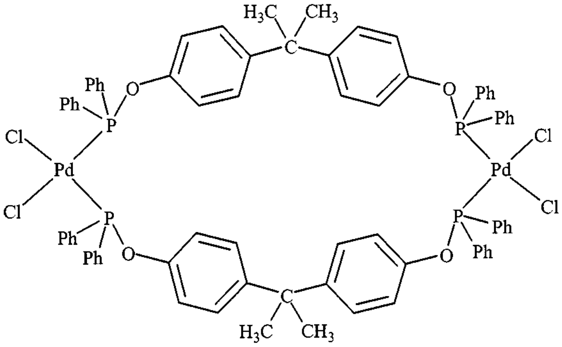
Ligand **4** was synthesised by treating 4,4′,6,6′-di-*tert*-butyl-2,2′-thiobisphenol[7] with PPh_2Cl and an excess of NEt_3 in toluene at room temperature. Several recrystallisations from hexane gave the pure product **4** as a white moderately air-stable powder, which was analysed by $^{31}P\{^1H\}$, ^1H NMR spectroscopy and GCMAS. In the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$ solution), a singlet appears at $\delta = 117.1$ and in the ^1H NMR two singlets at $\delta = 1.26$ and 1.31 due to *tert*-butyl groups as well as signals due to aromatic groups are seen. In the mass spectrum, a molecular peak at 810 was observed.

Ligand **5** has the same backbone as **3**, but it is chiral owing to the presence of two chiral configurationally resolved binaphthol groups. It was prepared by lithiation of 2,2-bis(4-hydroxyphenyl)propane in THF and subsequent addition of the lithium derivative to a solution of (*S*)-(1,1′-binaphthalene-2,2′-dioxy)chlorophosphane[8] in the same solvent at room temperature. The pure product was isolated as a white, air-sensitive powder and characterised by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6 solution), shows a singlet at $\delta = 144.79$ while the ^1H NMR exhibits a signal at $\delta = 1.47$ due to the CH_3 groups as well as two doublets at $\delta = 6.96$ and 7.0 ($J = 3$ Hz) due to the *p*-substituted phenyl groups. Multiplets in the range $\delta = 7.45-7.64$ due to the binaphthyl protons are also observed.

Ligands **3−5** were designed to induce a bridging coordination to transition metal centres. Structural determination of dinuclear Ru^{II} complexes containing ligand **3** proved that the P−P distance is longer than 9 Å[6] and therefore a *cis* or *trans* chelating bonding mode for ligands **3** and **5** is not expected.

Reactions of Ligands 3−5 with Palladium(II), Platinum(II) and Copper(I) Complexes

The reaction of **3** with $[Pd(PhCN)_2Cl_2]$ in a 1:1 molar ratio in toluene produced a yellow precipitate which was analysed as metallamacrocycle $[PdCl_2(\mu\text{-}\mathbf{3})]_2$ (**6**).



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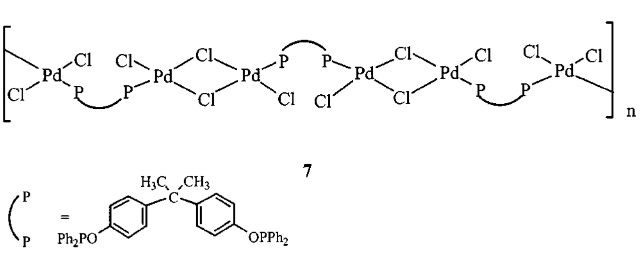
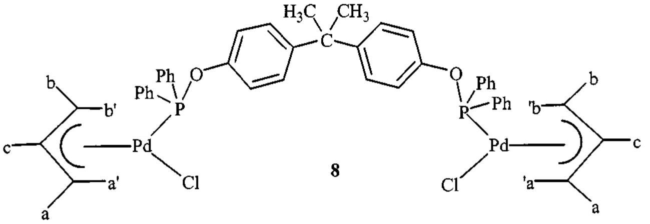
It is air-stable, soluble in chlorinated solvents and proved to be non-conducting in acetone solution. In agreement with the proposed structure, the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), shows a singlet at $\delta = 109.0$ while the ^1H NMR spectrum features a singlet at $\delta = 1.46$ due to the $C(CH_3)_2$ group together with the characteristic resonances of phenyl rings.

When a solution of **3** in toluene was added to a solution of $[Pd(PhCN)_2Cl_2]$ in the same solvent in a 1:2 molar ratio, an orange-brown precipitate quickly formed which was insoluble in common organic solvents and analysed as $[Pd_2Cl_4(\mathbf{3})]$ (**7**). Compound **7** dissolves moderately only in coordinating solvents such as CH_3CN and DMF.



7

The $^{31}P\{^1H\}$ NMR spectrum of **7** in CD_3CN shows a resonance at $\delta = 106.3$ as a sharp singlet which is consistent with a symmetric geometry. The ^1H NMR spectrum shows a singlet at $\delta = 1.37$ due to the isopropyl group, together with the signals of the aromatic rings in the correct integration ratio. Although it was not possible to obtain useful information from the mass spectrum because of the wide fragmentation of the compound **7**, on the basis of NMR spectroscopic data and the observed chemical properties, we deduced that **7** was an oligomer, $[Pd_2Cl_4(\mu\text{-}\mathbf{3})]_n$, in which the chloride and the phosphinito ligands alternately coordinate as bridges to palladium(II) centres. In coordinating solvents such as CH_3CN and DMF, a break of the chloro bridge probably occurs but the oligomeric structure is maintained. Furthermore, the ^1H NMR spectra of **7** (CD_3CN solution) shows features which indicate that scrambling processes take place. The proposed structure of **7** is in agreement with the trend of the palladium(II) to give bi- and polynuclear chloro-bridged compounds.[9] Reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with **3** in a 1:1 molar ratio afforded the expected dinuclear compound $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2(\mu\text{-}\mathbf{3})\}$ (**8**) in which the two metal atoms are bridged by only one phosphinito ligand.



