Isolation of 1,4-Li₂-C₆H₄ and its reaction with [(Ph₃P)AuCl]⁺

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The difficulty in generating $1,4-Li_2-C_6H_4$ utilising the lithium halogen exchange reaction on 1,4-Br₂-C₆H₄, 1,4-I₂-C₆H₄ and 1-Br-4-I-C₆H₄ is revisited and only on treatment of 1,4-I₂-C₆H₄ with 2 molar equivalents of n-BuLi can 1,4-Li₂-C₆H₄ 1 be isolated in excellent yield. Treatment of 1 with two equivalents of [ClAu(PPh₃)] gives [1,4-(Ph₃PAu)₂-C₆H₄] 2a in excellent yield. Subsequent treatment of 2a with 2.5 molar equivalents of PPh₂Me, PPhMe₂ or PMe₃ affords the PPh₃ substituted compounds $[1,4-(LAu)_2-C_6H_4]$ (L = PPh₂Me **2b**, PPhMe₂ **2c**, PMe₃ **2d**) in essentially quantitative yields. On treatment of 1,4-Br₂-C₆H₄ or 1-Br-4-I-C₆H₄ with 2 molar equivalents of n-BuLi only mono-lithiation takes place to give 1-Br-4-Li- C_6H_4 3 as shown through the isolation of essentially 1 : 1 molar equivalents of Ph₂PC₆H₄-4-Br and Ph₂PBu on treatment with 2 molar equivalents of ClPPh₂. Treatment of 3, prepared by lithium/iodine exchange on 1-Br-4-I-C₆H₄, with [ClAu(PPh₃)] affords $[(Ph_3P)Au(C_6H_4-4-Br)]$ 4 as expected and in addition $[(Ph_3P)Au(n-Bu)(C_6H_4-4-Br)_2]$ 5, indicating the straightforward chloride/aryl exchange at gold may proceed in competition with oxidative addition of the n-BuI, generated in the initial lithium/iodine exchange reaction, to some 'aurate' complex $Li[Au(C_6H_4-4-Br)_2]$ 6 formed *in situ* followed by reductive elimination of Br-C₆H₄-4-n-Bu in a manner that mimics lithium diorganocuprate chemistry. All of the gold-containing compounds have been spectroscopically characterised by ¹H and ³¹P-{¹H} NMR and in addition compounds **2a-d** and **5** by single crystal X-ray diffraction studies. The solid state structures observed for 2a-d are dictated by non-conventional hydrogen bonding and the packing requirements of the phosphine ligands. For 2a and 2b there is no close Au \cdots Au approach, however for 2c and 2d the reduction in the number of phenyl rings allows the formation of Au \cdots Au contacts. For 2c and 2d the extended structures appear to be helical chains with Au ··· Au contact parameters of 3.855(5) Å and C-Au-Au-C 104.1(3)° for 2c and 3.139(4) Å and C-Au-Au-C -92.0(2)° for 2d. The Au \cdots Au approach in 2c is longer than is normally accepted for an Au ··· Au contact and is dictated by ligand directed non-conventional hydrogen bonding to the aurated benzene ring and the π -stacking requirements of the phosphine ligand. By comparison of the structures 2a-2d with other structures in the database it is evident that the aurophilic interaction is a poor supramolecular synthon in the presence of non-conventional hydrogen bond donors. Searches of the CCDC database suggest that the observed parameters for the Au \cdots Au contact in 2c sit close to the cut-off point for observing this type of contact. In addition to aurophilic contacts and non-conventional hydrogen bonds there are a number of halogenated solvent C-Cl···Au contacts observed in the structures of 2a and 2d. The nature of these contacts have implications for the accepted van der Waals radius of gold which should be extended to 2 Å.

Introduction

Compounds containing a gold-aryl bond have been known¹ for nearly 80 years although full characterisation did not take place until 1959.² Regular reviews³ on this branch of chemistry have appeared since the 1970 s with an extensive review published in 2005.⁴ Aryl groups are typically introduced to the gold centre on reaction of an appropriate gold(I) precursor with an organolithium or Grignard reagent.⁵ Other routes have been utilised, for example, Schmidbaur *et al.*⁶ and Fackler *et al.*⁷ independently showed that NaBPh₄ acted as a phenylating agent towards gold(I) and more recently the use of boronic acids to effect aryl transfer to gold(I) in the presence of a base has been developed.⁸ This latter methodology shows that incorporation of functional groups not classically tolerated by either Grignard or lithium reagents is now possible and broadens the potential scope for this class of compound. In 2003 Schmidbaur *et al.* reported the preparation of bis(triphenylphosphine)gold(I) hydrocarbon species including those based on alkanes and arenes and noted that analogous complexes of benzene could not be prepared.⁹ More recently Gray *et al.* have made some diaurated naphthalene and pyrene based compounds.⁸⁴

One much discussed characteristic of gold(1) complexes in the solid state is the closed shell $d^{10}\cdots d^{10}$ aurophilic interaction

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[†] Electronic supplementary information (ESI) available: Packing diagrams and additional scattering diagrams generated from CCDC. CCDC reference numbers 756405 for **2a**, 756406 for **2b**, 756407 for **2c**, 756408 for **2d** and 688498 for **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b925355f

(Au...Au).¹⁰ Calculations have shown this interaction to be due to correlation and relativistic effects¹¹ and can be comparable in strength to hydrogen bonds. In some cases compounds with aurophilic contacts have been found to display packing similarities to classically hydrogen-bonded systems.¹² Other work has suggested that the Au...Au interaction exhibits no specific features and it is unreasonable to use the term aurophilic and metallophilic interactions.¹³ The nature and scope of the Au ··· Au interaction has been subject to several CCDC database searches in attempts to understand the nature of this solid state interaction.¹⁴ We have recently shown that phosphorane dihalogen adducts of the charge transfer spoke type are a good starting point in attempting to mimic the solid state structures of phosphine gold(I) halides and are helpful in teasing out issues that influence the formation of Au...Au contacts in the solid state.¹⁵ Herein we describe the problems associated with the double lithiation of 1,4dihalobenzenes, a suitable method for the isolation of 1,4-Li₂C₆H₄ 1 and its subsequent use for the preparation of the compounds $[1,4-(LAu)-C_6H_4]$ (L = PPh₃ 2a, PPh₂Me 2b, PPhMe₂ 2c, PMe₃ 2d). In addition we report the lithium/halogen exchange reaction carried out on Br-C₆H₄-4-I gives 1-Br-C₆H₄-4-Li which when quenched with [(Ph₃P)AuCl] leads to the isolation of both [(4- $Br-C_6H_4$ Au(PPh₃)] 4 and [(4-Br-C_6H_4)₂Au(n-Bu)PPh₃] 5 and a similarity of this chemistry to that of lithium diorganocuprate chemistry is drawn. The solid state structures of 2a-d along with a number of new database searches are used to discuss the relative merits of the Au \cdots Au and Au \cdots X (X = halogen) interactions, the distance to which they can be considered a valid contact and the implication this has for the van der Waals radius of gold.

