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Invited review

Complexes of gold(I) with polyaromatic phosphine ligands

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Abstract

Gold complexes of the polyaromatic ligands $PArPh_2$, PAr_2Ph and PAr_3 (Ar = naphthyl, or anthracenyl) have been synthesised and their chemical and structural properties are reviewed.

Keywords: Tolman cone angles; Bulky phosphines; C–H ··· π interaction; Ethyne; Hydrogen bond; Variable temperature NMR

1. Prologue

In September 1965 I arrived at the University of Sussex as a freshly graduated student from the University of Manchester Institute of Science and Technology to work with Professor Joseph Chatt on a research project which would lead to a D.Phil. Degree. In those days it was slightly unusual in Britain for students to move universities to do graduate work but the name of Joseph Chatt kept coming up in the third year tutorials which were given by Jeff Leigh. We had discussed the historical development of Chatt's ideas on the bonding in ethene complexes of platinum, the *trans*-effect model which he had developed with Venanzi, and the rational isolation of metal alkyls and hydrides of the platinum metals with Shaw. He seemed to be everywhere in a chemical sense, but from my point of view in the wrong place geographically at the ICI Laboratories at Welwyn Garden City, not a place well noted for its Ph.D. studies. Therefore, I was delighted to hear, halfway through my final year, that Chatt had left ICI and was setting up a laboratory at the University of Sussex which was to be funded by the Agricultural Research Council. I visited Chatt in the Spring of 1965 and he agreed to take me on as a research student the following academic year. During the interview he described the beautiful work which he had completed with Davidson at ICI on the reduction of ruthenium diphosphine complexes with sodium naphthalide [1]. It is now universally recognised as a classic piece of organometallic chemistry which was seminal in the development of C–H activation and of the concept that my later colleague Malcolm Green was to describe as agostic interactions [2]. He proposed that when I joined the group I might like to take on this project and explore its implications for related metals such as osmium.

When I arrived in Sussex in the autumn of 1965 Chatt must have realised that the experimental skills of a new graduate student, and in particular this graduate student, were an order of magnitude less than those of an experienced postdoctoral worker such as Davidson and no more was said about the C–H activation project, and my attention was drawn to a project which was an outgrowth of work being done by Brian Heaton and required the synthesis of binuclear iridium phosphine complexes first made by Bernard Shaw. These proved to be rather insoluble and therefore not particularly good precursors for the bridge splitting reaction required to emulate the chemistry being done on platinum by Brian. Coincidentally an Italian chemist was visiting Chatt's laboratory on a NATO fellowship for six months prior to taking up a Professorship at the University of Milan — it was Paulo Chini. Therefore it was decided by Chatt and his newly arrived Deputy, Jeff Leigh, that it might be a good idea if I were to take on an apprenticeship with Paulo with a view to continuing his chemistry when he departed for Italy. It was a pleasure to work with Paulo for approximately a month and to see so intimately how a really great synthetic chemist worked on a day to day basis [3].

Joseph Chatt proved to be a somewhat different chemist from that which I had come to know through

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his papers as an undergraduate. His major contributions to the conceptual framework of inorganic chemistry had not prepared me for someone who was essentially an intuitive chemist with a real feel for what were important compounds to make and a good grasp of how to achieve the synthetic goal. He had a tremendous knowledge of the detailed aspects of chemistry and a love of the crystallisation process and the resulting crystals. His enthusiasm for the subject was boundless. He would appear at one's shoulder at the bench twice a day and enquire "What new results have you obtained?" As a new research student this was daunting and at those times when you had no new results a bit irksome, but nevertheless I gained much from these discussions. His wealth of experience and his endless stream of anecdotes did much to provide me with an appreciation of the history and culture of inorganic chemistry. Initially it was a mystery to me how such an intuitive chemist could have been responsible for the development of many of the important concepts in modern inorganic chemistry. I think the following aspects of his character were important in understanding this. He did not have a profound theoretical knowledge himself, but he was so interested in his own compounds that he would be very interested to enrich his understanding of them by discussing them with theoretical chemists. Thus he had an open and receptive mind and he incorporated and developed the theoretical insights of theoretical chemists such as Dewar and Orgel. Also when he came to writing up his work his intuitive mantle was replaced by a much more dogmatic and pointed approach. He thought a great deal about how he should place his own results in a broader and more rational context, and his great attention to detail and high standards would not let him publish anything until he felt it was all correct and made a complete and polished story. His papers with Bernard Shaw on metal alkyls illustrate this point. What was initially an intuitive feeling that platinum might form stable alkyls was eventually transformed into a series of papers which not only reported a wide range of new alkyl complexes but also had a distinctive theoretical rationale.