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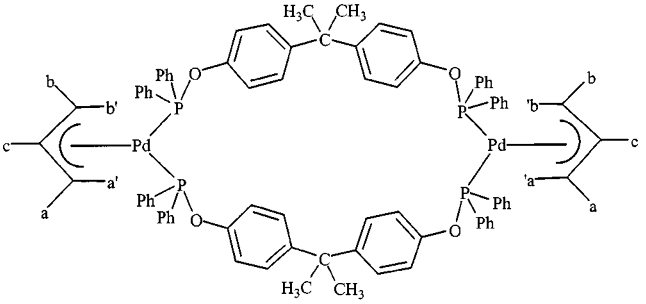
This is corroborated by the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$ solution), which shows a sharp singlet at $\delta = 123.29$, indicating a plane of symmetry in the molecule. In the ^1H NMR spectrum, the singlet at $\delta = 1.55$ was assigned to the isopropyl group. A ^1H NOESY experiment made the assignment of each allylic proton signal possible: two broad multiplets at $\delta = 2.20$ ($^3J = 12$ Hz, $H_{b'}$) and at $\delta = 3.13$ ($J = 6$ Hz, H_b), two doublets of doublets at $\delta = 3.57$ ($^3J = 11$ Hz, $J_{PH} = 15$ Hz, Ha′) and at $\delta = 4.67$ ($J_{PH} = 7$ Hz, H_a), one multiplet at $\delta = 5.22$ (H_c). Phase-sensitive 2D-^1H NOESY spectrum shows NOE peaks between H_c and its vicinal H_a and H_b protons. The analysis of the NMR spectroscopic data led us to conclude that a dynamic process, fast on the NMR time scale, was taking place and that it involved all the allylic protons in the molecule. This process is due to two concurrent $\eta^3-\eta^1-\eta^3$ rearrangements of the allylic fragment.[10]



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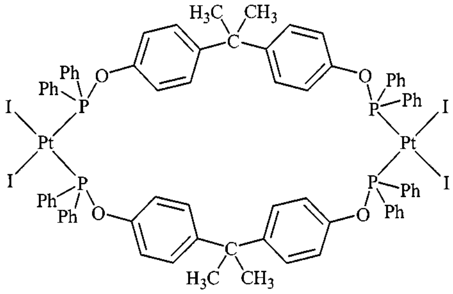
In order to prepare an allylpalladium macrocycle, a solution of $\{Pd(\eta^3\text{-}C_3H_5)Cl]_2(\mu\text{-}\mathbf{3})\}$ (**8**) in THF was initially treated with $AgCF_3SO_3$ in a 1:2 molar ratio, and after filtration of the AgCl precipitate, was further treated with 1 equivalent of **3**. The white dinuclear allylpalladium macrocycle $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}\mathbf{3})]_2[OTf]_2$ (**9**) was obtained in good yield and was characterised by microanalysis, NMR spectroscopy and conductivity measurements.

The presence of a broad signal at $\delta = 120.6$ in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), revealed a complex fluxional process in the complex. This was further supported by the broadness of the signals observed in the ^1H NMR spectra recorded over a wide range of temperatures.

Reaction of $[Pt(COD)I_2]$ with ligand **3** in an equimolar ratio proceed in a similar way to that with $[Pd(PhCN)_2Cl_2]$. Addition of ligand **3** to a toluene solution of $[Pt(COD)I_2]$ led to the formation of metallamacrocycle $[PtI_2(\mu\text{-}\mathbf{3})]_2$ (**10**) as a yellow precipitate which was characterized by NMR spectroscopy and X-ray analysis. As expected, the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) displays a peak at $\delta = 81.81$, together with satellites due to $^{195}Pt-P$ coupling ($J_{PtP} = 3968$ Hz), and the ^1H NMR spectrum features all ligand signals in the correct integration ratio.



10

Crystal Structure of $[PtI_2(\mu\text{-}\mathbf{3})]_2\cdot 2CH_2Cl_2$ ($\mathbf{10}\cdot 2CH_2Cl_2$)

A view of the structure of complex **10** is shown in Figure 1, together with the numbering system. Selected bond lengths and angles are given in Table 1. The metallamacrocycle has an imposed crystallographic C_2 symmetry.

The coordination at Pt is square-planar and involves two P atoms mutually in *cis* position and two I atoms. The two Pt−I [2.6523(11) and 2.6562(9) Å] and Pt−P [both 2.259(2) Å] bond lengths are equal. The most interesting feature is the 28-membered metallacycle; the conformation of the ring is shown in Figure 2. The central cavity seems to be too small to bind even small guest molecules. Critical cross-ring interatomic distances are C23···C23′ (3.983 Å), C23−C24′ and C23′−C24 (4.078 Å). The apex indicates an atom related by the twofold axis. The Pt−Pt′ and C7−C7′ separations are 13.071 and 8.974 Å, respectively. Furthermore, two phenyl groups at P2 point to the same side of the ring, facing one another, the shortest contacts involving C31···C31′ (3.690 Å), C31−C32′ and C31′−C32 (3.983 Å). It is worth noting that the O2 atom is involved in an intermolecular hydrogen bond with the Cl2 atom [O2···Cl2 = 3.048(5), Cl2···H2 = 2.32(5) Å; 02−H2−Cl2 = 157(5)°].

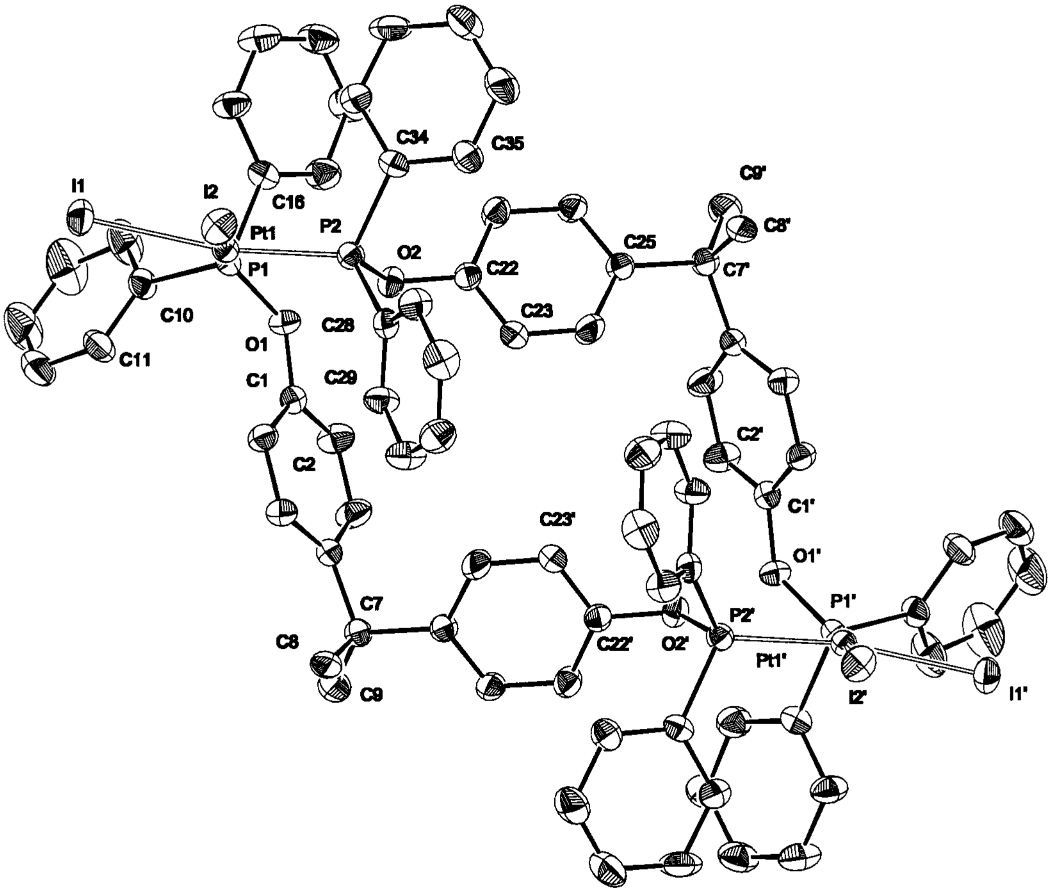
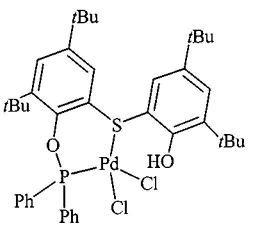