Results and discussion

Many approaches for the dilithiation of 1,4-Br₂-C₆H₄ have been described in the literature. The earliest being that of Gilman and Melstrom¹⁶ in which 3 eq. of n-BuLi were reacted with 1,4-Br₂-C₆H₄ in Et₂O at low temperature. Many variations based on this protocol have since been published, with those of Ipaktschi¹⁷ and Buchwald¹⁸ using 4 eq. of t-BuLi to dilithiate 1,4-Br₂-C₆H₄, and others in which n-BuLi is refluxed for up to 48 h with 1,4-Br₂-C₆H₄.^{19,20} Screttas²¹ has described the dilithiation of 1,4-Cl₂-C₆H₄ by reacting 1,4-Cl₂-C₆H₄ with 4 eq. of lithium naphthalide at low temperature and the reaction of Li metal with 1,4-Br₂-C₆H₄ described by Bloomfield.²² Attempts to utilise many of these methods for the preparation of 2a only resulted in mixtures and none of the desired product. An attempt to prepare 1,4-(Ph₂P)₂C₆H₄ by dilithiation of 1,4-Br₂-C₆H₄ using n-BuLi followed by reaction with 2 molar equivalents of Ph₂PCl, to check whether dilithiation was actually taking place, resulted in two main components: $Ph_2P(4-Br-C_6H_4)$ and $Ph_2P(n-Bu)$ in essentially 1:1 molar ratio. Only minute quantities of 1,4-(Ph₂P)₂C₆H₄ could be observed in the crude material indicating that dilithiation was definitely not taking place prior to the addition of ClPPh₂. This is consistent with the report of Baldwin²⁰ who reported low yields of $1,4-(Ph_2P)_2C_6H_4$ and suggested that the reaction should be carried out in a sequential fashion: this approach gives $1,4-(Ph_2P)_2C_6H_4$ in 80% yield. Unfortunately the sequential lithiation approach does not work for the preparation of **2a** as $\text{Li}[(n-Bu)\text{Au}(\text{C}_6\text{H}_4-4-$ Br)] is formed through PPh₃ displacement rather than the desired lithium/halogen exchange, see later. A reproducible approach to

achieve direct dilithiation was sought and an adaptation of the method of Fossatelli et al.23 was developed. They suggest that when attempting to dilithiate $[1,4-Br_2-C_6H_4]$ where the quench is effected by reactive electrophiles n-BuLi and the electrophile may co-exist, thereby giving the desired di-substituted product after a sequence of lithium/bromine exchange and derivatisation reactions. On investigation of the dilithiation of [1,4-I₂-C₆H₄] they concluded that 100% dilithiation could be achieved when the diiodobenzene was used along with three equivalents of n-BuLi, with the key to dilithiation being the absolute need to keep the mono-lithio species in solution. This approach although repeatable is not satisfactory for the clean preparation of 2a. We have found, however, that by carrying out the lithium/iodine exchange reaction with n-BuLi in diethylether only 2 molar equivalents are required to effect 100% conversion of $1,4-I_2-C_6H_4$ to 1 and that 1 can be readily isolated as a pyrophoric off-white crystalline solid, in essentially quantitative yield, on addition of hexane to the reaction mixture after 20 min. 1 can be reacted prior to isolation with electrophiles such as Ph₂PCl to give 1,4-(Ph₂P)₂C₆H₄ and [(Ph₃P)AuCl] to give the sought after $[1,4-(Ph_3PAu)_2(C_6H_4)]$ 2a in excellent yield, Scheme 1. However, the purity and yields of 1,4-(Ph₂P)₂C₆H₄ and $[1,4-(Ph_3PAu)_2(C_6H_4)]$ 2a are significantly improved through reaction with the relevant electrophile and isolated 1. It should be noted here that the lithium/iodine exchange reaction appears to be solvent specific and does not proceed cleanly to give 1 in THF or hexane.



Scheme 1 Synthesis 2a–2d:(i) 2 n-BuLi, Et₂O, 253 K, 20 min; (ii) 2 [(Ph₃P)AuCl], Et₂O, 24 h; (iii) 2.5 L, CH₂Cl₂, 15 min.

2a reacts cleanly with 2.5 molar equivalents of PPh₂Me, PPhMe₂ or PMe₃ in CH₂Cl₂ to give the PPh₃ exchanged products [1,4-(LAu)₂(C₆H₄)] (L = PPh₂Me **2b**, PPhMe₂ **2c**, PMe₃ **2d**) in essentially quantitative yield. All of the compounds **2a–d** have been characterised by microanalysis (C, H and P), ¹H and ³¹P{¹H} NMR spectroscopy see experimental and by single crystal X-ray diffraction studies, see Table 1 for crystallographic data and Fig. 1–4 for ORTEP representations of the molecular structures showing the atomic numbering schemes and selected bond lengths (Å) and angles (°).

