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One-dimensional phosphinite platinum chains based on hydrogen bonding interactions and phosphinite tetranuclear platinum(II)–thallium(I) complexes†‡§

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The mononuclear pentafluorophenyl platinum complex containing the chelated diphenylphosphinous acid/diphenylphosphinite system $[Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]$ **1** has been prepared and characterised. **1** and the related alkynyl complex $[Pt(C\equiv CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ **2** form infinite one-dimensional chains in the solid state based on intermolecular O–H···O hydrogen bonding interactions. Deprotonation reactions of $[PtL\{(PPh_2O)_2H\}(PPh_2OH)]$ ($L = C_6F_5$ **1**, $C\equiv CBu^t$ **2**, $C\equiv CPh$ **3**) with [Tl(acac)] yields tetranuclear Pt_2Tl_2 complexes $[PtL\{(PPh_2O)_2H\}(PPh_2O)Tl]_2$ ($L = C_6F_5$ **4**, $C\equiv CBu^t$ **5**, $C\equiv CPh$ **6**). The structure of the *tert*-butylalkynyl derivative **5**, established by X-ray diffraction, shows two anionic discrete units $[Pt(C\equiv CBu^t)\{(PPh_2O)_2H\}(PPh_2O)]^-$ joined by two Tl(I) centres *via* Tl–O and Pt–Tl bonds. Despite the existence of Pt–Tl interactions, they do not show luminescence.

Introduction

The dialkyl or diaryl phosphinous acids $[PR_2(O)H]$ and their anions phosphinite $[PR_2(O)^-]$ together with the strong hydrogen bonded mixed system $PR_2(O)\cdots H\text{-}OPR_2$ have been extensively used as ligands for the synthesis of transition metal complexes.[1–24] In this area, phosphinite platinum and palladium complexes have been recently reported as efficient catalysts in general C–C bond forming processes[25–34] as well as in hydrophosphinylation reactions,[35,36] hydrophosphorylation of alkenes and alkynes[37–39] and hydrogenation or hydroformylation of alkenes.[40–42]

We have been interested in the synthesis and reactivity of alkynyl phosphinite platinum complexes. Thus, the neutral derivatives $[Pt(C\equiv CR)\{(PPh_2O)_2H\}(PPh_2OH)]$ and $(NBu_4)[cis\text{-}Pt(C\equiv CR)_2\{(PPh_2O)_2H\}]$ ($R = Bu^t$, Ph) have proven to be valuable precursors to unusual hexanuclear Pt_2Li_4 sandwiched complexes of the type $[Pt(C\equiv CR)(PPh_2O)_3Li_2(H_2O)(THF)]_2$ and $[Pt(C\equiv CBu^t)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2]_2$[43,44] and platinum–rhodium or iridium heterobridged $[\{(PPh_2O)_2H\}Pt(\mu\text{-}\kappa^{\alpha}:\eta^2\text{-}C\equiv CR)(\mu\text{-}\kappa P:\kappa O\text{-}PPh_2O)ML_2]$ (ML_2 = Rh/Ir(COD); $Rh(CO)_2$] complexes,[45] while *cis*-bis(alkynyl) anionic complexes $(NBu_4)[cis\text{-}Pt(C\equiv CR)_2\{(PPh_2O)_2H\}]$ react with Ag(I) and Cu(I) salts to give tetra $[Pt_2M_2]$ or bimetallic [PtCu] derivatives, which show strong luminescence in frozen CH_2Cl_2 solutions.[46]

For comparative purposes, we considered it of interest to explore the reactivity of chelating diphenylphosphinous acid/diphenylphosphinite platinum complexes towards Tl(I). Numerous reports on platinum(II)–thallium(I) complexes have appeared in the literature over the last few years[47–63] and it now seems clear that their structural chemistry is characterised by attractive platinum–thallium interactions, which, on some occasions, compete with other Tl–X (X = N, O, π,. . .) bonds. Many of the Pt(II)–Tl(I) derivatives have been found to display luminescent properties, just like $[PtTl_2(CN)_4]$, which have been invariably related to the formation of the Pt–Tl bonds and attributed to a metal–metal' charge transfer transition MM'CT.[48–51,59–64] We have previously shown that with the homoleptic substrates $[Pt(C\equiv CR)_4]^{2-}$ ($R = Bu^t$, Ph, $SiMe_3$, Tol, 1-Naph), the Tl(I) centre exhibits a strong bonding preference towards the electron rich alkynyl entities, yielding final sandwich hexanuclear clusters $[Pt_2Tl_4(C\equiv CR)_8]$. However, in similar reactions with the electron-poor alkynyl derivative $[Pt\{C\equiv CC_6H_4\text{-}(p\text{-}CF_3)\}_4]^{2-}$ as well as with the heteroleptic *cis* (R = Ph) or *trans* ($R = Bu^t$) anionic substrates $[Pt(C_6F_5)_2(C\equiv CR)_2]^{2-}$, metallophilic platinum–thallium bonding interactions become preferential and the resulting platinum entities contain two Pt–Tl bonds that dimerise $[trans,cis,cis\text{-}PtTl_2(C_6F_5)_2(C\equiv CPh)_2]$[61] or polymerise $[PtTl_2\{C\equiv CC_6H_4\text{-}(p\text{-}CF_3)\}_4]_\infty$,[62] $[trans,trans,trans\text{-}PtTl_2(C_6F_5)_2(C\equiv CBu^t)_2]$[59] through secondary Tl–alkynyl (C_α) contacts.

We report here the preparation of the pentafluorophenyl derivative $[Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]$ **1** and the crystallographic characterisation of **1** and the related alkynyl derivative $[Pt(C\equiv CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ **2**. The reactivity of $[PtL\{(PPh_2O)_2H\}(PPh_2OH)]$ ($L = C_6F_5$ **1**, $C\equiv CBu^t$ **2**, $C\equiv CPh$ **3**) towards [Tl(acac)] led to tetranuclear Pt(II)–Tl(I) complexes. It is worth noting that despite the relatively strong Pt–Tl bonding

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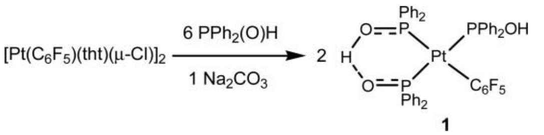
‡ The HTML version of this article has been enhanced with colour images.

§ Dedicated to Prof. Miguel Yus (University of Alicante) on the occasion of his 60th birthday.

interactions in these complexes, they do not show emissive properties.