Figure 1. ORTEP view of the structure of the complex **10** together with the numbering scheme; the ellipsoids for the atoms are drawn at the 30% probability level

The reaction between $[Cu(NCCH_3)_4]BF_4$ and ligand **3** in a 1:1 molar ratio in dichloromethane solution, afforded the metallamacrocycle $[Cu_2(\mu\text{-}\mathbf{3})_2][BF_4]_2\cdot 2CH_3CN$ (**11**) as a white solid. Conductivity measurements in methanol solution proved that compound **11** is a 2:1 electrolyte. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at $\delta = 99.06$, while the ^1H NMR spectrum ($CDCl_3$ solution) in addition to the expected signals, also shows a singlet at $\delta = 1.55$ due to the CH_3CN molecule of crystallisation. The coordination of acetonitrile to the metal centre can be excluded, since the observed chemical shift is the same as that of the free CH_3CN.

Reactions of **4** with Pd^{II} and Pt^{II} complexes gave different results from those reported for ligands **3**. Addition of one equivalent of **4** to a solution of $[Pd(PhCN)_2Cl_2]$ in toluene afforded a mixture of two very different compounds, **12** and **13**, in a 42:58 ratio, each giving rise to a singlet at $\delta = 135.66$ and 78.79, respectively, in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$).



12

Fractional crystallisation from CH_2Cl_2/hexane allowed us to separate the two compounds. Thus, **12** was obtained as yellow crystals which exhibit only a signal at $\delta = 135.66$ in the $^{31}P\{^1H\}$ NMR in $CDCl_3$. An X-ray analysis carried out on these crystals established that it has formula $[PdCl_2\{[2\text{-}Ph_2PO\text{-}3,5\text{-}(CMe_3)_2C_6H_2][3,5\text{-}(CMe_3)_2\text{-}C_6H_2OH]S\}]$.

Crystal Structure of $[PdCl_2\{[2\text{-}Ph_2PO\text{-}3,5\text{-}(CMe_3)_2C_6H_2]\text{-}[3,5\text{-}(CMe_3)_2\text{-}C_6H_2OH]S\}]\cdot 2CH_2Cl_2$ ($\mathbf{12}\cdot 2CH_2Cl_2$)

A view of the structure of complex **12** is shown in Figure 3 together with the numbering system. Selected bond lengths and angles are given in Table 2. The coordination at Pd is square-planar and involves two Cl atoms and the P1 and S1 from the chelating ligand, obtained by fragmentation of **4**. The six-membered chelating ligand is in a boat conformation with the two near-planar S1PdP101 and 01C13C18S1 moieties forming a dihedral angle of 41.1(1)°. The Pd−P1 and Pd−S1 bond lengths are 2.1985(15) and 2.2770(13) Å, respectively. The Pd−Cl1 and Pd−Cl2 bond lengths, 2.3149(14) and 2.3769(15) Å respectively, are rather different; the bond *trans* to the P atom is longer.

In light of the structure determined for **12**, we may consider two hypotheses based on this result. One could explain the hydrolysis of one P−O bond in the pure ligand as being due to the presence of water in the solvent. However, this can be excluded since the reaction was repeated several

Table 1. Selected bond lengths [Å] and angles [°] for **$10\cdot 2CH_2Cl_2$** (symmetry transformations used to generate equivalent atoms: ′ $-x + 1, y, -z + 1/2$)

Bond lengths	
Pt(1)−P(2)	2.259(2)
Pt(1)−P(1)	2.259(2)
Pt(1)−I(1)	2.6523(11)
Pt(1)−I(2)	2.6562(9)
P(1)−O(1)	1.625(5)
P(2)−O(2)	1.632(5)
O(1)−C(1)	1.399(8)
O(2)−C(22)	1.400(8)
C(1)−C(2)	1.365(10)
C(1)−C(6)	1.380(10)
C(2)−C(3)	1.380(11)
C(3)−C(4)	1.384(11)
C(4)−C(5)	1.396(10)
C(4)−C(7)	1.533(10)
C(5)−C(6)	1.372(10)
C(7)−C(25)′	1.541(10)
C(22)−C(27)	1.367(10)
C(22)−C(23)	1.372(10)
C(23)−C(24)	1.385(11)
C(24)−C(25)	1.384(11)
C(25)−C(26)	1.379(10)
C(25)−C(7)′	1.541(10)
C(26)−C(27)	1.398(10)
Bond angles	
P(2)−Pt(1)−P(1)	96.86(7)
P(2)−Pt(1)−I(1)	168.82(5)
P(1)−Pt(1)−I(1)	89.90(5)
P(2)−Pt(1)−I(2)	84.73(5)
P(1)−Pt(1)−I(2)	176.53(5)
I(1)−Pt(1)−I(2)	88.07(2)
C(25)′−C(7)−C(4)	108.1(6)
O(1)−P(1)−Pt(1)	120.0(2)
O(2)−P(2)−Pt(1)	109.11(19)
C(1)−O(1)−P(1)	128.5(4)
C(22)−O(2)−P(2)	123.8(4)
C(2)−C(1)−O(1)	114.7(6)

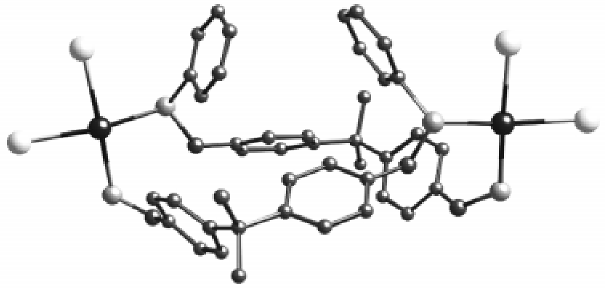
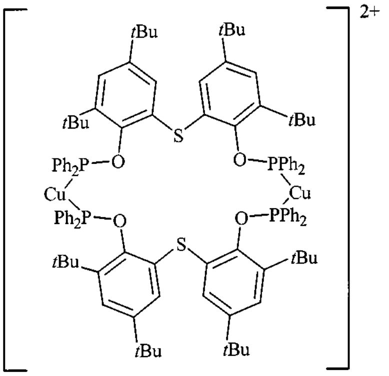