Compounds **2a–d** were found to crystallise in one of two space groups either P21/n for **2a** and **2b** or C2/c for **2c** and **2d**, see supplementary material† for packing diagrams. Considering initially the nearest neighbour Au··· Au contact distances the data suggest that there is no meaningful aurophilic interaction in compounds **2a–c**. However, consideration of the torsion angles^{14a} raises the possibility of an Au··· Au contact in **2c**. The skew

Table 1 Crystallographic data for 2a-d and 5

	$2\mathbf{a} \cdot 1.8 \mathrm{CH}_2 \mathrm{Cl}_2$	2b	2c	2d . 2CHCl ₃	5
Empirical Formula	C _{21.9} H _{18.8} PCl _{1.8} Au	$C_{32}H_{30}P_2Au_2$	$C_{22}H_{26}P_2Au_2$	$C_{14}H_{24}P_2Cl_6Au_2$	C ₃₄ H ₃₂ PBr ₂ Au
Fw	573.93	870.2	746.3	860.91	828.35
T/K	150	200	200	200	150
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	P21/n	P21/n	C2/c	C2/c	<i>P</i> 1̄ (No 2)
a/Å	8.2662(5)	8.4871(3)	11.5373(3)	24.5474(3)	10.8504(6)
b/Å	17.3899(11)	10.8176(4)	13.6031(3)	9.1914(2)	11.4943(6)
c/Å	14.2615(9)	15.1648(7)	14.1294(3)	12.2193(2)	14.3012(8)
α (°)					91.006(3)
β(°)	91.437(1)	90.89(1)	95.933(1)	113.807(1)	110.699(3)
γ (°)					111.903(2)
$V/Å^3$	2049.4(2)	1392.11(10)	2205.63(9)	2522.39(8)	1524.94(8)
Z	2	2	4	4	2
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.860	2.077	2.247	2.267	1.804
Crystal size/mm	$0.07 \times 0.03 \times 0.03$	$0.08 \times 0.15 \times 0.15$	$0.07 \times 0.12 \times 0.18$	$0.10 \times 0.15 \times 0.15$	$0.10 \times 0.15 \times 0.15$
θ Range for data collections	1.74-27.77	3.0-26.5	3.3-26.5	3.3-27.5	3.0-24.88
(°)					
λ/A	0.67100	0.71703	0.71703	0.71703	0.71703
Reflections collected	21858	6795	8775	25385	8162
Unique reflections	5700	2849	2291	2881	5179
<i>R</i> (int)	0.030	0.073	0.050	0.077	0.137
Absorption correction	Semi-empirical from	Semi-empirical from	Semi-empirical from	Semi-empirical from	Semi-empirical from
T	equivalents	equivalents	equivalents	equivalents	equivalents
Largest diff. between peak	2.158 and -0.771	-2.64 and 4.73	-2.59 and 2.77	-1.88 and 2.94	-1.907 and 0.251
and hole/e A ⁻³					
R indices observed data	0.0227	0.0504	0.0452	0.0402	0.0700
K_1	0.0327	0.0584	0.0453	0.0403	0.0789
WK ₂ Data (restraints (response to the	0.0840	0.1/82	0.1200	0.1034	0.23/9
Goodness of fit	1.04	2049/0/104	1.06	2001/0/115	1 02
Goodiless-oi-ilt	1.04	1.00	1.00	1.07	1.02



Fig. 1 ORTEP representation of the molecular structure of **2a**. Ellipsoids at 30%.^a Selected bond lengths (Å) and angles (°) Au(1)–C(1) 2.041(4), Au(1)–P(1) 2.293(1), Au(1)···Au(1)^b 8.266(4), C(1)–Au(1)···Au(1)^b 105.0(3), P(1)–Au(1)···Au(1)^b 88.9(4), C(1)–Au(1)–P(1) 175.49(12), C(1)–Au(1)···Au(1)^b–C(1)^b 180.0, P(1)–Au(1)···Au(1)^b–P(1)^b 180.0. Symmetry related atoms generated by: ^a(-x, -2y, -z), ^b(1+x, y, z).

orientation of the P–Au–C vector^{14a} in **2c** is comparable to that seen in **2d**, Fig. 5, however the Au \cdots Au contact distance at 3.855(5) Å is significantly longer than for **2d** 3.139(3) Å and would normally be considered to be too long for it to be a meaningful, notwithstanding the crystallographic similarities between the two compounds. This Au \cdots Au contact distance anomaly in crystallographically similar compounds has been observed previously in the isomorphous compounds [(Me₃P)AuX] (X = Cl I,²⁴ Br, II²⁵) where I is considered to be an infinite helical chain linked by Au \cdots Au contacts and II a trimer as one Au \cdots Au contact is beyond the normally accepted range at 3.980(2) Å. That



Fig. 2 ORTEP representation of the molecular structure of **2b**. Ellipsoids at 30%.^a Selected bond lengths (Å) and angles (°) Au(1)–C(1) 2.064(12), Au(1)–P(1) 2.295(3), Au(1)···Au(1)^b 5.936(5), C(1)–Au(1)···Au(1)^b 91.9(3), P(1)–Au(1)···Au(1)^b 65.4(4), C(1)–Au(1)–P(1) 178.5(4), C(1)–Au(1)···Au(1)^b–C(1)^b - 180.0, P(1)–Au(1)···Au(1)^b–P(1)^b–180.0. Symmetry related atoms generated by: ^a(-x, -2y, -z), ^b(1+x, y, z).

said this is quite a remarkable change in the nature the aurophilic contact resulting from a single phenyl-for-methyl group exchange in the phosphine ligand or is it? Perusal of the literature shows the closest related matched pair to **2c** and **2d** is $[(LAu)_2C_2]$ (L = PMe₃ III and PPhMe₂ IV) reported by Schmidbaur in 2003.²⁶ In both III and IV there are strong aurophilic contacts: 3.0747(8) Å in III and 3.3016(3) Å in IV. So why the substantial difference in **2c** and



Fig. 3 ORTEP representation of the molecular structure of 2c. Ellipsoids at 30%.^a Selected bond lengths (Å) and angles (°) Au(1)–C(1) 2.067(8), Au(1)–P(1) 2.291(2), Au(1)···Au(1)^b 3.855(3), C(1)–Au(1)···Au(1)^b 93.6(2), P(1)–Au(1)···Au(1)^b 91.2(4), C(1)–Au(1)–P(1) 175.2(2), C(1)–Au(1)···Au(1)^b–C(1)^b 104.1(2), P(1)–Au(1)···Au(1)^b–P(1)^b–103.4(2). Symmetry related atoms generated by: ^a(1-x, -y, 1-z), ^b(1-x, y, 1.5-z).