2. Introduction

In recognition of Professor Chatt's major contributions to our understanding of phosphine complexes I have chosen to review some of our recent results on polyaromatic phosphine ligands. Phosphine ligands, and particularly triphenylphosphine have been widely used in organometallic chemistry to stabilise and solubilise low oxidation complexes [4]. The resultant complexes have shown a remarkable versatility in their reactions, particularly with small molecules such as H_2, CO, olefins, etc. Indeed a search of the Cambridge Crystallographic Structural Data Files [5] has established that no fewer than 3819 complexes containing triphenylphosphine have been structurally characterised by X-ray crystallographic techniques. In contrast the corresponding polyaromatic ligands $PArPh_2$, PAr_2Ph and PAr_3 (Ar = naphthyl (Np), or anthracenyl (An)) have barely been studied.

The synthesis of some of the naphthyl and anthracenyl phosphine ligands had been reported previously. Specifically Issleib reported a Grignard synthesis for $PNpPh_2$ in 1961 [6] and subsequently this was developed in 1964 by Zorn, who also reported alternative syntheses based on Ph_2PM (M = Li, K) and either NpBr [7] or $NpSO_3Na$ [8] (see also Ref. [9]). The syntheses were repeated and extended to PNp_2Ph, PNp_3 and $PAnPh_2$ by Schindlbauer [10], Boaz [11], Berlin [12], Heck [13], Horner [14], Sakurai [15], Akasaka [16] and their coworkers. More recently Schmutzler et al. [17] improved the synthesis of $PAnPh_2$ and reported for the first time the synthesis of PAn_3. He also structurally characterised PAn_3.

The electrochemical properties of $PNpPh_2$, PNp_2Ph and PNp_3 have been described [18,19] and it has been established that the complexes become progressively easier to reduce when the naphthyl substituents are introduced. In contrast to the other members of the series, PNp_2Ph and PNp_3 show two half wave reduction potentials. The anions once formed preferentially lose phenyl rings leading to the naphthyl phosphido anions [20]. The substituted ligands react with dioxygen to form the corresponding phosphine oxides, the rate decreasing in the sequence $PAnPh_2 > PPh_3 > PNpPh_2$, although with hydroperoxides the order is $PPh_3 > PNpPh_2 > PAnPh_2$ [16]. Interestingly, although the phosphines show no fluorescence, the corresponding phosphine oxides show blue fluorescence [10]. This effect was developed for the fluorometric analysis of peroxides in organic solvents [16,21].

The following complexes of these ligands have been previously reported *trans*-$[MCl_2(PNpPh_2)_2]$ (M = Pd [22] or Pt [23]), *cis*-$[PtMe_2(PNpPh_2)]$ [23], $[W(CO)_5(PAnPh_2)]$ [17] and $[WI_2(CO)(Me_2C_2)(PNpPh_2)_2]$ [24]. An *ortho*-metallated product has been observed in the photochemical reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2(SiMePh_2)]$ and PNp_2Ph and characterised spectroscopically [25].

The polyaromatic ligands have also been mentioned in patent applications for olefin carbonylation (PNp_2Ph) [26], aromatic hydrocarbonylation (PNp_3) [27], as well as in publications for the Heck coupling reaction (PNp_3) [13], and homogeneous hydrogenation catalytic processes ($PNpPh_2$) [28].

Bidentate phosphine ligands with polyaromatic spacer groups between PR_2 donor groups have been studied in some detail as ligands. The BINAP ligand has proved particularly useful as a ligand for metal catalysed asymmetric hydrogenation catalytic reactions. These ligands have been described in some detail in a recent review [29]. The ligating properties of the chiral ligand PMeNpPh have also been studied extensively [25,30].

As part of our investigation of homo- and heterometallic gold cluster compounds [31] we recognised that interaromatic interactions may be providing a cumulative stabilising effect in the higher nuclearity clusters. Therefore, in order to maximise such effects we decided to make a systematic investigation of gold(I) complexes of polyaromatic phosphine ligands and their subsequent conversion to gold cluster compounds. Surprisingly a detailed investigation of these ligands had not previously been made.

3. Discussion

The ligands $PArPh_2$, PAr_2Ph and PAr_3 (Ar = Np and An) were synthesised following literature procedures [17]. With the exception of PAn_3 the ligands were obtained in high yields (40%–80%) from the appropriate chlorophosphine and the polyaromatic organolithium salt. The PAn_3 ligand was obtained only in 2% yield (literature 7%). The naphthyl containing ligands are virtually colourless and the anthracenyl containing ligands are yellow–orange crystalline solids. The ligands are air stable as solids, but convert slowly in solution to the corresponding phosphine oxides.