Figure 2. View of the 28-membered metallacycle of **10**; six phenyl groups (two at P1 and P1′ and one at P2 and P2′) are omitted for clarity

times under rigorously anhydrous conditions and the same result was obtained. Furthermore, the reaction between the Cu complex and the same sample of ligand **4** used in the reaction with $[Pd(PhCN)_2Cl_2]$ in toluene, gave a product (see below) which does not arise from P−O bond hydrolysis in ligand **4**. Another possibility is that a very complicated reaction takes place which could involve sulfur coordination to the palladium centre. In this case, a lengthening and breaking of one P−O bond can occur by a probable, but not experimentally proven, contribution of the solvent. Undoubtedly, the characterization of **13** is fundamental to the understanding of this reaction. Unfortunately, several attempts to obtain suitable crystals for X-ray analysis of **13** failed so far. However, other studies have to be conducted to give insight into this reaction.

Reaction of $[Pt(COD)I_2]$ with 1 equivalent of ligand **4** produced a mixture of compounds, as could be inferred by the presence of several peaks in the $^{31}P\{^1H\}$ NMR spectrum. It is also likely that a product similar to **12** can be formed in this reaction. Differently from palladium, reaction between $[Cu(NCCH_3)_4]BF_4$ and ligand **4** in a 1:1 molar ratio in toluene afforded the white ionic metallamacrocycle $[Cu(\mu\text{-}\mathbf{4})][BF_4]_2\cdot 2CH_3CN$ (**14**), which was soluble in chlorinated solvents, acetone and methanol. Compound **14** was found to be a 1:2 electrolyte in methanol solution.



14

Complex **14** presents elemental analysis and NMR spectroscopic data fully consistent with the proposed structure. Indeed, only two sharp singlets are present for *tert*-butyl groups in the ^1H NMR spectrum, consistent with the proposed symmetric structure. Furthermore, a sharp singlet at $\delta = 108.81$ is present in the $^{31}P\{^1H\}$ NMR spectrum.

On the basis of the similar structural features of ligands **3** and **5**, we expect a similar behaviour in the reactions between **5** and Pd, Pt and Cu complexes. Only in the case of the reaction with the Cu complex, was it not possible synthesise a product in pure form. A rapid degradation of the initially formed macrocycle probably occurs in solution.

The reaction of $[Pd(PhCN)_2Cl_2]$ with ligand **5** in toluene and in a 1:1 molar ratio, led to the formation of an orange-brown precipitate, which shows a singlet at $\delta = 107.68$ together with two signals of very low intensity at $\delta = 86.6$ and 85.7 in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$). However, several recrystallisations from toluene/hexane made it possible to obtain the pure chiral metallamacrocycle $[Pd(\mu\text{-}\mathbf{5})Cl_2]_2$ (**15**).

Its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) features only the signal at $\delta = 107.68$, while all expected signals in the correct integration ratio are present in the ^1H NMR spectrum. By adding ligand **5** to a solution of $[Pt(COD)I_2]$ in toluene, the metallamacrocycle $[Pt(\mu\text{-}\mathbf{5})I_2]_2$ (**16**) precipitated as a yellow solid. The resulting compound was not in a pure form, but

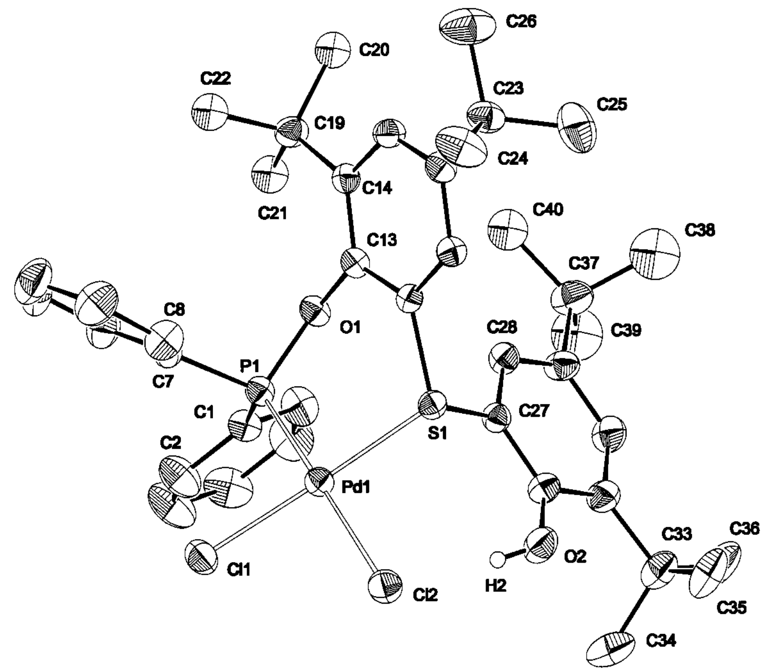
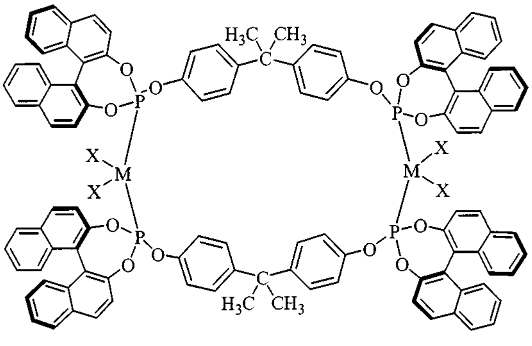


Figure 3. ORTEP view of the structure of the complex **12** together with the numbering scheme; the ellipsoids for the atoms are drawn at the 30% probability level

Table 2. Selected bond lengths [Å] and angles [°] for **12·2CH$_2$Cl$_2$**

Bond lengths	
Pd(1)−P(1)	2.1985(15)
Pd(1)−S(1)	2.2770(13)
Pd(1)−Cl(1)	2.3149(14)
Pd(1)−Cl(2)	2.3769(15)
S(1)−C(18)	1.784(5)
S(1)−C(27)	1.796(5)
P(1)−O(1)	1.633(3)
O(1)−C(13)	1.385(6)
O(2)−C(32)	1.343(7)
C(13)−C(18)	1.400(6)
Bond angles	
P(1)−Pd(1)−S(1)	93.41(6)
P(1)−Pd(1)−Cl(1)	87.13(6)
S(1−Pd(1)−Cl(1)	176.52(5)
P(1)−Pd(1)−Cl(2)	175.24(5)
S(1)−Pd(1)−Cl(2)	87.72(6)
Cl(1)−Pd(1)−Cl(2)	92.01(6)
C(18)−S(1)−C(27)	103.1(2)
C(18)−S(1)−Pd(1)	110.87(15)
C(27)−S(1)−Pd(1)	110.57(17)
O(1)−P(1)−Pd(1)	114.31(13)
C(13)−O(1)−P(1)	125.8(3)
C(18)−C(13)−O(1)	119.9(4)
C(13)−C(18)−S(1)	124.4(4)

repeated recrystallisations from toluene/hexane allowed us to obtain the pure compound **16**. It was characterised by elemental analyses, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet at $\delta = 84.06$ (J_{PtP} 5543) is present.