2d? It appears to be the result of differences in hydrogen bonding. In the extended structures of III and IV it is evident that there are hydrogen bond contacts between the H₃CP groups and the π -cloud of the ethyne bridge circa 2.8 Å for III and H₃CP circa 2.7 Å and Ph-H 2.8 Å contacts for IV in addition to the Au ··· Au contacts, see Fig. 6. For 2d two CHCl₃ molecules of crystallisation hydrogen bond to the π -cloud of the benzene ring CH- π circa 2.4 Å, and happily co-exist with the formation of an aurophilic contact. The H₃CP groups no longer engage in hydrogen bonding. So, on exchanging an ethynyl bridge for a benzene bridge noticeably changes the hydrogen bonding pattern. Considering 2c it is immediately evident that there is a considerable difference in the hydrogen bonding motif than seen for 2d. The PhMe₂P ligand hydrogen bonds to the π -cloud of the benzene ring with three non-conventional hydrogen bonds27 on each side of the benzene ring circa 3.2 Å which prevents the formation of an analogous aurophilic contact as seen in 2d. This observation can not be solely dependent upon the steric bulk of the phosphine ligand leading to an interpretation that non-conventional hydrogen bonding exerts far more influence as a supramolecular synthon than the aurophilic contact, notwithstanding the calculated strength of aurophilic contacts.¹¹ It appears that the ligand phenyl and methyl group hydrogen bonding to the aurated benzene ring must exert a greater stabilising affect than the formation of a strong aurophilic contact. In addition to this hydrogen bonding there are also phenyl embraces²⁸ that add additional stability to the molecular crystal and augment the stabilisation effect of the hydrogen bonds. These observations fit well with our recent suggestion that the hydrogen bond acceptor strength of the Au-X bond exerts more influence in the crystal packing than the aurophilic interaction based upon



Fig. 5 ORTEP representation of the Au \cdots Au linked helical chains in 2c and 2d, ellipsoids at 30% and Ph group of the PPhMe₂ ligand in 2c omitted for clarity.

the similarities and dissimilarities of solid state structures of matched [LAuX] (L = phosphine and X = halide) and R_3EX_2 (R = alkyl, aryl; E = P, As: X = Br, I).¹⁵ From an empirical perspective, therefore, hydrogen bonding and phenyl embraces as well as the Au–X bond behaving as a hydrogen bond acceptor appear to be more important supramolecular synthons than aurophilic contacts in determining the overall crystal packing in these systems. This interpretation accounts nicely for the drastic change in the nature of the aurophilic contact on going from **2c** to **2d**.

As previously mentioned, in **2d** the only phenyl ring present is the central benzene core and it engages in strong nonconventional hydrogen bonding²⁷ to two chloroform solvate molecules [C(7)–H(7) 1.00 Å, C(7)–H(7)–C(1) 174.29(3)°, C(7)– H(7)…C(1) 2.389(4) Å], Fig. 7. The CHCl₃ is also involved in a close C–C1…Au approach [C(7)–Cl(3) 1.716(3) Å, C(7)– H(7)–C(1) 140.76(3)°, C(7)–Cl(3)…Au(1) 3.625(4) Å]. A search of the CCDC database (HCl₂C–C1…Au) shows this example to be the closest yet observed approach of this type. The typical distances previously observed being 3.9–4 Å.²⁹ Shorter Cl…Au approaches have been observed in gold(1) complexes



Fig. 6 Hydrogen bond and aurophilic contacts in III, IV, 2c and 2d.

of the type [ClAuL] with the shortest being 3.472 Å.³⁰ In addition to there being a close (HCl₂C–Cl···Au) contact the chloroform molecules also form infinite chains linked by $\{Cl \cdots ClC(HCl)Cl \cdots Cl \cdots ClC(HCl)Cl \cdots \}$ contacts, see supplementary material. The Cl···Cl distance at 3.316 Å is noticeably shorter than that observed in the solid state structure of CHCl₃, 3.596 Å.³¹ Infinite chains of this type are not without precedent in



Fig. 7 ORTEP representation of Cl₃CH ··· Ph interactions in 2d.

the database.³² The chloroform solvates also prevent the formation of any aryl stacking motifs. The PMe₃ methyl groups are also prevented from engaging in any hydrogen bonding interactions. This is also seen in the solid state structure of $[(Me_3P)AuI] V$,³³ but in this case is due to the poor hydrogen bond acceptor capability of the Au–I bond.¹⁵

The complete absence of an Au \cdots Au contact in 2a and 2b is therefore a direct result of the increasing number of phenyl rings and their solid state interactions, rather than simply the increasing bulk of the ligand as many compounds containing either PPh₃³⁴ or PPh₂Me³⁵ ligands are known that contain close Au · · · Au contacts. In 2a the CH₂Cl₂ solvates engage in a series of close contacts to the gold centres. Like the CHCl₃ solvate in 2d one CH bond points at the aurated C(1) atom [C(1 s)-H(1 s) 0.991(5) Å, C(1 s)-H-C(1) 172.22(6)°, C(1 s)–H(1 s)···C(1) 2.913(5) Å]. This contact distance is longer than that observed in 2a and is presumably due to the differing acidities of the respective C-H bonds. It also appears to bridge two Au centres [C(1 s)-Cl(1 s) 1.757(3) Å, C(1 s)-Cl(1 s)- $C(1) 163.70(3)^{\circ}, C(1 s)-Cl(1 s) \cdots Au(1) 3.663(4) Å], [C(1 s)-Cl(2 s)$ 1.768(3) Å, C(1 s)–Cl(2 s)–C(1) 80.54(3)°, C(1 s)–Cl(2 s) · · · Au(1) 3.840(5) Å], giving rise to an extended Au \cdots Cl–(CH₂)–Cl \cdots Au chain, Fig. 8.

In an early search of the CCDC database Parthasarathy et al.³⁶ showed that the C–X bonds (X = F, Cl, Br, I), although considered to be poor ligands, behave as electron donors to metal centres by making close approaches, within the sum of the van der Waals radii,³⁷ to metal centres. The favoured M-Cl \cdots C angle was found to be clustered around 100°. In the same study³⁶ it was found that when the C-X bond behaves as an electron acceptor, engaging in halogen bonding,³⁸ the favoured angle of approach is clustered around 165°. A repeat search of the CCDC database looking for C–Cl··· M (M = any transition metal) contacts still shows the preference to clustered around 100° for the M \cdots Cl–C angle with the presence of a second cluster centred around 155° is beginning to emerge, see supplementary material. Clearly the bridging CH₂Cl₂ in 2a fulfils the generic criteria for these contacts to be real. It presumably also accounts for the virtual insolubility of this compound after recrystallisation from CH₂Cl₂. Narrowing the search to consider just CH₂Cl₂ approaches to a gold(I) centre by a C-Cl bond in compounds of the type [LAuC] the average



Fig. 8 ORTEP representation of the secondary Cl_2CH_2 interactions in 2a.

approach is found to be about 4 Å.³⁹ Similar results were found for searches carried out on the analogous gold chlorides [LAuCl]. If these are van der Waals rather than strong $M \cdots Cl-CH_2Cl$ contacts this would suggest a more realistic van der Waals radius for gold of approximately 2 Å. Due to the limited number of data points available for C-Cl··· Au contacts an additional search was carried out to look at all close non-bonded Au··· Cl-Au contacts in two coordinate [LAuCl] systems to see if the nature of the two contacts show any similarities. The search parameters used are illustrated in Fig. 9.