4. Gold(I) halide and nitrate complexes

The corresponding gold(I) complexes $[AuCl(PAr_xPh_{3-x})]$ were readily synthesised from $[AuCl(SMe_2)]$ and the appropriate phosphine (yields > 95%) and interconverted into the related nitrate salts $[Au(NO_3)(PAr_xPh_{3-x})]$ using $AgNO_3$ (yields > 80%). Both series of compounds are stable crystalline solids and have the same colour as the parent phosphines. The chloro-compounds are soluble in halogenated solvents, and the nitrato-compounds are soluble in these solvents and also in THF. This series of compounds represents the first complete series of polyaromatic phosphine complexes and provide the first examples of PAn_2Ph and PAn_3 complexes.

Fig. 1 contrasts the $^{31}P(^1H)$ chemical shifts of $[AuCl(PAr_xPh_{3-x})]$ and $[Au(NO_3)(PAr_xPh_{3-x})]$ with those for the free ligand and the phosphine oxide. Interestingly, the complexes show the same trends in chemical shifts as those observed in the free ligands, and opposite to those for the corresponding phosphine oxides. The chemical shifts for the corresponding triphenylphosphine and trimethylphosphine compounds are given also in the Figure for comparative purposes. Compared to the PPh_3 compounds the ^{31}P chemical shift becomes more negative (more downfield) as the number of polyaromatic substituents is increased and the shifts for the anthracenyl compounds are slightly more negative than those for the corresponding naphthyl compounds. The range of chemical shifts observed for the PNp_3 and the PAn_3 compounds is, however, larger than that for PPh_3 compounds, and more closely resembles those for PMe_3 compounds.

As the number of polyaromatic substituents is increased the rotation about the P–C bonds becomes more restricted. This behaviour is clearly illustrated in the variable temperature ^1H NMR spectral data for $[Au(NO_3)(PAn_3)]$ shown in Fig. 2.

The usual numbering for the anthracenyl group is shown in Scheme 1, and the relevant assignments of the peaks in the spectra are shown in Fig. 2 are made on the basis of this numbering scheme. The ^1H chemical shift differences between the protons which are symmetry inequivalent in the complex because of the restricted rotation follow the order $H_1–H_8 > H_2–H_7 > H_3–H_6$, reflecting their relative position in relation to the metal. At the low temperature limit the resonances associated with H_1 and H_8 are clearly visible and coalescence occurs at -30 ± 5°C leading to an averaged room temperature signal. Using the Gutowsky equation [32] the activation energy is calculated as $\Delta G^\ddagger = 51.0 \pm 1.1$ kJ mol^{-1}. In the corresponding free ligand PAn_3 the activation energy is much smaller and the coalescence temperature is lower than -100°C. The conformational aspect will be discussed in more detail below in the context of the calculation of the cone angles of the ligands.

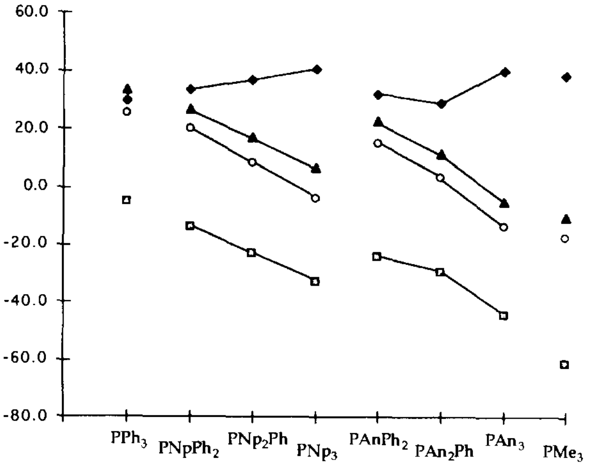


Fig. 1. The ^{31}P (^1H) chemical shifts of the polyaromatic phosphines (□), $[Au(NO_3)(PAr_xPh_{3-x})]$ (○), $[AuCl(PAr_xPh_{3-x})]$ (▲) and of the phosphine oxides (◆) in comparison to the corresponding PPh_3 and PMe_3 compounds.