M = Pd, X = Cl, **15** M = Pt, X = I, **16**

Conclusion

A new class of dinuclear metallamacrocycles [M(μ-**L**)X$_2$]$_2$ [M = Pd^{II}, Pt^{II}, Cu^{I}] characterised by a 28-membered ring was obtained using the ditopic ligands **3** and **5**. In the case of **4**, only the Cu^{I}-based dinuclear macrocycle was formed with this ligand. Different results were achieved with Pd^{II} and Pt^{II} complexes on account of sulfur being involving in the course of the reaction. The lack of formation of cyclic tri- and tetranuclear species in the reaction of **3** with Pd^{II}, Pt^{II} and Cu^{I} substrates is a consequence both of the geometry of ligand **3** and of thermodynamic factors owing to the very strong metal−phosphorus bond. Another consequence of the ligand geometry is that when ligand **3** was used in the reaction with [Ru(η^6-*p*-cymene)Cl$_2$]$_2$, only the dinuclear complex {[Ru(η^6-*p*-cymene)Cl$_2$]$_2$[μ-(*p*-Ph$_2$POC$_6$H$_4$)$_2$C(Me)$_2$]} was obtained[6] and attempts to obtain bi- and tetranuclear metallamacrocycles were unsuccessful. The formation of the dinuclear metallamacrocycles $[M(\mu\text{-}L)X_2]_2$ (M = Pd^{II}, Pt^{II}, Cu^{I}, L = **3**, **5**) was promoted by the presence of *cis*-coordinated labile ligands in the starting complexes. Thus, the reaction of $[M(PPh_3)_4]$ (M = Pt, Pd) with dihalobenzophenone afforded the dinuclear complex $\{[MX(PPh_3)_2]_2[\mu\text{-}(C_6H_4)_2CO]\}$ (M = Pt, X = I, M = Pd, X = Br, I) and failed to give $\{[MX_2(PPh_3)]_2[\mu\text{-}(C_6H_4)_2CO]_2\}$.[11]

A very interesting aspect connected with the formation of metallamacrocycles is the introduction of chirality by suitable self-assembly building blocks. At least five different ways of rationally designed chiral supramolecular species have been indicated.[12] Stang successfully used an appropriate metal complex bearing (*R*)-(+)-BINAP as the chiral ancillary ligand for the synthesis of chiral palladium(II) and platinum(II) supramolecular square-planar species.[12] The use of the ditopic chiral ligand **5** made the synthesis of chiral palladium(II)- and platinum(II)-based macrocycles possible.

From this work we conclude that chiral dinuclear square-planar metallamacrocycles can be obtained by spontaneous self-assembly of building units of palladium(II) and platinum(II) complexes containing labile ligands and the chiral bidentate ligand **5**. This methodology can be extensively used owing to the great number of chiral ligands, with different geometric properties, which should prove to be bi- and tridentate functional building blocks for the synthesis of chiral supramolecular squares. Up to now, the use of chiral dinuclear square-planar metallamacrocycles as organometallic reagents is an unexplored topic.

The ability for molecular recognition of these new metallamacrocycles depends on the size of the cavity formed. On the basis of the X-ray crystal structure of the complex **10·2CH$_2$Cl$_2$** the cavity determined by meaningful cross-ring interatomic distances seems to be too small to bind guest molecules. We are actually trying to synthesize different types of bis(phosphinito) ligands with the aim of obtaining metallamacrocycles that can act as host molecules in the formation of supramolecular species.

Experimental Section

All syntheses were performed under argon or nitrogen using standard Schlenk-tube techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. [D$_6$]Benzene (99.5+%) and [D$_3$]chloroform (99.8+%) were used as received from Aldrich Chemical Co. All other reagents were of the highest purity grade commercially available and were used without further purification. Redox Analytical Laboratories, Milan, performed microanalyses. ^{1}H, ^{31}P and ^{13}C NMR spectra were obtained with a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13, 121.49 and 75.46 MHz, respectively [δ (ppm) relative to Me_4Si, *J* (Hz)]. $^{31}P\{^{1}H\}$ spectra were run using an aqueous H_3PO_4 sample (85%) as external reference (δ = 0). Standard pulse sequences were employed for ^{1}H-2D-NOESY. Mixing times of 0.8 s were used for the phase-sensitive NOESY experiments. $[Cu(NCCH_3)_4]BF_4$[13], $[\{p\text{-}(Ph_2PO)C_6H_4\}_2CMe_2]$,[6] and 4,4′,6,6′-di-*tert*-butyl-2,2′-thiobisphenol[7] were prepared by standard methods. IR spectra of KBr pellets were recorded with a Perkin−Elmer FT-IR 1720 spectrometer. GLC analyses were performed with a Carlo Erba HRGC 5160 series Mega instrument using a 25-m Mega OV1 column.

$[\{2\text{-}Ph_2PO\text{-}3,5\text{-}(CMe_3)_2C_6H_2\}_2S]$ (4): The synthetic procedure was essentially the same as previous described for **1**, using a solution of PPh_2Cl (1.98 g, 9.00 mmol) and a solution of 4,4′,6,6′-di-*tert*-butyl-2,2′-thiobisphenol (2.00 g, 4.50 mmol) and NEt_3 (1.45 g, 14.3 mmol) in toluene (40 mL each). The reaction mixture was warmed to room temperature and then kept under continuous stirring for 72 h. The ligand **4** was obtained as a white solid by filtration of the resulting mixture and crystallisation from toluene/hexane (1:3, v/v). Yield 87% (3.17 g, 3.90 mmol). − $C_{52}H_{60}O_2P_2S$ (811.0): calcd. C 77.01, H 7.46, S 3.95; found C 76.97, H 7.49, S 3.91. − ^{1}H NMR ($CDCl_3$): δ = 1.26 [s, 18 H, $C(CH_3)_3$], 1.31 [s, 18 H, $C(CH_3)_3$], 7−7.12 (m, 12 H, CH), 7.28 (d, ^{3}J = 2.5 Hz, 2 H, CH), 7.39 (d, ^{3}J = 2.5 Hz, 2 H, CH), 7.61−7.67(m, 8 H, CH). − $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 117.21 (s).