Fig. 9 Parameters used in the search of the CCDC.

The search examined contacts up to 5 Å much longer than the normally accepted range, to see if any clear cut off could be determined. The data obtained are illustrated in a series of scatter plots, Fig. 10–12. Fig. 10 indicates that the closest non-bonded Au– $Cl \cdots Au$ approaches occur, as might be expected, when the Au– $Cl \cdots Au$ angle approaches 90 (±) 10° and cluster in the range 3.4– 4 Å and as the angle opens up beyond 120° the $Cl \cdots Au$ distance increases rapidly. Since the nature of the C– $Cl \cdots Au$ contacts observed in **2a** and **2d** appear comparable in nature to the nonbonded contacts Au– $Cl \cdots Au$ observed in compounds of the type [ClAuL] and they further support a van der Waals radius for gold



Fig. 11 Scatter plot of $Au \cdots Cl-Au$ (°) *versus* $Au \cdots Au$ (Å).

to be approximately 2 Å. Considering the scatter plots of Au · · · Cl-Au (°) versus Au ··· Au (Å) and Cl-Au ··· Au-Cl torsion angle versus Au ··· Au represented as Fig. 11 and 12 significant clustering is again observed in both. If the compact nature of the clusters can be taken to indicate the range and scope of a meaningful Au · · · Au contact, the data represented in both plots suggest that Au...Au contacts are possible out to at least 3.8 Å and compare favourably with the data observed for Au-Cl··· Au and C-Cl··· Au contacts. A close inspection of the structures represented by the data points in the region 3.9–4.2 Å show that the two ClAuL fragments tend to line up with each other in a head to tail fashion, torsion angles $\pm 180^{\circ}$. This orientation is dictated by the packing requirements of the ligands, which are not necessarily sterically bulky. The illusion that is created however is that as the ligand volume increases so the molecular Au-X vectors slide past each other as if moving along an upward inclined arc (to $\theta \approx 90^{\circ}$) until the Au–X bonds are parallel. This initially decreases the Au · · · Cl distance while the Au · · · Au distance increases until both simultaneously increase. The search criteria used to investigate the nature of Au-Cl... Au interactions were then used to look at analogous bromo- and iodo-containing



Fig. 12 Scatter plot of Cl–Au \cdots Au–Cl torsion angle *versus* Au \cdots Au. Note: the hits with a torsion angle of 0° at circa 4.4 Å are the result of non-next nearest neighbour interactions.

compounds. Essentially the same scatter patterns are observed, but indicate that the maximal distance for an Au...Au contact could be extended to 3.98 Å, II.25 The final search carried out looked at the related two coordinate [LAuC] system. Once again identical clustering patterns are observed. What is remarkable about these searches is that they all show the same clustering patterns, see supplementary material for a series of scatter plots (similar to Fig. 11-12) that combine data points from all of the searches. They appear to indicate a similar broad region in which aurophilic contacts may be observed and they all indicate that this is out to about 4 Å. What also becomes apparent is that above 4 Å the nearest neighbour contact is generally expected to give a torsion angle of \pm 180°. A significant anomaly to this observation is seen for the compounds $[1,9-(Ph_2PAuX)_2-C_{14}H_8]$ $(X = Cl VI, Br VII)^{40}$ which have Au ··· Au contact distances of 4.449(5) and 4.451(5) Å with torsion angles of 90°. What is immediately evident though, Fig. 13, is that the orientation of the "Au ... Au contact" is a result of the packing being driven by the packing requirements of the diphenylanthracenylphosphine ligand, further supporting the argument¹⁵ that: the nature of the Au ··· Au contact is determined by the requirements of the ligands,



Fig. 13 Illustration of the Au ··· Au approach in VI.

not the requirements of the Au...Au contact and the presence of an Au...Au contact is not simply related to the perceived bulk of the ligand. So, what do these observations mean for the range of Au... Au contacts and its utility as supramolecular synthon? It is has been suggested elsewhere for the Au...Au contact to be a good supramolecular synthon,^{14a} ie. one that directs the crystal packing, the two L-Au-X vectors have to be at essentially 90° to each other and with the Au \cdots Au distance less than 3.32 Å. The data presented for 2d support this suggestion in principle. The structure found for 2d displays an Au ··· Au contact distance of 3.139(4) Å with a C-Au ··· Au-C torsion angle of - 92.0(2)°, but can the Au \cdots Au contact really be considered a good supramolecular synthon in general? In this case possibly, but only because there is no strong alternative director of the packing present. As soon as a phenyl ring is incorporated into the ligand system, 2c, the parameters of the Au \cdots Au contact fall to the very fringes of what can be interpreted as a meaningful attractive aurophilic contact. The ligand cannot be considered sterically demanding and so negates the steric argument for weak or absent aurophilic contacts. Hydrogen bonding is clearly more important. The hydrogen bonds that are observed may be weaker than calculated aurophilic contacts but there are more of them and it appears the sum of the whole is more important. Once again these observations seem to fit nicely with a view expressed by Dance in a review:^{28b} "It is important to consider the complete structure of the molecular crystal and all of the intermolecular space." As for the maximum length of a meaningful Au...Au contact, the data from the CCDC database searches, presented here, suggest that aurophilic contacts are observable up to about 4 Å. This in turn impacts on the value quoted for the van der Waals radius used in such searches.37 Based on the available data from the CCDC database it ought to be considered to be in the region 1.9–2.1 Å. Is there any other data to support this assertion? It has been reported that Au ··· Au interactions may occur in the range 2.47 = R_e^{di} < $R_e(Au \cdots Au)$ < $R_e^{vdw}(Au \cdots Au)$ = 3.22-4.0 Å, where \mathbf{R}_{e}^{di} is the distance in the ¹⁹⁷Au₂ (gas) molecule in the $X^{1} \Sigma_{\alpha}^{+}$ state,⁴¹ so there is other experimental evidence to support using this value. Further there is ample evidence to suggest the van der Waals radius of neighbouring mercury be considered to be 2.1 Å⁴² rather than the often quoted 1.55 Å.³⁷ The nature of any observed interaction at this extreme is going to be weak. For VI and VII, even though the skew torsion angle is 90°, and this feature is normally considered a good criteria for an aurophilic contact,^{14a} there can be no attractive aurophilic contact there.