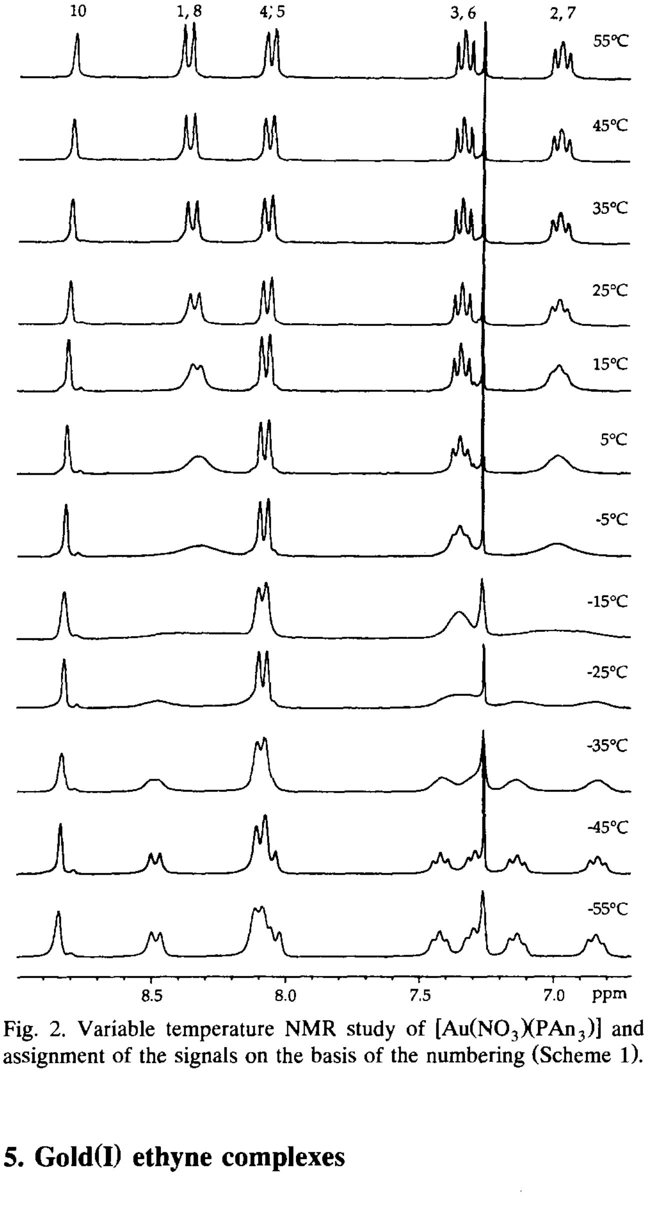


Fig. 2. Variable temperature NMR study of [Au(NO$_3$)(PAn$_3$)] and assignment of the signals on the basis of the numbering (Scheme 1).

5. Gold(I) ethyne complexes

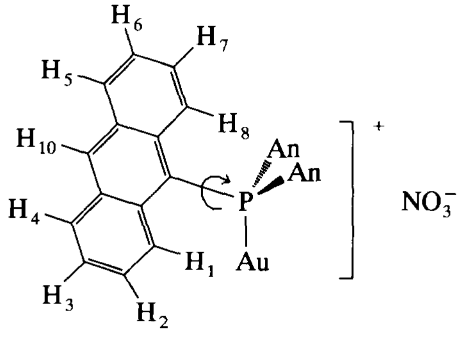
The ethynylgold complexes Np$_x$Ph$_{3-x}$P–Au–C≡C–Au–PNp$_x$Ph$_{3-x}$ and NpPh$_2$P–Au–C≡CH were made using modifications of the synthesis reported by Cross and Davidson [33]. A colloidal suspension of [AuCl(PR$_3$)] in ethanol, to which sodium ethoxide had been added was reacted with acetylene. The product is insoluble in ethanol and precipitates from the solution.

The synthesis of the ethynediyl digold complexes has some interesting subtleties. If phosphines like PNp$_x$Ph$_{3-x}$ are used the synthesis from [AuCl(PR$_3$)] results in a mixture of mono- and di-aurated ethyne complexes, R$_3$P–Au–C≡CH and R$_3$P–Au–C≡C–Au–PR$_3$. At times these compounds are difficult to separate because of their very low solubilities in organic solvents. To increase the reactivity of the [AuCl(PR$_3$)] it was dissolved in a small volume of THF and the filtered solution was run into ethanol. This resulted in a very reactive colloidal suspension. After the solution was made alkaline with KO^{t}Bu in ethanol, acetylene was bubbled through the solution. After a short period, 1–30 min depending on the phosphine an intense white precipitate formed which proved to be R$_3$P–Au–C≡C–Au–PR$_3$. Prolonged reaction times led to an increasingly higher proportion of the monoaurated ethyne R$_3$P–Au–C≡CH in the product mixture. By optimising the conditions the reaction could be directed into formation of either product. Good-to-excellent yields of the products were obtained. The compounds [Np$_3$P–Au–C≡C–Au–PNp$_3$]; [Np$_2$PhP–Au–C≡C–Au–PNp$_2$Ph]; [NpPh$_2$P–Au–C≡C–Au–PNpPh$_2$]; [Ph$_3$P–Au–C≡C–Au–PPh$_3$] and [NpPh$_2$P–Au–C≡CH] were isolated and characterised using this methodology.