$[\{p\text{-}[(C_{10}H_6O)_2PO]C_6H_4\}_2CMe_2]$ (5): *n*BuLi solution in hexanes (1.6 M, 1.09 mL, 0.112 g, 1.75 mmol) was added dropwise to a solution of 2,2-bis(4-hydroxyphenyl)propane (0.200 g, 0.876 mmol) in THF (20 mL) at −78 °C. The white mixture was added to a solution of (*S*)-(1,1′-binaphthalene-2,2′-dioxy)chlorophosphane in THF (3 mL) at 0 °C. The resulting pale yellow solution was allowed to reach room temperature and stirred for ca. 2 h. The solution was then dried under vacuum and extracted with toluene (3 × 5 mL). Decreasing the solution volume followed by the addition of hexane led to the formation of a white solid. The pure ligand **3** was isolated, washed with small volumes of hexane and finally dried under vacuum with a yield of 70% (0.525 g, 0.613 mmol). − $C_{55}H_{38}O_6P_2$ (856.8): calcd. C 77.10, H 4.47; found C 77.3, H 4.49. − ^{1}H NMR (C_6D_6): δ = 1.47 [s, 6 H, $C(CH_3)_2$], 6.96−7.65 (m, 24 H, CH). − $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 144.79 (s).

$[PdCl_2(\mu\text{-}3)]_2$ (6): Ligand **3** (0.165 g, 0.260 mmol), dissolved in toluene (5 mL), was treated with a solution of $[Pd(PhCN)_2Cl_2]$ (0.100 g, 0.260 mmol) in toluene (30 mL). A yellow solid precipitated immediately and was separated from the mother solution after ca. 1 h, washed with toluene (3 × 1 mL), diethyl ether (1 × 1 mL) and then dried under vacuum. Yield 82% (0.166 g, 0.107 mmol). − $C_{78}H_{68}Cl_4O_4P_4Pd_2$ (1548): calcd. C 60.52, H 4.43; Cl, 9.16; found C 60.16, H 4.34; Cl, 8.93. − ^{1}H NMR ($CDCl_3$): δ = 1.46 [s, 6 H, $C(CH_3)_2$], 6.45 (d, ^{3}J = 8.4 Hz, 4 H, CH), 6.70 (d, ^{3}J = 8.7 Hz, 4 H, CH), 7.28−7.46 (m, 12 H, CH), 7.66−7.69 (m, 8 H, CH). − $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 109.03 (s).

$[Pd_2Cl_4(\mu\text{-}3)]_n$ (7): The orange compound **7** was prepared from $[Pd(PhCN)_2Cl_2]$ (0.080 g, 0.208 mmol) and **3** (0.062 g, 0.104 mmol) as described above for compound **6**. Yield 75% (0.074 g, 0.078 mmol). − $C_{39}H_{34}Cl_4O_2P_2Pd_2$ (951.3): C. 49,24; H. 3,60; Cl. 14,91; found C. 49,20; H. 3,63; Cl. 14,87. − ^{1}H NMR (CD_3CN): δ = 1.37 [s, 6 H, $C(CH_3)_2$], 6.25 (d, ^{3}J = 8.7 Hz, 4 H, CH), 6.52 (d, ^{3}J = 8.9 Hz, 4 H, CH), 6.86−7.69 (m, 20 H, CH). − $^{31}P\{^{1}H\}$ NMR (CD_3CN): δ = 106.32 (s).

$\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2(\mu\text{-}3)\}$ (8): To a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.05 g, 0.137 mmol) in dichloromethane (10 mL) was added ligand **3** (0.082 g, 0.137 mmol). The resulting yellow solution was stirred for 1 h and then reduced to 3 mL in vacuo. Addition of hexane (10 mL) led to the formation of a yellow precipitate. Yield 72% (0.048 g, 0.050 mmol). − $C_{45}H_{44}Cl_2O_2P_2Pd_2$(962.5): calcd. C 56.15, H 4.61; Cl, 7.37; found C 56.25, H 4.53; Cl, 6.99. − ^{1}H NMR ($CDCl_3$): δ = 1.55 [s, 6 H, $C(CH_3)_2$], 2.20 [d (br.), ^{3}J = 12 Hz, 2

H, $H_{b'}$], 3.13 [d (br.), ^3J = 6 Hz, 2 H, H_b], 3.57 [dd (br.), ^3J = 11 Hz, J_{HP} 15 Hz, 2 H, $H_{a'}$], 4,67 [dd (br.), J_{HP} 7 Hz, 2 H, H_a], 5.22 [m (br.), 2 H, H_c], 6.99 (d, ^3J = 5 Hz, 4 H, H_e), 7.01 (d, ^3J = 5 Hz, 4 H, H_d), 7.43−7.45 (m, 12 H, $H_{m,p}$), 7.85−7.93 (m, 8 H, H_o). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 123.29 (s).

[Pd(η^3-C_3H_5)(μ-3)]$_2$[OTf]$_2$ (9): The bridge complex **8** (0.077 g, 0.080 mmol) was dissolved in dichloromethane (10 mL) and $AgCF_3SO_3$ (0.041 g, 0.16 mmol) was added with continuous stirring. After 5 min, ligand **3** (0.048 g, 0.080 mmol), dissolved in THF (2 mL), was added to the suspension and the mixture stirred for a further 1 h. The mixture was filtered through Celite, and the solution was concentrated to a small volume; addition of hexane and vigorous shaking led to the formation of **9** as a white solid. Yield 65% (0.093 g, 0.050 mmol). − $C_{86}H_{78}F_6O_{10}P_4S_2Pd_2$ (1786): calcd. C 57.82, H 4.40, S 3.59; found C 57.3, H 4.20, S 3.74. − ^1H NMR ($CDCl_3$): δ = 1.53 [s, 12 H, $C(CH_3)_2$], 3.33 [s (br.), 2H, $H_{b'}$], 3.48 [s (br.), 2 H, H_b], 3.87 [s (br.), 2 H, $H_{a'}$], 3.95 [s (br.), 2 H, H_a], 5.32 [m (br.), 2 H, H_c], 6,48 [d (br.), ^3J = 8 Hz, 8 H, H_e], 7,02 [d (br.), ^3J = 10 Hz, 4 H, H_d], 7,41−7.46 [m (br.), $H_{m,p}$, 24 H], 7,83−7.86 [m (br.), 16 H, H_o]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 120,6 [s (br.)].