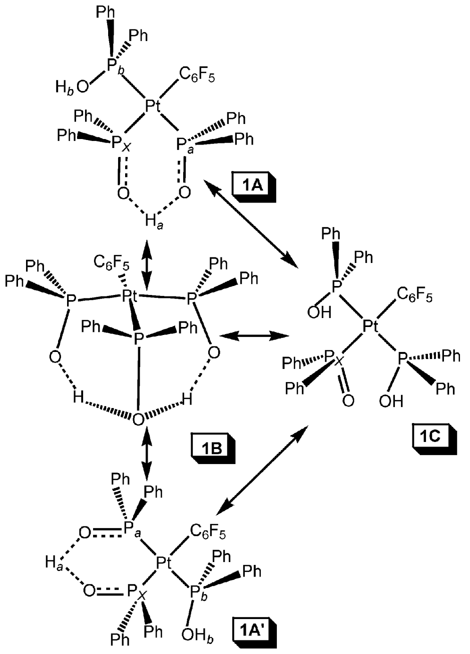
Results and discussion

As shown in eqn (1), treatment of $[Pt(C_6F_5)(tht)(\mu\text{-}Cl)]_2$ in acetone at room temperature with 6 equiv of $PPh_2(O)H$ in the presence of Na_2CO_3 (1 equiv) leads to the formation of the neutral phosphinite/hydroxyphosphine containing derivative $[Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]$ **1** in moderate yield (59%). Complex **1** is an air-stable white solid, slightly soluble in common organic solvents, the spectral properties of which are consistent with their formulation. Thus, in its FAB(+) spectrum, **1** shows the expected peak corresponding to the molecular ion and in its IR spectrum absorptions in the ν(P=O) region (890–1106 cm^{-1}) and one ν(X-sensitive C_6F_5) band at 781 cm^{-1}. As has been previously noted,[1,12–24,44–46] the lack of bands due to ν(O–H) in the usual spectral region is consistent with the presence of symmetrical hydrogen bond O···H···O formation, given that the vibrations assigned to this system appear below 2000 cm^{-1}.[65] The most interesting feature of its ^1H NMR spectrum (−50 °C) is the presence of a broad downfield signal at δ 17.25, attributable to the hydrogen bridging the oxygen atoms, which compares well to those found in related platinum complexes (δ 13.2–17.2).[14,15,22,35,44–46]



(1)

At −50 °C complex **1** exhibits the expected ABX pattern with ^{195}Pt satellites in its $^{31}P\{^1H\}$ NMR spectrum. In accordance with previous assignments,[44] the most deshielded signals (δ P_A/P_X 88.92/71.25; $^2J_{PA,PB\,trans}/^2J_{PA,PX\,cis}$ 435 Hz/26.1 Hz) are assigned (tentatively for P_A) to the inequivalent phosphorus atoms of the $PPh_2O\cdots H\cdots OPPh_2$ system and the highfield resonance [δ P_B 70.20] to the hydroxydiphenylphosphine PPh_2OH. The lower value of the coupling constant found for the P_x phosphorus atom *trans* to the C_6F_5 group, confirms the high *trans* influence of this group. The $^{31}P\{^1H\}$ NMR spectrum of **1** is temperature dependent. When the temperature is increased, the mutually *trans* phosphorus resonances P_A and P_B disappear into the baseline at ~25 °C, while the central signal (P_X) due to PPh_2O^- *trans* to C_6F_5 is seen as a broad singlet. This behaviour indicates that at high temperature P_A and P_B become magnetically equivalent, implying a fast migration of the acidic proton H_a and H_b between the forms **1A** an **1A′** showed in Scheme 1. The motion of a proton between donor and acceptor atoms is one of the simplest chemical reactions and has been studied[66,67] in detail. The transformation of **1A** to **1A′** form may occur intramolecularly through the concerted motion of the two hydrogens *via* an intermediate such as **1B**, or by two successive motions through the *trans*-pentafluorophenyl bis(hydroxyphosphine)phosphinite platinum intermediate **1C**. However, although an intramolecular pathway seems reasonable, isomerization involving intermolecular interaction through hydrogen bonding cannot be excluded. In fact, the extended intermolecular aggregation observed in the solid state for **1** (see below) suggests that, in solution, the presence of this type of intermolecular interactions cannot be excluded.



Scheme 1

X-Ray diffraction studies of complex **1** and of the related complex $[Pt(C\equiv CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ **2** were carried out on single crystals obtained by slow evaporation of the reaction mixture in acetone at −30 °C (**1**) or by diffusion of *n*-hexane into a CH_2Cl_2 solution of **2** at −30 °C (**2**). The molecular structures of the complexes **1·Me₂CO** and **2** are depicted in Fig. 1–4. Relevant bond lengths and angles are given in Tables 1 and 2. The most significant structural feature in these derivatives is the formation of an extended 1-D chain formed by $[Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**1**) or $[Pt(C\equiv CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**2**) units connected through O···H···O hydrogen bonds between the terminal PPh_2OH of one molecule and a PPh_2O unit of the chelating $\{(PPh_2O)_2H\}$ group of the next molecule (Fig. 2 and 4). The main difference between both structures is that in **1**, the H(2) atom corresponding to the terminal phosphinite ligand interacts intermolecularly with the O(2′) atom corresponding to the phosphinite ligand of the chelate ring *trans* to C_6F_5 group, whereas in **2**,

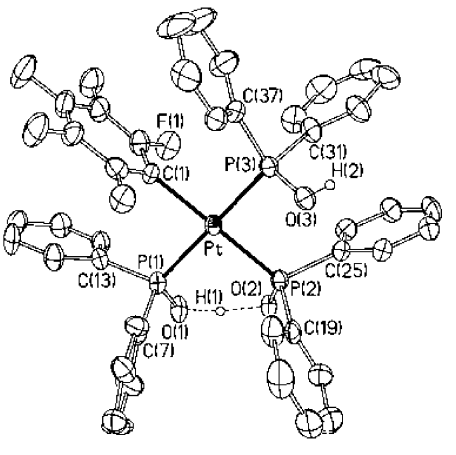


Fig. 1 Molecular structure of $[(Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]\cdot Me_2CO$ (**1·Me₂CO**). Ellipsoids are drawn at the 50% probability level.

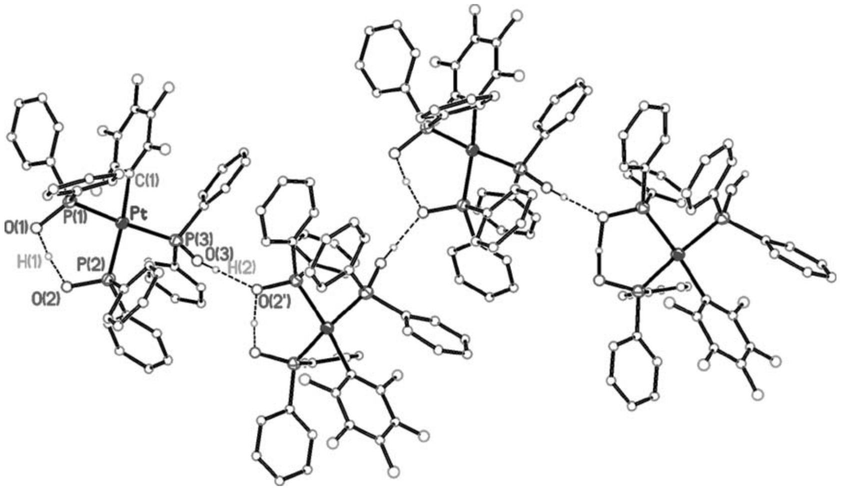


Fig. 2 View of the polymeric one-dimensional chain formed in $[(Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]_n$ $[\mathbf{1}]_n$. O(2′) is at equivalent position (2−*x*, 1/2 + *y*, 1/2−*z*).