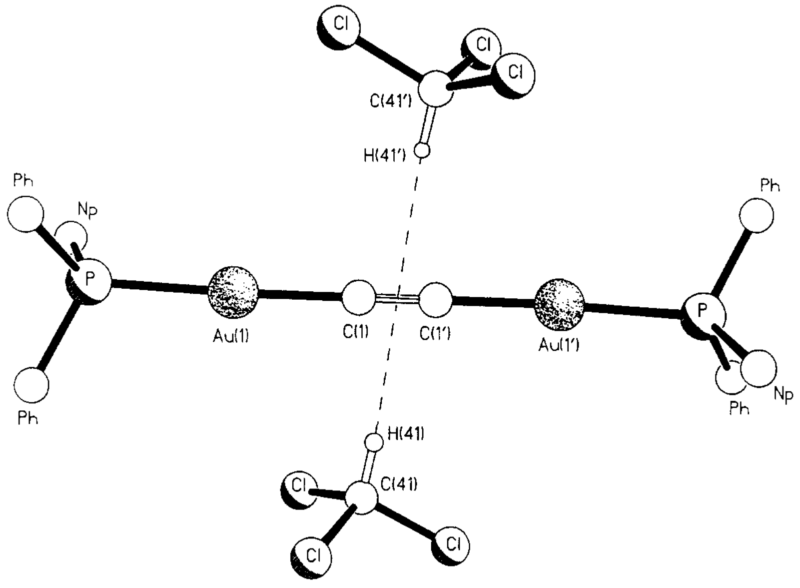
An interesting feature of the compounds [NpPh$_2$P–Au–C≡C–Au–PNpPh$_2$] and [Np$_2$PhP–Au–C≡C–Au–PNp$_2$Ph] is their solubility. When these compounds are synthesised and precipitate from the ethanol solution they are fairly soluble in CH$_2$Cl$_2$ and CHCl$_3$. Yet after recrystallisation it is nearly impossible to redissolve them in the same solvent. For further experiments the compounds were therefore not recrystallised, but stirred with MeOH/H$_2$O (1 : 1) overnight to remove all impurities and used as obtained after drying. Crystals were obtained by recrystallisation of the complexes from chloroform. The observations concerning the solubilities of these compounds led us to investigate their structures using single crystal X-ray diffraction and discover a novel interaction between the CHCl$_3$ molecules and the triple bond of the gold ethyne complexes.

Generalised, the geometry of these ethynylgold complexes resembles a dumb-bell with the Au–C≡C–Au bond representing the bar between two large spherical triaryl phosphine end groups. The two halves of the complex NpPh$_2$R–Au–C≡C–Au–PNpPh$_2$ · 2CHCl$_3$, (**1**) are related by a crystallographic centre of symmetry at the centre of the ethyne bond. The central C≡C bond has a length of 1.222(16) Å and the Au–C bond 1.938(8) Å. These compare well with those reported previously for gold ethyne complexes [34]. The P–Au–C≡C unit deviates slightly from linearity with an angle at C(1) of 174(1)° and at Au(1) of 175.8(2)°.

Although many gold(I) compounds frequently exhibit short Au–Au intermolecular contacts, the gold atom in (**1**) shows no close approaches to the other gold atoms.



Scheme 1.



Interestingly, centrosymmetrically related pairs of chloroform molecules are positioned with their C–H bonds directed orthogonally towards the centre of the ethyne C(1)≡C(1') bond (Fig. 3). The distance of the chloroform hydrogen H(41) to the bond centre of the triple bond is 2.42 Å. The vector H(41)–bond centre–H(41') is inclined by 85° to the triple bond and the C–H-centroid angle is 174.3°. The distances of H(41) to C(1) and C(1') are 2.45 and 2.55 Å, respectively. This arrangement is clearly indicative of pairs of C-H · · · π interactions which are favoured both by the acidic nature of the $CHCl_3$ protons and by the donation of electrons by the gold atoms into the triple bond. The geometry of-the-Cl_3CH–π(C≡C) interactions are very close to the optimal T-shaped geometry predicted theoretically. It is noteworthy that the $CHCl_3$ molecules "dock" with C≡C in a pairwise fashion which utilises the same π-orbital rather than a pair of orthogonal π-orbitals.

The complex Np_2PhP–Au–C≡C–Au–PNp_2Ph · $6CHCl_3$ (**2**) also has a crystallographic symmetry centre which is located in the middle of the C≡C bond. Bond lengths for the Au–C≡C–Au chain are 1.225(34) Å for C≡C and 1.986(17) Å for Au–C; these are comparable to those in (**1**). The P–Au–C≡C unit is close to linear with an angle at C(1) of 178(2)° and at Au(1) of 176.6(6)°. As in structure (**1**) there are no close approaches to the gold centres.