[PtI$_2$(μ-3)]$_2$ (10): The dinuclear complex was prepared by reaction of ligand **3** (0.089 mg, 0.143 mmol) with a solution of [Pt(COD)I_2] (0.080 g, 0.143 mmol) in toluene (30 mL). A yellow precipitate was immediately obtained. The reaction mixture was stirred for 1 h and then the solvent was removed. The precipitate was washed with toluene (3 × 1 mL) and finally dried in vacuo. Yield 78% (0.117 g, 0.056 mmol). − $C_{78}H_{68}I_4O_4P_4Pt_2$ (2091): calcd. C 44.8, H 3.28, I 24.28; found C 45.15, H 3.39, I 24.60. − ^1H NMR ($CDCl_3$): δ = 1.51 [s, 6 H, $C(CH_3)_2$], 6.35 (d, ^3J = 8.4 Hz, 4 H, CH), 6.72 (d, ^3J = 8.3 Hz, 4 H, CH), 7.16−7.41 (m, 12 H, CH), 7.63−7.70 (m, 8H, CH). − ^{31}P {^1H} ($CDCl_3$): δ = 81.81 (s, J_{PtP} = 3968 Hz).

[Cu(μ-3)]$_2$[BF$_4$]$_2$·2CH$_3$CN (11): A dichloromethane solution containing ligand **3** (0.095 g, 0.159 mmol) was added dropwise to a solution of [$Cu(CH_3CN)_4$]BF_4 (0.050 g, 0.159 mmol) in CH_2Cl_2 (10 mL). The colourless solution was kept under continuous stirring for ca. 1 h, filtered through Celite and concentrated under vacuum until a volume of 1 mL was achieved. Further addition of hexane (10 mL) led to the formation of a white solid which was isolated, washed several times with hexane and dried. Yield 87% (0.109 g, 0.069 mmol). − $C_{82}H_{74}B_2Cu_2F_8N_2O_4P_4$ (1576): calcd. C 62.49, H 4.73, N 1.78; found C 62.29, H 4.93, N 1.59. − ^1H NMR ($CDCl_3$): δ = 1.49 [s, 6 H, $C(CH_3)_2$], 1.98 (s, 6 H, CH_3), 6.7 (d, ^3J = 8.4 Hz, 4 H, CH), 6.93 (d, ^3J = 8.3 Hz, 4 H, CH), 7.35−7.43 (m, 20 H, CH). − ^{31}P {^1H} NMR ($CDCl_3$): δ = 99.06 (s). − Λ [ohm^{-1} cm^2 mol^{-1}] (5 10^{-4} − 10^{-3} M CH_3OH) = 182.

[PdCl$_2${[2-Ph$_2$PO-3,5-(MeC)$_2$C$_6$H$_2$][3,5-(Me$_3$Cl$_2$C$_6$H$_2$OH]S}] (12): A solution of [$Pd(PhCN)_2Cl_2$] (0.050 g, 0.130 mmol) in toluene (10 mL) was treated with a toluene solution of ligand **4** (0.105 g, 0.130 mmol). The yellow solution was stirred for ca. 30 min and then reduced to a small volume (1 mL). By crystallization from a toluene/hexane mixture, a yellow solid was obtained. Yield 78% (0.081 g, 0.101 mmol). − $C_{40}H_{51}Cl_2O_2PSPd$ (804.2): calcd. C 59.74, H 6.39, Cl 8.82, S 3.99; found C 59.37, H 6.31, Cl 8.26, S 4.23. − ^1H NMR ($CDCl_3$): δ = 0.99 [s, 9 H, $C(CH_3)_3$], 1.03 [s, 9 H, $C(CH_3)_3$], 1.30 [s, 9 H, $C(CH_3)_3$], 1.31 [s, 9 H, $C(CH_3)_3$], 6.34 (d, ^3J = 2.1 Hz, 1 H, CH_{Ar}), 7.21−7.71 (m, 14 H, CH). − ^{31}P {^1H} ($CDCl_3$): δ = 135.66 (s).

[Cu(μ-4)]$_2$[BF$_4$]$_2$·CH$_3$CN (14): The white compound **13** was prepared from [$Cu(CH_3CN)_4$]BF_4 (0.080 g, 0.254 mmol) and the ligand **4** (0.206 g, 0.254 mmol) as described above for the compound **11**. Yield 89% (0.222 g, 0.113 mmol). − $C_{106}H_{123}B_2Cu_2F_8NO_4P_4S_2$ (1963): calcd. C 64.83, H 6.31, N 0.71, S 3.26; found C 64.48, H 6.42, N 0.80, S 2.95. − ^1H NMR ($CDCl_3$): δ = 0.87 [s, 18 H, $C(CH_3)_3$], 1.24 [s, 18 H, $C(CH_3)_3$], 2.26 (s, 3 H, CH_3), 7.01−7.40 (m, 24 H, CH). − ^{31}P {^1H} NMR ($CDCl_3$): δ = 108.81 (s). − Λ [ohm^{-1} cm^2 mol^{-1}] (5 10^{-4} − 10^{-3} M CH_3OH) = 183.

[PdCl$_2$(μ-5)]$_2$ (15): Ligand **5** (0.110 g, 0.128 mmol), dissolved in toluene (5 mL), was added dropwise with continuous stirring to a solution of [$Pd(PhCN)_2Cl_2$] (0.05 g, 0.128 mmol) in toluene (10 mL). A yellow-orange solid began to precipitate. After 2 h, the solid was isolated from the reaction mixture, washed with toluene (3 × 1 mL), and dried under vacuum. Yield 73% (0.097 g, 0.046 mmol). − $C_{110}H_{76}Cl_4O_{12}P_4Pd_2$ (2068): calcd. C 63.88, H 3.70, Cl 6.86; found C 63.56, H 4.04, Cl 6.93. − ^1H NMR ($CDCl_3$): δ = 1.27 [s, 6 H, $C(CH_3)_2$], 6.25 (d, ^3J = 6.6 Hz, CH, 4 H), 5.5 (d, ^3J = 6.6 Hz, 4 H, CH), 7.27−7.65 (m, 12 H, CH), 7.89−8.01 (m, 8 H, CH). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 107.68 (s).

[PtI$_2$(μ-5)]$_2$ (16): The yellow bridge species was synthesized by the reaction of a solution of [Pt(COD)I_2] (0.050 g, 0.089 mmol) in toluene (10 mL) with a toluene solution of ligand **5** (0.076 mg, 0.089 mmol), using the same procedure for the synthesis of **16**. Yield 78% (0.116 g, 0.045 mmol). − $C_{110}H_{76}I_4O_{12}P_4Pt_2$ (2611): calcd. C 50.59, H 2.93, I 19.44; found C 50.28, H 2.59, I 19,60. − ^1H NMR ($CDCl_3$): δ = 1.27 [s, 6 H, $C(CH_3)_2$], 6.36 (d, ^3J = 8.8 Hz, 4 H, CH), 6.63 (d, ^3J = 8.3 Hz, 4 H, CH), 7.16−7.88 (m, 20 H, CH). − ^{31}P {^1H} NMR ($CDCl_3$): δ = 84.06 (s, J_{PtP} 5543 Hz).