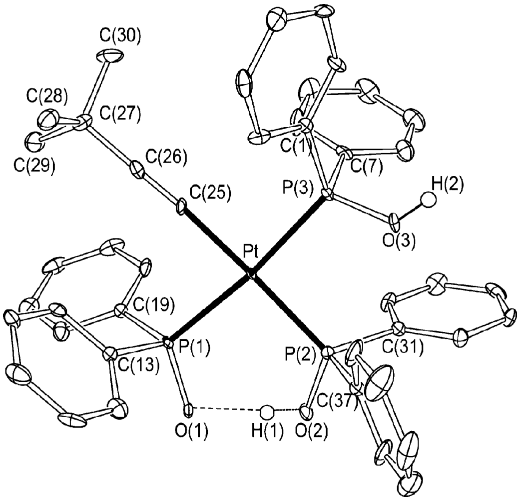


Fig. 3 Molecular structure of $[(Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**2**). Ellipsoids are drawn at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for $[(Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]\cdot Me_2CO$ ($\mathbf{1\cdot Me_2CO}$)

Pt–P(1)	2.3087(15)	Pt–P(2)	2.3113(14)
Pt–P(3)	2.3043(14)	Pt–C(1)	2.095(5)
P(1)–O(1)	1.572(4)	P(2)–O(2)	1.557(4)
P(3)–O(3)	1.576(4)	O(1)–H(1)	1.14(8)
O(2)–H(1)	1.34(8)	O(3)–H(2)	0.80(8)
C(1)–Pt–P(1)	88.07(16)	C(1)–Pt–P(3)	90.69(16)
P(1)–Pt–P(2)	89.27(5)	P(3)–Pt–P(2)	92.49(5)
O(1)–P(1)–Pt	114.77(16)	O(2)–P(2)-Pt	111.92(15)
O(3)–P(3)–Pt	108.61(16)	P(1)–O(1)–H(1)	106(4)
P(2)–O(2)–H(1)	109(3)	P(3)–O(3)–H(2)	124(6)
O(1)–H(1)–O(2)	170.8		

the terminal H(2) atom interacts intermolecularly with the O(1′) atom of the phosphinite group *trans* to the terminal phosphinite ligand. The low solubility of these products in common organic solvents is probably due to the existence of these intermolecular interactions. The O(3)–O(2′) (**1**) or O(3)–O(1′) (**2**) distances (the marks ′ indicate atoms of a different molecule) between oxygen atoms of the two adjacent units are 2.547 Å and 2.517 Å, respectively with clear asymmetry in the O–H distances [O(3)–H(2) 0.80(8) Å (**1**), 0.83(7) Å (**2**) in the same molecule and H(2)···O(2′) 1.749 Å (**1**), H(2)···O(1′) 1.700 Å (**2**), between two different molecules] and angles P(3)–O(3)···O′ of 126.4° (**1**) and 122.40° (**2**). The formation of supramolecular aggregates by the self assembling of individual entities through secondary classical O–H···O intermolecular hydrogen bonding is now a well recognized process.[68–72]

In both cases, the platinum atom is in a square planar environment formed by the C_{ipso} of the C_6F_5 ring (**1**) or the C_α

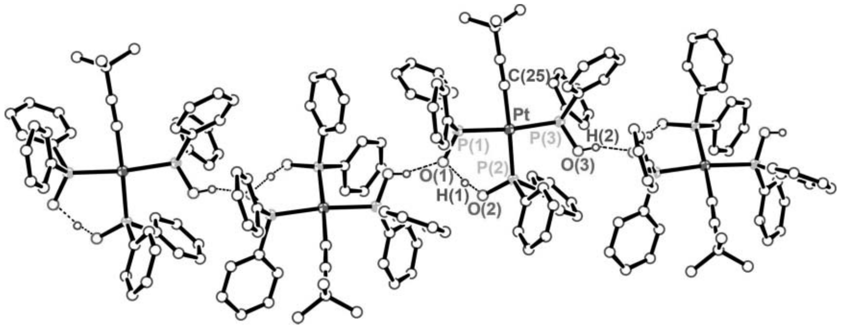


Fig. 4 View of the polymeric one-dimensional chain formed in $[(Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]_n$ $[\mathbf{2}]_n$.

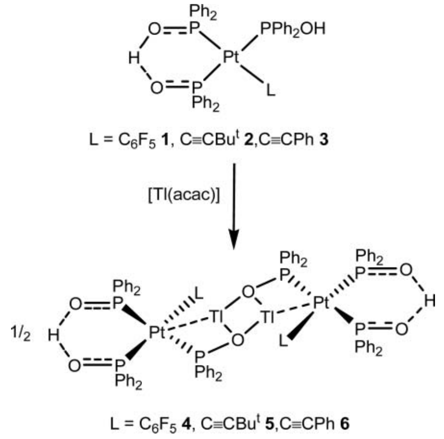
Table 2 Selected bond lengths (Å) and angles (°) for $[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**2**)

Pt–P(1)	2.3202(15)	Pt–P(2)	2.2892(16)
Pt–P(3)	2.3141(15)	Pt–C(25)	2.013(6)
P(1)–O(1)	1.557(4)	C(25)–C(26)	1.191(8)
P(3)–O(3)	1.574(5)	P(2)–O(2)	1.591(5)
O(1)–H(1)	1.68(7)	O(3)–H(2)	0.83(7)
O(2)–H(1)	0.84(7)		
C(25)–Pt–P(3)	89.33(19)	C(25)–Pt–P(1)	83.77(19)
P(2)–Pt–P(3)	93.01(6)	P(2)–Pt–P(1)	93.87(6)
O(1)–P(1)-Pt	114.98(17)	O(2)–P(2)–Pt	115.4(2)
O(3)–P(3)–Pt	111.44(19)	P(1)–O(1)–H(1)	109.80
P(2)–O(2)–H(1)	110.51	P(3)–O(3)–H(2)	121.96
O(1)–H(1)–O(2)	165.49		

alkynyl carbon (**2**), the phosphorus atom of the terminal PPh_2OH group and the two phosphorus atoms of the diphenylphosphinite/diphenylphosphinous chelate ring, with usual bond distances and angles. In the chelate ring the Pt–P distances, although nearly identical, show a slight asymmetry [Pt–P(1) 2.3087(15) **1**, 2.3202(15) Å **2** and Pt–P(2) 2.3113(14) **1**, 2.2892(16) Å **2**], which is in agreement with the observed platinum–phosphorus coupling constants (see Experimental section and ref. 44). The 5-membered ring (Pt–P–O–O–P) is not flat. Representative torsion angles into the ring for **1** are Pt–P(1)–O(1) $\cdots$ O(2) 25.1°; P(1)–O(1) $\cdots$ O(2)–P(2) 1.3°, O(1) $\cdots$ O(2)–P(2)–Pt −26.4°; P(2)–Pt–P(1)–O(1) −36.5°. The O–O bond distances in the anionic chelate systems (O(1)–O(2) 2.470 Å **1**, 2.502 Å **2**) are shorter than the sum of the van der Waals radii, indicative of a strong hydrogen bond.[73] The observed O–H distances [O(1)–H(1) 1.14(8) Å, O(2)–H(1) 1.34(8) Å **1**, O(2)–H(1) 0.84(7) Å, O(1)–H(1) 1.68(7) Å **2**] and the angles O(1)–H(1)–O(2) (170.8° **1**, 165.49° **2**), indicate that the hydrogen bond system is more asymmetric[22,23,26,42] in **2** than in **1**.