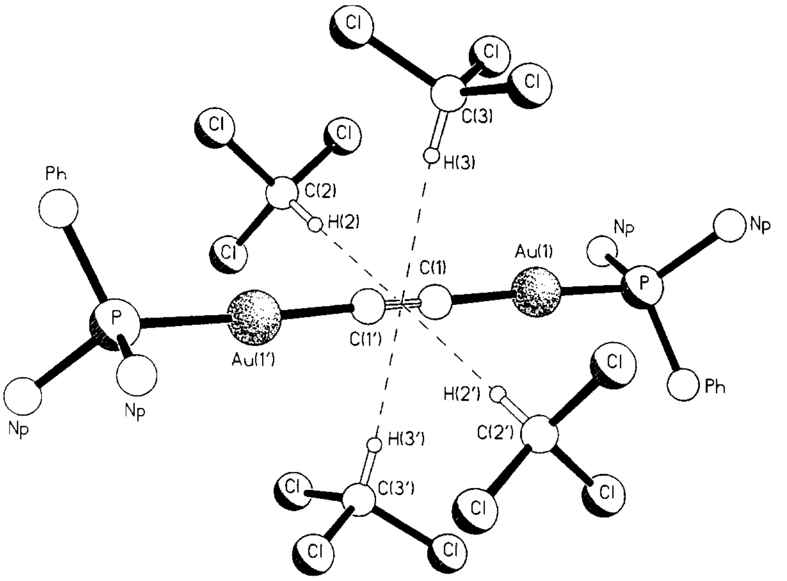


Fig. 4. Pseudo-octahedral arrangement of $CHCl_3$ around the C(1)≡C(1') ethyne bond in (2), showing the C–H · · · π interactions.

The complex is heavily solvated, with six $CHCl_3$ molecules per gold dimer, four of which are positioned with their C–H bonds directed orthogonally towards the centre of the ethyne bond (Fig. 4). This arrangement is directly analogous to that observed in (**1**) except that in (**2**) two pairs of $CHCl_3$ molecules are involved with their CH ··· π ··· HC axes oriented approximately orthogonally with respect to each other. The distances of H(2) and H(3) to the centre of the ethyne bond are 2.58 and 2.50 Å, respectively. The H(2)–H(2′) and H(3)–H(3′) vectors are inclined by 84.8° and 89.1° to the C(1)≡C(1′) bond and by 89.1° to each other, thus forming a pseudo-octahedral arrangement. The associated C–H-centroid angles are 166.6° at H(2) and 172.7° at H(3). Intermolecular distances of H(2) to C(1) and C(1′) are 2.70 and 2.59 Å, of H(3) to C(1) and C(1′) 2.59 and 2.57 Å, respectively. Although the C–H-centroid distances are slightly longer than those observed in (**1**) they still constitute significant C-H ··· π interactions.

Complexes (**1**) and (**2**) may be also viewed as reversed square-planar and octahedral coordination complexes of C_2^{2-} which forms σ-dative bonds to two *trans*-$[AuPR_3]^+$ fragments and π-dative bonds to the $CHCl_3$ molecules. Clearly the dumb-bell shape of the R_3P–Au–C≡C–Au–PR_3 molecules enhanced by the bulky polyaromatic phosphine ligands provides an excellent sheltered cavity which is favourable for the docking of small molecules with the ethyne bond. The above results have provided the first examples of C-H ··· π(C≡C) interactions which have the optimal theoretically predicted T-shaped geometry. However, the H ··· π distances observed here (2.42–2.58 Å) are significantly shorter than those indicated by the theoretical calculations (> 3.02 Å) [35,36] and must therefore be appreciably stronger. Density functional molecular orbital calculations [37] have confirmed that this unusual form of hydrogen bonding is quite strong (10–15 kJ mol^{-1} per $CHCl_3$ molecule) and the gold atoms play an important function in strengthening this interaction. In these complexes the C≡C fragment bears a higher negative charge than that in HC≡CH and therefore the charge transfer to $CHCl_3$ is encouraged. At the same time the polyaromatic phosphines protect the C≡C from electrophiles and provide a cavity with the appropriate dimensions to capture $CHCl_3$ molecules.

6. Estimation of the steric requirement of the phosphines

Since the structures of naphthyl and anthracenyl phosphine complexes have not previously been described in any detail it was of interest to use the structural data to compare the Tolman cone angles [38] of these ligands with those for the more widely studied triphenylphosphine [39,40]. The Tolman cone angle comparisons which we have made are based on crystallographic data rather than the mechanical model procedures first described by Tolman. This has the advantage that the conformations of the ligands actually observed in the structures are used as the basis for the cone angle calculations. It is noteworthy that Brown et al. [41] have reported alternative molecular mechanics procedures for estimating the cone angles in ligands. However, the crystallographic data was not used directly.