In an attempt to prepare **2a** by a stepwise lithiation process using n-BuLi and 1-Br-4-I-C₆H₄, Scheme 2, the initial step proceeds to give 4-Li-C₆H₄Br **3** which reacts with [(Ph₃P)AuCl] to give [(Ph₃P)Au(C₆H₄-4-Br)] **4** (82%) and [(Ph₃P)Au(n-Bu)(C₆H₄-4-Br)₂] **5** (10%). The isolation of **5** was somewhat surprising and its presence was initially observed as a low intensity signal at 24.2 ppm in the ³¹P{¹H} NMR spectrum of crude **4**. Compound **5** could be extracted from the crude by washing with hexane. Slow evaporation of the hexane gave suitable crystals of **5** for a single crystal X-ray diffraction analysis, see Table 1 for crystallographic data and Fig. 14 for an ORTEP representation of the molecular structure showing the atomic numbering scheme and selected bond lengths (Å) and angles (°). From these observations it is evident that the reaction between 1-Br-4-Li-C₆H₄ and [ClAu(PPh₃)] is not just a simple metathesis reaction but must be made up of a



Scheme 2 Reagents: (i) n-BuLi, Et₂O, 253 K, 30 min; (ii) [ClAu(PPh₃)] 18 h



Fig. 14 ORTEP representation of the molecular structure of 5 showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°):Au(1)–C(19) 2.101(17); Au(1)–C(25) 2.082(17); Au(1)–C(31) 2.113(16); Au(1)–P(1) 2.381(4); C(19)–Au(1)–C(25) 171.5(6); C(19)–Au(1)–C(31) 87,6(7); C(25)–Au(1)–C(31) 87.8(7); C(31)–Au(1)–P(1) 176.0(6); C(19)–Au(1)–P(1) 93.9(5); C(25)–Au(1)–P(1) 91.3(4).

series of interlinked reactions which ultimately lead to the expected product **4**.

Compound 4 formed by the expected metathesis reaction must readily react with excess 3 in the reaction mixture to give the aurate complex Li[(4-Br-C₆H₄)₂Au] 6 and with time 6 equilibrates with the remaining [ClAu(PPh₃)] to give 4. During this equilibration process the n-BuI that was generated in the lithium/iodine exchange reaction, Scheme 2, is not an innocent by-stander. It slowly, and competitively oxidatively adds to 6 affording 5. In an attempt to maximise the yield of 5, 6 was generated directly from the reaction of [ClAu(PPh₃)] and 2 equivalents of 3 and left to react with n-BuI for 24 h. The crude reaction mixture was found to contain 4, 5 and 1-Br-4-n-Bu-C₆H₄. 5 was extracted from the crude mixture with hexane and spectroscopically characterised, see experimental. While recording the NMR spectra it became evident that 5 slowly decomposes to 4 by reductive elimination of 1-Br-4-n-Bu-C₆H₄ and with a half life of approximately 24 h. Notwithstanding the slow decomposition of 5 an interpretable ¹³C{¹H}-NMR spectrum was recorded. The data obtained are interesting when considered in conjunction with the data of Ogle et al.⁴³ who have recently reported the preparation and spectral characterisation of some neutral triorganocopper(III) complexes at low temperature using rapid injection nuclear magnetic resonance spectroscopy (RI-NMR); a technique they have applied to look at other reactive copper systems.⁴⁴ For 4 the aurated aromatic carbon resonates at 170.4 ppm ${}^{2}J_{PC} = 118.1$ Hz which is as expected for a linear gold(I) phosphine species.45 On oxidative addition of n-BuI the aurated phenyl carbon resonance shifts to 162.7 ppm and displays a much reduced ${}^{2}J_{PC} = 10.0$ Hz which is consistent with a cis P-C orientation. The aurated n-butyl carbon atom resonates at 38.1 ppm with a ${}^{2}J_{PC} = 104.7$ Hz consistent with a trans P-C geometry, Fig. 15, and is consistent with the crystallographically determined structure. These data therefore correlate nicely with the RI-NMR data observed for related thermally unstable triorganocopper complexes of the type [R₂R'CuL],⁴³ where for [Me₂(Et)Cu(PPh₃)] the observed trans ${}^{2}J_{\rm PC}$ = 118.0 Hz and is similar to that seen for 3, 104.7 Hz. Unfortunately the cis coupling was not resolved, but it is likely to be similar in magnitude to that observed for 5.

The similarity in behaviour between Li[Me₂Au] and Li[Me₂Cu] was originally remarked upon by Teutsch when studying the ring opening of epoxides where he postulated the presence of a transient Cu(III) intermediate.⁴⁶ As long ago as 1973 Tamaki and Kochi reported⁴⁷ that the oxidative addition of alkyl halides to Li[Me₂Au] gave rise to the trans products [(Me)₂AuR(PPh₃)] which on heating led to three decomposition processes:48 (i) alkyl rearrangement, (ii) cis trans isomerisation and (iii) reductive elimination. The nature of these process was studied theoretically and compared to related copper systems.⁴⁹ Considering, the renaissance of gold in homogeneous catalysis⁵⁰ we wondered whether any other oxidative addition/reductive elimination process was feasible for the formation of C-C bonds in this system. An attempted oxidative addition of acetyl chloride to $Li[(F_5C_6)_2Au]$ was reported by Uson et al. in 1977 in the expectation of generating a gold(III) complex.⁵¹ Unfortunately they were unable to isolate a Au(III) species and only isolated the gold(I) compound $[(F_5C_6)AuCl]^-$ from the reaction mixture. We suspected, based on the observations above, that their reaction would also have led to the formation of the pentafluorophenylmethyl ketone $C_6F_5C(O)$ Me via an oxidative addition reductive elimination pathway. So in a related reaction, 6 was reacted with 2-Br-benzoylchloride in ether and found to give the expected asymmetric diphenyl ketone via an oxidative addition reductive elimination pathway, Scheme 3.