As we noted in the Introduction, we have been interested in recent years in studying the structure–properties relationship of Pt–Tl heteropolynuclear complexes. Previously, we have reported that the homoleptic derivatives $[Pt(C{\equiv}CR)_4]^{2-}$ (R = Bu^t, Ph, SiMe$_3$, Tol, 1-Naph) react with Tl(I) salts giving hexanuclear luminescent complexes of the type $[Pt_2Tl_4(C{\equiv}CR)_8]$ by sandwiching naked Tl^I centres through the preferred Tl^I–alkyne interactions.[60,62] However with R = 4-$CF_3C_6H_4$, the platinum has a stronger preference for the Tl(I) centre yielding supramolecular columnar species $[PtTl_2(C{\equiv}C\text{-}4\text{-}CF_3C_6H_4)_4(acetone)S]_\infty$ (S = acetone, dioxane) stabilized by Pt–Tl bonds and secondary Tl $\cdots$ (η^2-acetylenic) interactions. Similar reactions with heteroleptic *cis* or *trans*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ (R = Bu^t, Ph) yield also six-coordinated platinum entities with two direct Pt–Tl bonds that dimerise (*cis*)[61] or polymerise (*trans*)[59] through Tl^I–alkynyl (C_α) contacts. With $[Pt(C_6F_5)_4]^{2-}$ we have described a trimetallic complex and two different anionic $[Pt\text{–}Tl]_\infty{}^-$ chain systems formed by alternate anionic fragments and naked Tl$^+$ centres joined through Pt–Tl bonds.[74] All complexes display interesting luminescent properties, which can be modulated through Pt $\cdots$ Tl and/or η^2-alkynyl–Tl bonding interactions.

With this in mind, we decided to study the reactivity of the phosphinite complexes $[PtL\{(PPh_2O)_2H\}(PPh_2OH)]$ (L = C_6F_5 **1**, C≡CBu^t **2**, C≡CPh **3**) towards Tl^I. These derivatives may be viewed as potential metalloligands if one deprotonated oxygen atom of a phosphinite ligand, the alkynyl and the platinum atom are considered.



(2)

The treatment of $[PtL\{(PPh_2O)_2H\}(PPh_2OH)]$ (L = C_6F_5 **1**, C≡CR;[44] R = Bu^t **2**, Ph **3**) in acetone or THF with [Tl(acac)] in a 1 : 1 molar ratio causes the dissolution of the initial suspensions and subsequent formation of complexes **4–6** as white precipitates. The solids obtained present very low solubility in common solvents, especially complex **4**, which is extremely insoluble precluding its characterisation in solution. These complexes analyse as $[PtL\{(PPh_2O)_2H\}PPh_2OTl]$ but their dimeric formulation as tetrametallic species $[PtL\{(PPh_2O)_2H\}(PPh_2O)Tl]_2$ (L = C_6F_5 **4**, C≡CBu^t **5**, C≡CPh **6**) (eqn (2)) was carried out on the basis of an X-ray diffraction study of **5**. Single crystals of **5** were grown by slow diffusion of *n*-hexane into a saturated solution of **5** in $CHCl_3$ at −30 °C (Fig. 5 and Table 3). The crystals contain two molecules of $CHCl_3$ per complex molecule. This study shows the formation of an unusual centrosymmetric dimer Pt_2Tl_2, $[Pt(C{\equiv}CBu^t)\{PPh_2O)_2H\}(PPh_2O)Tl]_2$, stabilised by bridging diphenylphosphinite ligands, displaying a μ_3-1κP,2κO,3$\kappa O'$ (Pt,Tl,Tl) bonding mode. As far as we know, this is the first reported example containing phosphinite ligands and thallium centres. The coordination bonding of the phosphinite group to

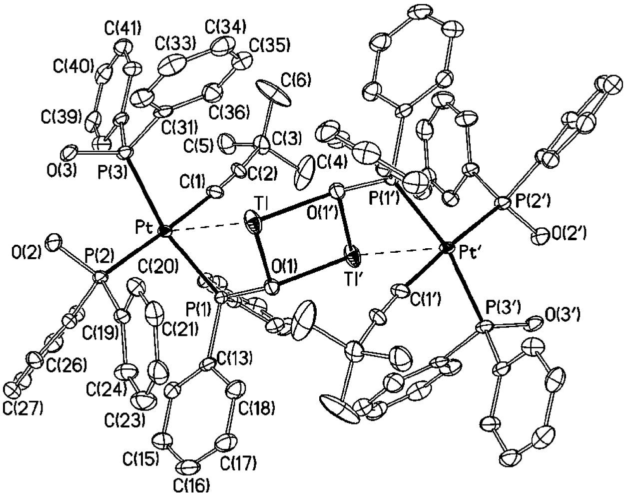


Fig. 5 View of the molecular structure of $[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O)Tl]_2{\cdot}2CHCl_3$ (**5·2CHCl$_3$**). Ellipsoids are drawn at the 50% probability level. The prime (′) character in the atom labels indicates that these atoms are at equivalent position (−*x*, −*y*, −*z*).