X-ray Structure Determination of 10·2CH$_2$Cl$_2$ and 12·2CH$_2$Cl$_2$: The crystals of both complexes were obtained by crystallization from dichloromethane solutions and molecules of solvent were found in them. The intensity data of both complexes were collected at room temperature with a Siemens AED (**10·2CH$_2$Cl$_2$**) and with an Enraf−Nonius CAD 4 (**12·2CH$_2$Cl$_2$**) single-crystal diffractometer using graphite-monochromated Mo-K_α (**10·2CH$_2$Cl$_2$**) and Cu-K_α (**12·2CH$_2$Cl$_2$**) radiation and the θ/2θ scan technique. Crystallographic and experimental details for both structures are summarized in Table 3. A correction for absorption was made for both complexes [maximum and minimum value for the transmission coefficient was 1.000 and 0.487 (**10·2CH$_2$Cl$_2$**), 1.000 and 0.697 (**12·2CH$_2$Cl$_2$**).[14] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms, except for the carbon and chlorine atoms of the solvent molecules (**10·2CH$_2$Cl$_2$**) and except for the carbon atoms of the two isobutyl groups which were found disordered in two positions with an occupancy factor of 0.5 (**12·2CH$_2$Cl$_2$**). In both structures, the hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2 + (0.0533\ P)^2]$ (**10·2CH$_2$Cl$_2$**) and $w = 1/[\sigma^2 F_o^2 + (0.1271\ P)^2]$ (**12·2CH$_2$Cl$_2$**) where $P = (F_o^2 + 2\ F_c^2)/3$ was used. All calculations were carried out with the DIGITAL AlphaStation 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.[15] The supplementary material for the structures includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. The details of the crystal structure investigations have been deposited in the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-143608 (**10·2CH$_2$Cl$_2$**) and -143609 (**12·2CH$_2$Cl$_2$**). Copies of the data can be obtained free of charge on application to CCDC,

Table 3. Crystal data and structure refinement for **$10\cdot2CH_2Cl_2$** and **$12\cdot2CH_2Cl_2$**; $R1 = \Sigma|F_o - F_c|/|\Sigma(F_o)$ $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

	$10\cdot2CH_2Cl_2$	**$12\cdot2CH_2Cl_2$**
Empirical formula	$C_{78}H_{68}I_4O_4P_4Pt_2\cdot2CH_2Cl_2$	$C_{40}H_{51}Cl_2PPdS\cdot2CH_2Cl_2$
Formula mass	2260.84	973.99
Temperature	293(2) K	293(2) K
Wavelength	0.71144 Å	1.54184 Å
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*n*
Unit cell dimensions	a = 31.436(5)Å b = 16.563(4)Å c = 15.894(4)Å β = 101.28(6)°	a = 14.740(4)Å b = 19.851(5)Å c = 16.272(4)Å β = 93.17(6)°
Volume	8116(3) Å^3	4754(2) Å^3
Z	4	4
Density (calcd.)	1.850 Mg/m^3	1.361 Mg/m^3
Absorption coefficient	52.23 cm^{-1}	72.28 cm^{-1}
F(000)	4320	2008
Crystal size	0.32 × 0.25 × 0.21 mm	0.12 × 0.22 × 0.22 mm
θ range [°]	3.08−27.10	3.52−70.02
Index ranges	$-40 \le h \le 39, -6 \le k \le 21, -19 \le l \le 20$	$-17 \le h \le 17, 0 \le k \le 24, 0 \le l \le 19$
Reflections collected	11581	9313
Independent reflections	8909 [*R*(int) = 0.1353]	8995 [*R*(int) = 0.0554]
Obs. refl [$I > 2\sigma(I)$]	4772	6097
Data/restr./param.	8909/6/448	8995/0/482
Goodness-of-fit on F^2	0.838	0.981
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0421, $wR2$ = 0.0905	$R1$ = 0.0589, $wR2$ = 0.1704
R indices (all data)	$R1$ = 0.0959, $wR2$ = 0.1035	$R1$ = 0.0831, $wR2$ = 0.1883

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[1] [1a] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. − [1b] P. J. Stang, Chem. *Eur. J.* **1998**, *4*, 19. − [1c] P. N. W. Baxter, *Metal Ion Directed Assembly of Complex Molecular Architectures and nanostructures* in *Comphrensive Supramolecular Chemistry*, vol. 9 (Series Ed.: J-M. Lehn; Volume Eds.: J. P. Sauvage, M. W. Hosseini), Pergamon, Oxford, **1996**, chapter 5, p. 165. − [1d] G. X. Liu, R. Puddephatt, *Organometallics* **1996**, *15*, 5257. − [1e] S. Achar, J. J. Vittal, R. Puddephatt, *Organometallics* **1996**, *15*, 43.

[2] [2a] J. A Whiteford, C. V. Lu, P. J. Stang, *J. Am. Chem. Soc.* **1997**, *119*, 2524. − [2b] P. J. Stang, D. H. Cao, S. Saito, A. A. M. Arif, *J. Am. Chem. Soc.* **1994**, *117*, 6273. − [2c] P. J. Stang, D. H. Cao, *J. Am. Chem. Soc.* **1994**, *116*, 4981.

[3] C. J. Jones, *Chem. Soc. Rev.* **1998**, *27,* 289.

[4] [4a] P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502. − [4b] F. Makoto, K. Ogura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471.

[5] F. S. McQuillan, H. Chen, T. A. Hamor, C. J. Jones, H. A. Jones, P. Sidebotham, *Inorg. Chem.* **1999**, *38*, 1555.

[6] C. G. Arena, D. Drago, M. Panzalorto, G. Bruno, F. Faraone, *Inorg. Chim. Acta* **1999**, *292*, 84.

[7] S. D. Pastor, J. D Spivack, L. P Steinhuebel, *J. Heterocycl. Chem.* **1984**, *21*, 1285.

[8] G. Franciò, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219.

[9] F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publishers Ltd., Ripple Road, Barking, Essex, England, **1973**.

[10] P. S. Pregosin, R. Salzmann, *Coord. Chem. Rev.* **1996**, *155*, 35

[11] J. Manna, C. J. Kuchl, J. A. Whiteford, P. J. Stang, *Organometallics* **1997**, *16*, 1897.

[12] M. Fuss, H. U. Siehl, B. Olenyuk, P. J. Stang, *Organometallics* **1999**, *18*, 758.

[13] G.J. Kubas, *Inorg. Synth*. **1979**, *19*, 90.

[14] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39* 158. − F. Ugozzoli, *Comput. Chem.* **1987**, *11*, 109.

[15] G. M. Sheldrick, *SHELX-97, Program for the Solution and the refinement of Crystal Structures*, Universität Göttingen, Germany, **1997**.

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