The ¹³C{¹H}-NMR spectrum of the crude material displayed a ketone carbonyl resonance at 194.8 ppm. The aurated phenyl resonance observed for **4** at 170.4 ppm was also observed. This is indicative of oxidative addition of the acid chloride followed by reductive elimination of the ketone. Treatment of **4** with n-BuLi gives Li[(4-Br-C₆H₄)Au(n-Bu)] **7** which appears (by NMR) to react selectively with 2-Br-benzoylchloride to give exclusively the mixed n-butyl-2-bromo-phenyl ketone (C=O, 203.2 ppm) with no evidence for the diphenyl ketone and a resonance at 170.4 ppm indicating the presence of **4**. This observation is further supported by the ³¹P{¹H}-NMR data where only one





Fig. 15 Selected ¹³C-{¹H} spectral portions for 1 and 3 illustrating the magnitude of the coupling constants ${}^{2}J_{PC}$. (a) Au(I)-C(Ph); (b) Au(III)-C(Ph); (c) Au(III)-C(Bu).



Scheme 3 Ketone formation through reaction of benzoylchloride with $Li[(4-Br-C_6H_4)_2Au] 6$.

resonance ($\delta = 44.8 \text{ ppm}$) is observed and is again with consistent with the formation of **4**. No resonance corresponding to [(n-Bu)Au(PPh₃)]**8** ($\delta = 47.6 \text{ ppm}$) was seen. This pattern of reactivity is also consistent with the inability to form **2a** by a stepwise lithium/halogen exchange procedure.

Conclusion

1,4-Li₂-C₆H₄ **1** has been isolated for the first time as a pyrophoric off-white solid using a reproducible stoichiometric lithium/iodine exchange reaction. It has been used to prepare $[1,4-(Ph_3PAu)_2-C_6H_4]$ **2a** which readily undergoes ligand substitution reactions with more basic phosphines to give $[1,4-(LAu)_2-C_6H_4]$ (L = PPh₂Me **2b**, PPhMe₂ **2c**, PMe₃ **2d**). The presence of aurophilic contacts in these structures is determined by the non-conventional hydrogen bonding requirements of the ligands. The nature of the solid state interactions in **2c** and **2d** when considered in

conjunction with searches using the CCDC database strongly indicate that meaningful Au...Au contacts can be observed to a limit of 4 Å and that the van der Waals radius for gold ought to be increased to 2.0 Å. In the preparation of [(4-Br-C₆H₄)Au(PPh₃)] 4 via halide/aryl-group metathesis (using in situ generated 1-Br-4-Li- C_6H_4 3 via lithium iodine/exchange) also generates $Li[(4-Br-C_6H_4)_2Au]$ 6 in situ which slowly equilibrates with unreacted [(Ph₃P)AuCl] to give 4. Compound 6 behaves in an analogous manner to diorganocuprates utilising the n-BuI, generated in the lithium/iodine exchange reaction, to undergo oxidative addition to give 5 followed by reductive elimination to give 4 and 1-Br-4-n-Bu-C₆H₄. The related gold and copper complexes display comparable spectroscopic features including J_{PC} coupling constants. As expected the gold complexes are kinetically less labile. Compound 6 also reacts with acid chlorides to give ketones by an oxidative addition/reductive elimination process.

Experimental

General considerations: Hexane and diethyl-ether were dried by refluxing over sodium-potassium alloy and distilled prior to use. [ClAu(PPh₃)] was prepared on adding a stoichiometric amount of PPh₃ to [ClAu(THT)]⁵² in CH₂Cl₂. All other chemicals were obtained from commercial sources and used as received. ¹H-NMR (200.2 MHz) and ³¹P {¹H}-NMR (81.3 MHz) were recorded on a Bruker DPX200 spectrometer. Proton spectra were referenced either to CHCl₃ ($\delta = 7.26$) or CH₂Cl₂ ($\delta = 5.29$) and ³¹P {¹H}-NMR were referenced externally to 85% H₃PO₄ ($\delta =$ 0.0). Elemental analyses were performed by the Microanalytical Service, School of Chemistry, The University of Manchester, Manchester, UK. The syntheses of all compounds were carried out under an argon atmosphere using standard Schlenk techniques. Final purification of the gold-containing compounds was carried out in the open.

Syntheses

[1,4-Li₂-C₆H₄]·nEt₂O 1. n-BuLi (20 mL, 1.6 M) was added to a Schlenk flask (100 mL) under an atmosphere of dry argon and the hexane removed under reduced pressure. To the viscous residue was added Et₂O (25 mL) and the solution cooled to 253 K and 1,4-I₂-C₆H₄ (5.28 g, 16 mmol) added in one solid portion with vigorous stirring and the reaction stirred for an additional 20 min. The solvent volume was then reduced by approximately half and hexane (100 mL) added to effect full precipitation of [1,4-Li₂- C_6H_4]·nEt₂O The precipitated [1,4-Li₂-C₆H₄]·nEt₂O was collected on glass sinter (No 4) under argon, washed with hexane (3 \times 10 mL) and dried in vacuo. It was then transferred to a glovebox for storage. The number of Et₂O molecules of crystallisation were calculated by quenching a known mass of 1 with ClSiMe₃ in Et₂O and assuming 100% conversion to $[1,4-(Me_3Si)_2-C_6H_4]$ and from the yield back calculating the formula weight. The typical yield is 2-2.4 g, 70-75%; formula weight range 160-190 g mol⁻¹. Caution: this compound is extremely pyrophoric.

[1,4-(Ph₃PAu)₂-C₆H₄]·2CH₂Cl₂ 2a. To [1,4-Li₂-C₆H₄]·nEt₂O (0.09 g, 0.5 mmol) suspended in Et₂O (30 mL) was added [ClAuPPh₃] (0.495 g, 1 mmol) and the reaction mixture stirred under an argon atmosphere. After 72 h water (0.1 mL) was added and the mixture stirred for an additional 10 min. The precipitate was collected by filtration and washed with water (2×5 mL) and EtOH (2×5 mL) and dried under suction. The crude product was dissolved in boiling CH₂Cl₂ (100 mL) and filtered, quickly, through warm celite. Addition of EtOH (10 mL) and concentration of the solution under reduced pressure effected crystallisation of 2a·2CH₂Cl₂ (white, 0.49 g, 85%).