Table 3 Selected bond lengths (Å) and angles (°) for [Pt(C≡CBu^t)-{(PPh$_2$O)$_2$H}(PPh$_2$O)Tl]$_2$·2CHCl$_3$ (**5·2CHCl$_3$**)

Pt–C(1)	2.024(5)	Pt–P(1)	2.3446(13)
Pt–P(2)	2.2931(14)	Pt–P(3)	2.3232(14)
Pt–Tl	3.1090(11)	Tl–O(1)	2.538(3)
Tl–O(1′)	2.468(4)	P(1)–O(1)	1.550(4)
P(2)–O(2)	1.578(4)	P(3)–O(3)	1.542(4)
C(1)–C(2)	1.196(7)	C(2)–C(3)	1.482(7)
C(1)–Pt–P(1)	82.49(15)	P(2)–Pt–P(1)	99.46(5)
C(1)–Pt–P(3)	85.60(15)	P(2)–Pt–P(3)	92.86(5)
O(1′)–Tl–O(1)	77.69(12)	Tl′–O(1)–Tl	102.31(12)
C(2)–C(1)–Pt	170.6(5)	C(1)–C(2)–C(3)	173.1(6)
O(1)–Tl–Pt	67.44(8)	O(1′)–Tl–Pt	116.39(8)
P(1)–O(1)–Tl	107.36(18)	P(1)–O(1)–Tl′	131.2(2)

three metal centres (μ_3-κ^3:*P*,*O*,*O*′) bridging two hard Li centres through the oxygen atoms (μ-O) and also being *P*-bonded to a Pt centre, has been reported by us.[43,44] The Tl(I) centre of each half of the molecule is chelated by the anionic fragment [Pt(C≡CBu^t){PPh$_2$O)$_2$H}(PPh$_2$O)]$^-$ through the oxygen atom of the phosphinite ligand [Tl–O 2.538(3) Å] and the basic platinum centre (Tl···Pt 3.1090(11) Å), while the additional coordination of the phosphinite oxygen atom of the other half unit accomplishes a final trigonal pyramidal coordination [Tl–O(1′) 2.468(4) Å]. This geometry and the sum of angles O(1)–Tl–O(1′) [77.69(12)°], O(1)–Tl–Pt [67.44(18)°] and O(1′)–Tl–Pt [116.39(8)°] (261.52°) is indicative of the presence of the lone pair stereochemically active at each Tl(I) centre. The Tl–O distances are shorter than the sum of van der Waals radii and comparable to those found in carboxylate[75] and aryloxide[76–79] thallium derivatives, suggesting an appreciable formation of dative Tl–O bonds. The central four-membered ring {Tl$_2$O$_2$}, which shows a dihedral angle of the platinum coordination planes of 135.90°, is a well-known motif in aryloxide[76–79] and carboxylate[75] Tl(I) chemistry, being previously described in dimers [TlOR]$_2$ (R = (CF$_3$)$_3$C$_6$H$_2$,[76] (C$_6$H$_4$OH)C$_6$H$_4$)[77] and numerous cubane-like structures (Tl$_4$O$_4$).[78–81] A similar structural disposition was observed in (NBu$_4$)$_2$[{(C$_6$F$_5$)$_3$Pt}$_2${(μ_3-OOCCH$_3$)Tl}$_2$].[49]

The Tl(I)–Tl(I) separation is 3.899(1) Å, slightly shorter than the sum of van der Waals radii (3.92 Å)[73] but clearly out of the range of structurally characterised Tl(I)···Tl(I) bonding interactions (3.146–3.887 Å).[79,82] However, the Pt···Tl distance (3.1090(11) Å) is within of the range found for Pt(II)–Tl(I) complexes (2.7961(7)[58]–3.714(1) Å[48–63]). It is worth noting that the thallium atom does not show interaction with the alkynyl function [Tl···C(1) 3.451 Å, Tl–C(2) 4.271 Å]. Without considering the Pt–Tl interaction, each platinum centre has a slightly distorted square planar geometry formed by the chelate ligand PPh$_2$O···H–OPPh$_2$, the phosphorus atom of the PPh$_2$O$^-$ group and the C≡CBu^t ligand [Pt–C(1) 2.024(5) Å]. The Pt–P bond lengths [Pt–P(1) 2.3446(13) Å, Pt–P(2) 2.2931(14) Å, Pt–P(3) 2.3232(14) Å] are within the range found for **1**, **2** and related complexes, and show a slight asymmetry induced by the different *trans*-influence of the ligands. As a consequence of the interaction of the O(1) atom to the thallium centre, the sum of angles around O(1) is 340.87°, far from the planarity (360°), causing a distortion in the coordination plane of the platinum with an angle P(1)–Pt–P(3) [166.61(5)°] that is far from than the ideal value (180°). Curiously, in this distortion the platinum centre suffers a pyramidalisation pointing in the opposite direction to the thallium centre, and located at 0.015 Å of its best coordination plane.

All Pt–Tl compounds (**4–6**) show the expected absorptions in the P–O stretching region (962–1106 cm^{-1}) but only complex **6** exhibits one ν(C≡C) vibration in the expected region for the terminal alkynyl group (2100 cm^{-1}). As previously commented, the low solubility of **4** precludes its characterisation by NMR spectroscopy. However, the ^{1}H NMR spectra at room temperature (**5**) or at −50 °C (**6**) confirm the presence of the expected PPh$_2$O···H···OPPh$_2$ system (δ O–H–O 17.17 **5**, 17.21 **6**). Furthermore, at room temperature (**5**) or at −50 °C (**6**) display in their ^{31}P{^{1}H} NMR spectra the expected ABX pattern with platinum satellites compatible with the molecular structure of **5** in solid state (see Experimental for details).

Despite the presence of a relatively short Pt–Tl distance (3.1090(14) Å), these complexes do not display any detectable luminescence either at room temperature or at low temperature when irradiated with UV light.

Experimental

All reactions were carried out under argon using dried solvents purified by known procedures and distilled prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer as Nujol mulls between polyethylene sheets and NMR spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe$_4$, CFCl$_3$ and 85% H$_3$PO$_4$). Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer and mass spectra on a VG Autospec spectrometer (FAB$^+$). Literature methods were used to prepare the starting materials [Pt(C$_6$F$_5$)(tht)(μ-Cl)]$_2$[83] and [(Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (R = Bu^t **2**, Ph **3**).[44]

[(Pt(C$_6$F$_5$){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (1)

A suspension of *trans*-[Pt(C$_6$F$_5$)(tht)(μ-Cl)]$_2$ (0.450 g, 0.463 mmol) in acetone (20 mL) at room temperature was treated with Na$_2$CO$_3$ (0.049 g, 0.463 mmol) and PPh$_2$(O)H (97%) (0.579 g, 2.779 mmol) and the mixture stirred for 4 h. The resulting mixture was filtered off to give **1** (0.527 g, 59%) as a white solid. (Found: C, 52.33; H, 3.69. C$_{42}$H$_{32}$F$_5$O$_3$P$_3$Pt requires C, 52.13; H, 3.33%); ν_{max}(Nujol)/cm^{-1} 781 (m) (X-sensitive C$_6$F$_5$), 1106 (vs), 954 (s), 932 (m) and 890 (sh) (P–O); δ_H (300.1 MHz; CD$_3$COCD$_3$; −50 °C), 17.25 (br, tentatively assigned to O···H···O), 7.59 (6H, m, Ph) and 7.36–7.16 (24H, m, Ph); δ_F (282.4 MHz; CD$_3$COCD$_3$; −50 °C), −115.2 (2F, dd, $^3J_{Pt,F}$ ~360 Hz, *ortho*-F), −163.1 to −163.9 (3F, m, *para*-F + *meta*-F); δ_P (121.5 MHz, CD$_3$COCD$_3$, −50 °C) ABX pattern, 88.92 (P$_A$, PPh$_2$O$^-$), 70.20 (P$_B$, PPh$_2$OH) and 71.25 (P$_x$, P$_{trans}$ to $_{C6F5}$), $^2J_{PA,PB\ trans}$ 435 Hz, $^2J_{PA,Pxcis}$ 26.1 Hz, $^2J_{PB,Px\ cis}$ less than 10 Hz, $^1J_{Pt,PA}$ 2645 Hz, $^1J_{Pt,PB}$ 2579 Hz, $^1J_{Pt,PX}$ 2456 Hz; δ_P (121.5 MHz, CD$_3$COCD$_3$, 25 °C) 71.42 (s, br, $^1J_{Pt,PX}$ = 2497 Hz); *m*/*z* (FAB+) 968 ([M$^+$], 100%), 800 ([M$^+$ − C$_6$F$_5$], 5%) and 599 ([Pt(PPh$_2$O)$_2$H], 95%).