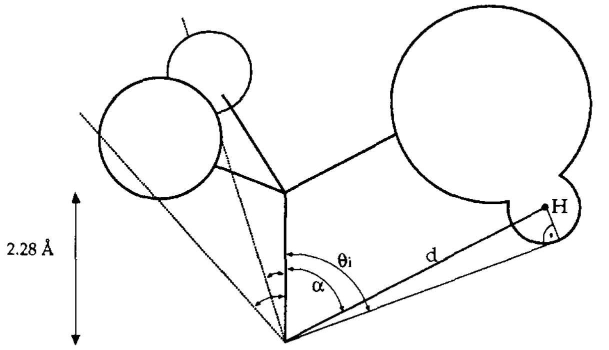


Fig. 5. Definition of the van der Waals' surface which in phosphorus ligands results in the calculation of the Tolman cone angle directly from crystallographic data.

The determination of the Tolman cone angles in this work required that the coordinates of the atoms be read into a molecular editing program [42]. For the coordinated complexes the distance from the phosphorus to the metal centre was adjusted to 2.28 Å. For the free phosphines a hypothetical metal atom X was placed in a distance of 2.28 Å from the phosphorus atom, so that all X–P–C angles were equal. For each substituent the hydrogen atom which gives the largest value for the cone angle was selected. Then the angle α between the phosphorus centre, the metal atom and the hydrogen atom and the distance d between the phosphorus atom and the hydrogen was calculated (Fig. 5). The half-angle θ_i was then calculated for each substituent according to the following formula:

$$\theta_i = \alpha + 180/\pi * \sin^{-1}(r_H/d)$$

r_H = van der Waals radius of hydrogen.

The Tolman cone angle Θ was then calculated as two times the average of the half-angles θ_i.

The method we have used is geometrically equivalent to Tolmans method. However, the algorithm we have developed uses the atomic centres instead of the surfaces of the van der Waals spheres of the atoms in the substituents to determine the cone angle. The angle α is thereby adjusted by the contribution of the van der Waals radius of the hydrogen (1.00 Å) to the cone angle. This methodology therefore leads to the calculation of cone angles in individual and structurally characterised molecules for the first time, rather than being based on idealised molecular models or geometries

Table 1
Average angles X^a–P–C and calculated cone angles (°) for polyaromatic phosphines

Compound	Average X^a–P–C	Cone angle calculated
$W(CO)_5(PAnPh_2)$ [17]	115.7	156
$Pd(dba)(PAnPh_2)_2$ [44]	113.9	164
$NpPh_2P$–Au–C≡C–Au–$PNpPh_2$ [45]	113.4	169
Np_2PhP–Au–C≡C–Au–PNp_2Ph [45]	113.1	177
PAn_3 [17]	108.5	218

[a] X is the metal atom for PAn_3 an imaginary atom in direction of the lone pair with all X–P–C angles being equal.

derived from molecular mechanics calculations. It also enables one to access the Cambridge Crystallographic Data Base and make a statistical analysis of the variation of cone angles as a function of metal, electron configuration, etc. More details of these computations and their application to a wide range of phosphine ligands will be discussed elsewhere [43].

Table 1 gives the values for the calculated cone angles and the average X–P–C and Au–P–C angles for the polyaromatic phosphines. The cone angle increases from $PAnPh_2$, $PNpPh_2$, PNp_2Ph to PAn_3. The cone of $PAnPh_2$ depends on the metal to which it is coordinated and on other factors. Coordination to the early transition metal tungsten leads to a larger cone angle than coordination to the late transition metal palladium. This is reflected in the average MPC angle which is 115.7° in the tungsten complex and 113.9° in the palladium complex. This is understandable in terms of the s character in the P–C bond which is larger in the palladium compound. This leads to an opening of the angle between the substituents resulting in a decreased average M–P–C angle and a larger cone angle. An analysis of 1 414 structures containing PPh_3 has shown [44] that the average cone angle has a standard deviation of $\pm 4.9°$ and therefore the conclusions drawn must be treated with some caution until more structural data is available.

The cone angle of $PNpPh_2$ in $NpPh_2P$–Au–C≡C–Au–$PNpPh_2$ is larger than the cone angle of $PAnPh_2$ in the complexes given in Table 1. This is counter intuitive, but can be explained if one considers the conformation of the aromatic substituents. This will be discussed in detail below.