Elemental Analysis: C₄₄H₃₈P₂Cl₄Au₂ requires: C, 45.4, H, 3.3, P 5.3; Found C, 45.6, H, 3.4, P, 5.2; ¹H CD₂Cl₂:7.5 (m, 15H, Ph-H); 7.32 (s, 4H, Ph-H); ³¹P-{¹H} CD₂Cl₂:44.5 (s).

[1,4-(Ph₂MePAu)₂-C₆H₄] 2b. To 2a (0.233 g, 0.2 mmol) slurried in CH₂Cl₂ (5 mL) with continuous stirring under a stream of argon was added PPh₂Me (0.07 mL, 0.5 mmol). After 1 h the solution was filtered through celite and EtOH (10 mL) added. Concentration of the solution under reduced pressure effected crystallisation of 2b (white, 0.155 g, 89%). Elemental Analysis: C₃₂H₃₀P₂Au₂ requires: C, 44.2, H, 3.5, P 7.1; found C, 44.4, H,3.8, P, 6.9; ¹H CDCl₃:7.6 (m, 20H, Ph-H); 7.38 (s, 4H, Ph-H), 2.12 (d, 6H, CH₃, J_{PH} 8.5 Hz; ³¹P-{¹H} CDCl₃:30.5 (s).

In a similar fashion compounds $[1,4-(PhMe_2PAu)_2-C_6H_4]$ **2c**, (white, 94%) elemental analysis: $C_{22}H_{26}P_2Au_2$ requires: C, 35.4, H, 3.5, P 8.3; found C, 35.6, H,3.5, P, 8.6; ¹H CDCl₃:7.6 (m, 10H, Ph-H); 7.38 (s, 4H, Ph-H), 1.76 (d, 12H, CH₃, J_{PH} 8.6 Hz; ³¹P-{¹H} CDCl₃:18.8 (s), and $[1,4-(Me_3PAu)_2-C_6H_4]$ ·2CHCl₃ **2d** (white, 92%) elemental analysis: $C_{14}H_{24}P_2Cl_6Au_2$ requires: C, 19.5, H, 2.8, P 7.2; found: C, 19.2, H, 3.1, P 7.4; ¹H CDCl₃:7.41 (s, 4H, Ph-H), 1.43 (d, 18H, CH₃, J_{PH} 8.6 Hz; ³¹P-{¹H} CDCl₃:8.4 (s), were prepared. **[(4-Br-C₆H₄)Au(PPh₃)] 4.** To 4-I-Br-C₆H₄ (0.227 g, 0.8 mmol) dissolved in Et₂O (10 mL) was added n-BuLi (0.5 mL, 1.6 M hexane) at -78 °C. After 15 min [ClAu(PPh₃)] (0.396 g, 0.8 mmol) was added and the solution allowed to warm to room temperature and stirred for 18 h. H₂O (0.2 mL) was added and after 10 min the solvent removed *in vacuo*. Redissolution in CH₂Cl₂, drying over MgSO₄, filtration through celite followed by slow addition of hexane effected the precipitation of **4** (0.4 g, 82%); Elemental analysis (Calc %):C 47.1 (46.9), H 3.2 (3.1), P 5.2 (5.0); NMR (CDCl₃ δ ppm, J = Hz): Bruker DPX 400; ¹H 7.48–7.0 (m, Ph-H); ¹³C-{¹H} 170.4 (d, J_{PC} 118.1); 140.71, 134.3 (d, J_{PC} 13.5); 131.2, 130.7 (d J_{PC} 49.8), 130.2, 129.0 (d, J_{PC} 10.5), 119.9; Bruker DPX 200: ³¹P-{¹H} 44.8 s.

[(4-Br-C₆H₄)₂Au(Bu)(PPh₃)] 5. The methodology was the same as for the preparation of 4 save [ClAu(PPh₃)] (0.198 g, 0.4 mmol) was added and after 18 h the solvent was removed and the crude extracted with hexane (10 mL). Reduction of the solvent volume afforded 5 (80 mg, 24%). Elemental analysis (Calc %): C 48.9 (49.3), H 3.6 (3.9), P 3.5 (3.7); NMR (CDCl₃, δ ppm, J = Hz) Bruker DPX 400: ¹H 7.8–7.0 (m, 23H, Ph-H), 2.1 (bm, 2H, CH₂), 1.4 (bm, 4H CH₂), 0.9 (bm 3H, CH₃); ¹³C-{¹H} 162.7 (d, J_{PC} 10.1); 136,7, 134.1 (d, J_{PC} 13.6); 130.6 130.4, 128.2 (d J_{PC} 10.8); 117.5; 38.1 (d, J_{PC} 10.1); 32.4 (d, J_{PC} 10.1); 26. 7 (d, J_{PC} 10.1) 13.9; Bruker DPX 200: ³¹P-{¹H} 24.2 s.

X-ray crystallography

Crystals suitable for X-ray crystallography for 2a were grown by slow cooling of a saturated CH_2Cl_2 solution for compounds 2b, 2c and 2d, slow evaporation of NMR samples and 5 by slow evaporation of a hexane solution.

Data collection for 2a: A suitable single crystal was coated in inert perfluoropolyether oil and mounted on a single glass wool strand of ca. 3 mm in length glued to a glass fibre. All measurements were carried out on Station 9.8. CCLRC Daresbury Laboratory, Daresbury, UK using a standard Bruker SMART charge-coupled device (CCD) 1 K area-detector diffractometer controlled using the SMART software package version 5.054.53 This software was also used for indexing, cell refinement and data reduction. For 2b, 2c, 2d and 5 data collections were carried out using ϕ and ω scans on a Nonius Kappa CCD diffractometer employing graphite monochromated Mo-K α radiation (λ = 0.71073 Å). Experimental details are presented in Table 1. The crystal structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97.54 Crystallographic data for the structural analysis (CIF)† has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 756405 for 2a and CCDC No. 756406 for 2b CCDC No. 756407 for 2c and CCDC No. 756408 for 2d and CCDC No. 688498 for 5. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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