[Pt(C$_6$F$_5$){(PPh$_2$O)$_2$H}(PPh$_2$O)Tl]$_2$ (4)

A solution of [Pt(C$_6$F$_5$){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (0.100 g, 0.103 mmol) in acetone (20 mL) was treated at −20 °C with [Tl(acac)] (0.032 g, 0.103 mmol) and the mixture was allowed to warm to room temperature. After 1 h of stirring, the resulting white solid (**2**) was filtered and washed with acetone (2 × 5 mL) (0.064 g, 64%). (Found: C, 51.88; H, 2.89. $C_{84}H_{62}F_{10}O_6P_6Pt_2$ requires C, 52.18; H, 3.23%); ν_{max} (Nujol)/cm^{-1} 804 (m) (X-sensitive C_6F_5), 1106 (s), 1008 (m), 985 (m) and 956 (s) (P–O).

$[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O)Tl]_2$ (5)

To a suspension of $[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ (0.150 g, 0.170 mmol) in acetone (20 mL) at −20 °C was added [Tl(acac)] (0.052 g, 0.170 mmol). The initial suspension was dissolved slowly (∼1 h) and a white precipitate formed. The mixture was stirred for 3 h and after that time the product was filtered off, washed with *n*-hexane and dried in vacuum (0.155 g, 84%). (Found: C, 46.11; H, 3.48. $C_{84}H_{80}O_6P_6Pt_2Tl_2$ requires C, 46.49; H, 3.72%); ν_{max}(Nujol)/cm^{-1} C≡C is not observed; 1099 (s), 1012 (m), 999 (m) and 962 (s) (P-O); δ_H (300.1 MHz; CD_3COCD_3, 20 °C) 17.17 (vbr, O···H···O), 7.91 (8H, m, Ph), 7.40, 7.37 (52H, m, Ph) and 0.54 (18H, s, Bu^t); δ_P (121.5 MHz, CD_3COCD_3, 20 °C) ABX pattern, 77.03 (P_A, PPh_2O^-), 59.04 (P_B, PPh_2OH) and 79.23 (P_x, $P_{trans\ to\ C6F5}$), $^2J_{PA,PB\ trans}$ 428 Hz, $^2J_{PA/PB,Px\ cis}$ cannot be calculated, $^1J_{Pt,PA}$ 2141 Hz, $^1J_{Pt,PB}$ 2167 Hz, $^1J_{Pt,PX}$ 2820 Hz); *m*/*z* (FAB+) 1289 ($[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O)Tl_2]$, 17%), 1087 ($[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O)Tl + 2H]$ 56%), 883 ($[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O) + 2H]$, 60%), 801 ($[Pt\{(PPh_2O)_2H\}(PPh_2O) + H]$, 100%) and 599 ($[Pt(PPh_2O)_2H)]$, 64%).

$[Pt(C{\equiv}CPh)\{(PPh_2O)_2H\}(PPh_2O)Tl]_2$ (6)

A white suspension of $[Pt(C{\equiv}CPh)\{(PPh_2O)_2H\}(PPh_2OH)]$ (0.150 g, 0.166 mmol) in THF (20 mL) at −20 °C was treated with [Tl(acac)] (0.051 g, 0.166 mmol), giving immediately a colourless solution. After a few minutes of stirring, a white solid began to precipitate and after 4 h of stirring, the white solid was filtered off and washed with THF (2 × 2 mL) (0.125 g, 68%) (Found: C, 48.23; H, 3.36. $C_{88}H_{72}O_6P_6Pt_2Tl_2$ requires C, 47.82; H, 3.28%); ν_{max}(KBr)/cm^{-1} 2100(m) (C≡C), 1100 (s), 1009 (s), 998 (sh) and 962 (s) (P-O); δ_H (300.1 MHz, $CDCl_3$, −50 °C) 17.21 (br, O···H···O), 7.86, 7.33, 6.96 and 5.94 (70 H, m, Ph); δ_P (121.5 MHz, $CDCl_3$, 20 °C) ABX pattern, 72.69 (2P, AB part) and 77.31 (P_X, $P_{trans\ to\ C{\equiv}CPh}$), $^2J_{PA/B,\ X}$ 23.2 Hz, $^1J_{Pt,PA/B}$ ∼ 2120 Hz, $^1J_{Pt,PX}$ 2762 Hz; at −50 °C, ABX pattern, 79.42 (P_A, PPh_2O^-), 72.49 (P_B, PPh_2OH) and 77.70 (P_X, br, $P_{trans\ to\ C{\equiv}CPh}$), $^2J_{PA,PB\ trans}$ 637 Hz, $^1J_{Pt,PA}$ 2090 Hz, $^1J_{Pt,PA/PB}$ 2133 Hz, $^1J_{Pt,PX}$ 2745 Hz.

X-Ray crystal structure determinations

Crystal data and other details of the structure analysis are presented in Table 4. Diffraction measurements were made at 150 K on a Enraf-Nonius CAD4 diffractometer (**1**, **5**) or at 100 K on a Nonius κ-CCD area diffractometer (**2**), using graphite monochromated Mo-Kα X-radiation. Lorentz and polarisation corrections were applied. The structures were solved by Patterson and Fourier methods (**1**, **5**) or by Direct methods (**2**). All non-hydrogen atoms were assigned anisotropic displacement parameters. In **1** and **2**, the positions of the two OH hydrogen atoms were found in the density maps. They were refined with no positional constraints and a common thermal isotropic parameter. The rest of the hydrogen atoms (and all hydrogen atoms in **5**) were constrained to idealised geometries fixing isotropic displacement parameters equal to 1.2 times the U_{iso} value of the attached carbon for the phenyl and methyne groups and 1.5 for methyl and hydroxyl

Table 4 Crystal data and structure refinement parameters for $[(Pt(C_6F_5)\{(PPh_2O)_2H\}(PPh_2OH)]\cdot Me_2CO$ (**1·Me₂CO**), $[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**2**) and $[Pt(C{\equiv}CBu^t)\{(PPh_2O)_2H\}(PPh_2O)Tl]_2\cdot 2CHCl_3$ (**5·2CHCl₃**)