The cone angle of the PNp_2Ph complex (177°) increases only slightly relative to the cone angle in the $PNpPh_2$ complex, because the additional phenyl ring of the naphthyl group is able to tuck into empty space within the cone. The introduction of three anthracenyl groups in PAn_3 leads then to a sharp increase of the cone angle to 218°. This is due to the inability of three aromatic groups to tuck into the space within the cone. The molecule is very strained and therefore it is not surprising that its synthesis gives low yields [17]. The van der Waals' surfaces of the anthracenyl groups touch each other so that the rotation around the P–C bond is hindered. The variable temperature experiment on $[Au(NO_3)(PAn_3)]$ described above has confirmed that this restricted rotation has $\Delta G^{\ddagger} = 51.0 \pm 1.1$ kJ mol^{-1}.

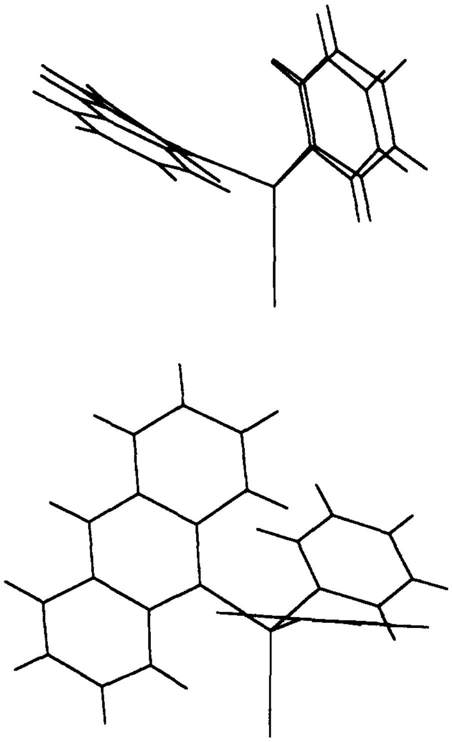


Fig. 6. Extreme conformations of the anthracenyl groups in the complexes $[W(CO)_5(PAnPh_2)]$ (top) and $[Pd(dba)(PAnPh_2)_2]$ (bottom).

The anthracenyl groups in the coordinated phosphines take up a range of conformations and two structures which illustrate the extremes are shown in Fig. 6. In $[Pd(dba)(PAnPh_2)_2]$ [44] the anthracene plane is virtually parallel to the M–P–C bond plane, whereas in $[W(CO)_5(PAnPh_2)]$ [17] it lies perpendicular to this plane. These conformational differences interestingly have relatively little effect on the overall cone angle as calculated by the methodology described above. In the former it is 164° and in the latter 156°. Although the half angles to the anthracenyl ligands are quite different, 100.6° in the former and 75.5° in the latter, the different conformations of the phenyl ligands compensate to equalise the cone angle.

The apparently anomalous cone angles for $PAnPh_2$ and $PNpPh_2$ mentioned above can be related to the conformations of the aromatic substituents. In the complex $[Pd(dba)(PAnPh_2)_2]$ a phenyl ring on each of the $PAnPh_2$ ligands takes up a perpendicular conformation relative to the M–P–C plane and is associated with a particularly small half angle ($\theta_i = 66.0$ and 70.3°). The other phenyl substituents make a dihedral angle of approximately 20° to the M–P–C plane giving half angles $\theta_i = 76.9$ and $75.3°$. The economical packing of the phenyl rings thereby more than compensates for the larger half angle made by the anthracenyl substituents ($\theta_i = 103.4$ and $100.6°$). Although in the $PNpPh_2$ complex the half angle of the naphthyl is smaller ($\theta_i = 95.6°$) the conformations of the phenyl substituents ($\theta_i = 76.2$ and $81.7°$) lead to a larger overall cone angle. In $[W(CO)_5(PAnPh_2)]$ the conformations of the phenyl ligands ($\theta_i = 78.7–80.0°$) are very similar to those observed in the $PNpPh_2$ compound, but the perpendicular conformation of the anthracenyl group leads again to a low overall cone angle.

This review has summarised the structural and spectroscopic properties of polyaromatic phosphine complexes of gold. These ligands, which have previously been neglected, show some interesting differences in their coordination properties compared with those of PPh_3. Specifically they have provided an unusual environment around the ethyne moiety in $R_3P–Au–C{\equiv}C–Au–PR_3$ which has resulted in the observation of novel coordination of $CHCl_3$ molecules to the ethyne bond. The ability of these ligands to adapt their steric requirements by adopting alternative ring conformations is useful in the context of coordination and organometallic chemistry and has raised the question of whether the Tolman cone angle can adequately describe these variations. A new structural definition of the cone angles introduced here has enabled us to access the crystallographic database and also address the question of cone angle variability as a function of ligand conformation, size of metal atoms and other variables associated with the environment in a complex. These polyaromatic phosphine complexes of gold also exhibit some interesting photophysical properties which have been described in detail elsewhere. Some show long lived luminescence and others alternative types of photoluminescence [45].

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