	$1\cdot Me_2CO$	2	$5\cdot 2CHCl_3$
Empirical formula	$C_{45}H_{38}F_5O_4P_3Pt$	$C_{42}H_{41}O_3P_3Pt$	$C_{86}H_{80}Cl_6O_6P_6Pt_2Tl_2$
Formula weight	1025.75	881.75	2406.94
Temperature/K	150(2)	100(1)	150(2)
Wavelength/Å	0.71073	0.71073	0.7173
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P*2(1)/*c*	*Pbca*	*P*-1
Crystal dimensions/mm	0.40 × 0.30 × 0.20	0.10 × 0.05 × 0.05	0.50 × 0.35 × 0.25
a/Å	12.5500(7)	17.1175(4)	12.126(2)
b/Å	13.5977(7)	18.3866(4)	12.961(2)
c/Å	24.6710(15)	24.3578(5)	15.926(2)
α/°	90	90	97.28(2)
β/°	97.102(12)	90	108.07(2)
γ/°	90	90	112.45(2)
V/Å^3	4177.8(4)	7666.2(3)	2111.7(6)
D_{calc}/Mg m^{-3}	1.631	1.528	1.893
Z value	4	8	1
μ(Mo Kα)/mm^{-1}	3.539	3.823	7.461
F(000)	2032	3520	1154
θ range/°	2.18–24.97	4.09–26.02	2.26–24.93
no. of reflns measd	7662	110865	7759
no. of obsd reflns	7301	7514	7377
Goodness of fit on F^{2a}	1.050	1.093	1.054
Final *R* indices [$I > 2\sigma(I)$]^a	$R1 = 0.0327$, $wR2 = 0.0848$	$R1 = 0.0559$, $wR2 = 0.0707$	$R1 = 0.0279$, $wR2 = 0.0604$
R indices (all data)	$R1 = 0.0543$, $wR2 = 0.0982$	$R1 = 0.0992$, $wR2 = 0.0796$	$R1 = 0.0379$, $wR2 = 0.0637$

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; Goodness of fit $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

groups. For **1·Me$_2$CO** an acetone solvent molecule is present in the asymmetric part of the unit cell and it is disordered over two sets of positions sharing the cetonic carbon atom and with partial occupancy 0.6/0.4. **5·2CHCl$_3$** contains two molecules of CHCl$_3$ per complex molecule. Full-matrix least-squares refinement of this model against F^2 converged to final residual indices given in Table 4. Calculations were carried out using the SHELXL-97[84] program and absorption correction using the MULTISCAN[85] program (**2**).

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References

1 B. Walther, *Coord. Chem. Rev.*, 1984, **60**, 67.
2 D. E. Fogg, N. J. Taylor, A. Meyer and A. J. Carty, *Organometallics*, 1987, **6**, 2252.
3 P. M. Veitch, J. R. Allan, A. J. Blake and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1987, 2853.
4 N. W. Alcock, P. Bergamini, T. M. Gomes-Carniero, R. D. Jackson, J. Nicholls, A. G. Orpen, P. G. Pringle, S. Sostero and O. Traverso, *J. Chem. Soc., Chem. Commun.*, 1990, 980.
5 N. W. Alcock, P. Bergamini, T. J. Kemp, P. G. Pringle, S. Sostero and O. Traverso, *Inorg. Chem.*, 1991, **30**, 1594.
6 J. Vicente, M. T. Chicote and P. G. Jones, *Inorg. Chem.*, 1993, **32**, 4960.
7 V. Riera, M. A. Ruiz, F. Villafane, C. Bois and Y. Jeannin, *Organometallics*, 1993, **12**, 124.
8 M. A. Esteruelas, A. M. Lopez, J. I. Tolosa and N. Vela, *Organometallics*, 2000, **19**, 4650.
9 C. Hollatz, A. Schier, J. Riede and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1999, 111.
10 P. Mastrorilli, C. F. Nobile, M. Latronico, V. Gallo, U. Englert, F. P. Fanizzi and O. Sciacorelli, *Inorg. Chem.*, 2005, **44**, 9097.
11 V. Gallo, M. Latronico, P. Mastrorilli, C. F. Nobile, G. P. Suranna, G. Ciccarella and U. Englert, *Eur. J. Inorg. Chem.*, 2005, 4607.
12 D. M. Roundhill, R. P. Sperline and W. B. Beaulieu, *Coord. Chem. Rev.*, 1978, **26**, 263.
13 P. C. Kong and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1974, 187.
14 W. B. Beaulieu, T. B. Rauchfuss and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 1732.
15 A. J. Carty, S. E. Jacobson, R. T. Simpson and N. J. Taylor, *J. Am. Chem. Soc.*, 1975, **97**, 7254.
16 K. R. Dixon and A. D. Rattray, *Can. J. Chem.*, 1971, **49**, 3997.
17 M. C. Cornock, R. O. Gould, C. L. Jones and T. A. Stephenson, *J. Chem. Soc.*, 1977, 1307.
18 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1992, 2425.
19 H. Alper and M. Sommovigo, *Tetrahedron Lett.*, 1993, **34**, 59.
20 C. S. Browning and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1995, 2005.
21 J. Powell, M. J. Horvath and A. Lough, *J. Chem. Soc., Dalton Trans.*, 1995, 2975.
22 P. Mastrorilli, M. Latronico, C. F. Nobile, G. P. Suranna, F. P. Fanizzi, U. Englert and G. Ciccarella, *J. Chem. Soc., Dalton Trans.*, 2004, 1117.
23 C. Hollatz, A. Schier and H. Schmidbaur, *J. Am. Chem. Soc.*, 1997, **119**, 8115.
24 C. Hollatz, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1997, 1333.
25 A. M. Trzeciak, H. Bartosz-Bechowski, Z. Ciunik, K. Niesyty and J. J. Ziólkowski, *Can. J. Chem.*, 2001, **79**, 752.
26 I. Pryjomska, H. Bartosz-Bechowski, Z. Ciunik, A. Trzeciak and J. J. Ziólkowski, *J. Chem. Soc., Dalton Trans.*, 2006, 213.
27 D. Morales-Morales, R. Redón, C. Yung and C. M. Jensen, *Chem. Commun.*, 2000, 1619.
28 R. B. Bedford, S. L. Hazelwood, M. E. Limmert, J. M. Brown, S. Ramdeehul, A. R. Cowley, S. J. Coles and M. B. Hursthouse, *Organometallics*, 2003, **22**, 1364.
29 R. B. Bedford and S. L. Welch, *Chem. Commun.*, 2001, 129.
30 I. D. Kostas, B. R. Steele, A. Terzis and S. V. Amosova, *Tetrahedron*, 2003, **59**, 3467.
31 G. Y. Li, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 1513.
32 G. Y. Li, *J. Org. Chem.*, 2002, **67**, 3643.
33 K. Yonehara, K. Mori, T. Hashizume, K. G. Chung, K. Ohe and S. Uemura, *J. Organomet. Chem.*, 2000, **603**, 40.
34 A. Mansour and M. Portnoy, *Tetrahedron Lett.*, 2003, **44**, 2195.
35 L. B. Han, N. Choi and M. Tanaka, *Organometallics*, 1996, **15**, 3259.
36 L. B. Han, R. Hua and M. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 94.
37 L. B. Han and M. Tanaka, *J. Am. Chem. Soc.*, 1996, **118**, 1571.
38 L. B. Han, F. Mirzaei, C. Q. Zhao and M. Tanaka, *J. Am. Chem. Soc.*, 2000, **122**, 5407.
39 C. Q. Zhao, L. B. Han and M. Tanaka, *Organometallics*, 2000, **19**, 4196.
40 P. W. N. M. van Leeuwen, C. F. Roobeek, R. L. Wife and J. H. G. Frijns, *J. Chem. Soc., Chem Commun.*, 1986, 31.
41 P. W. N. M. van Leeuwen, C. F. Roobeek and A. G. Orpen, *Organometallics*, 1990, **9**, 2179.
42 P. W. N. M. van Leeuwen, C. F. Roobeek, J. H. G. Frijns and A. G. Orpen, *Organometallics*, 1990, **9**, 1211.
43 L. R. Falvello, J. Forniés, E. Lalinde, A. Martín, M. T. Moreno and J. Sacristán, *J. Chem. Soc., Chem Commun.*, 1998, 141.
44 L. R. Falvello, J. Forniés, J. Gómez, E. Lalinde, A. Martín, M. T. Moreno and J. Sacristán, *Chem.–Eur. J.*, 1999, **5**, 474.
45 L. R. Falvello, J. Forniés, J. Gómez, E. Lalinde, A. Martín, M. T. Moreno and J. Sacristán, *Inorg. Chem.*, 1999, **38**, 3116.
46 J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Inorg. Chim. Acta*, 2003, **347**, 145.
47 L. H. Gade, *Angew. Chem., Int. Ed.*, 2001, **40**, 3573.
48 J. K. Nagle, A. L. Balch and M. M. Olmstead, *J. Am. Chem. Soc.*, 1988, **110**, 319.
49 R. Usón, J. Forniés, M. Tomás, R. Garde and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 1383.
50 A. L. Balch and S. P. Rowley, *J. Am. Chem. Soc.*, 1990, **112**, 6139.
51 W. Chen, F. Liu, D. Xu, K. Matsumoto, S. Kishi and M. Kato, *Inorg. Chem.*, 2006, **45**, 5552.
52 J. R. Stork, M. M. Olmstead, J. C. Fettinger and A. L. Balch, *Inorg. Chem.*, 2006, **45**, 849.
53 J. R. Stork, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 2005, **127**, 6512.
54 N. Oberbeckmann-Winter, P. Braunstein and R. Welter, *Organometallics*, 2004, **23**, 6311.
55 R. Stadnichenko, B. T. Sterenberg, A. M. Bradford, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2002, 1212.
56 E. A. Quadrelli, J. E. Davies, B. F. G. Johnson and N. Feeder, *Chem. Commun.*, 2000, 1031.
57 O. Renn, B. Lippert and I. Mutikainen, *Inorg. Chim. Acta*, 1993, **208**, 219.
58 H. B. Song, Z. Z. Zhang, Z. Hui, C. M. Che and T. C. W. Mak, *Inorg. Chem.*, 2002, **41**, 3146.
59 I. Ara, J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 6461.
60 J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Organometallics*, 2001, **20**, 4847.
61 J. P. H. Charmant, J. Forniés, J. Gómez, E. Lalinde, R. I. Merino, M. T. Moreno and A. G. Orpen, *Organometallics*, 2003, **22**, 652.
62 J. R. Berenguer, J. Forniés, B. Gil and E. Lalinde, *Chem.–Eur. J.*, 2006, **12**, 785.
63 L. R. Falvello, J. Forniés, R. Garde, A. García, E. Lalinde, M. T. Moreno, A. Steiner, M. Tomás and I. Usón, *Inorg. Chem.*, 2006, **45**, 2543.
64 B. Weissbart, A. L. Balch and D. S. Tinti, *Inorg. Chem.*, 1993, **32**, 2096.
65 W. C. Hamilton and J. A. Ibers, in *Hydrogen Bonding*, Benjamín, New York, 1968.
66 R. L. Schowen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1434.
67 A. Mezer, R. Friedman, O. Noivirt, E. Nachliel and M. Gutman, *J. Phys. Chem. B.*, 2005, **109**, 11379.
68 A. M. Beatty, *Coord. Chem. Rev.*, 2003, **246**, 131.
69 Molecular Self-Assembly Organic *versus* Inorganic Approaches in *Structure and Bonding*, ed. M. Fujita, Springer-Verlag, Berlín, 2000, vol. 96.

70 V. Chandrasekhar, R. Azhakar, J. F. Bickley and A. Steiner, *Cryst. Growth Des.*, 2006, **6**, 910.
71 M. B. Zaman, K. Udachin, J. A. Ripmeester, M. D. Smith and H. C. zur Loye, *Inorg. Chem.*, 2005, **44**, 5047.
72 C. J. Kuehl, F. M. Tabellion, A. M. Arif and P. J. Stang, *Organometallics*, 2001, **20**, 1956.
73 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
74 L. R. Falvello, J. Forniés, R. Garde, A. García, E. Lalinde, M. T. Moreno, A. Steiner, M. Tomás and R. Usón, *Inorg. Chem.*, 2006, **45**, 2543.
75 F. Wiesbrock and H. Schmidbaur, *J. Am. Chem. Soc.*, 2003, **125**, 3622.
76 H. W. Roesky, F. T. Edelman, M. Noltemeyer and M. Scholz, *Inorg. Chem.*, 1989, **28**, 3829.
77 A. A. El-Hadad, J. E. Kickham, S. J. Loeb, L. Taricani and D. G. Tuck, *Inorg. Chem.*, 1995, **34**, 120.
78 C. A. Zechmann, T. J. Boyle, D. M. Pedrotty, T. M. Alam, D. P. Lang and B. L. Scott, *Inorg. Chem.*, 2001, **40**, 2177.
79 M. V. Childress, D. Millar, T. M. Alam, K. A. Kreisel, G. P. A. Yap, L. V. Zakharov, J. A. Golen, A. L. Rheingold and L. H. Doerrer, *Inorg. Chem.*, 2006, **45**, 3864.
80 S. Harvey, M. F. Lappert, C. L. Raston, B. W. Skelton, G. Srivastova and A. H. White, *J. Chem. Soc., Chem Commun.*, 1988, 1216.
81 H. Rothfuss, K. Fofting and K. G. Coulton, *Inorg. Chim. Acta*, 1993, **212**, 165.
82 L. H. Gade, *Dalton Trans.*, 2003, 267.
83 I. Usón, J. Forniés, P. Espinet and G. Alfranca, *Synth. React. Inorg. Met. Org. Chem.*, 1980, **10**, 579.
84 G. M. Sheldrick, *SHELXL-97: A Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
85 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **A51**, 33.