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# Bulky triarylarsines are effective ligands for palladium catalysed Heck olefination

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The four arsines, As{$C_6H_3$(*o*-$CH_3$)(*p*-Z)}$_3$ {Z = H (**2a**) or OMe (**2b**)} and As{$C_6H_3$(*o*-$CHMe_2$)(*p*-Z)}$_3$ {Z = H (**2c**) or OMe (**2d**)} react with [$PdCl_2$(NCPh)$_2$] or [$PtCl_2$(NCBu$^t$)$_2$] to give *trans*-[$MCl_2L_2$] or *trans*-[$M_2Cl_2$(μ-Cl)$_2L_2$]. The crystal structures of *trans*-[$PdCl_2$(**2a**)$_2$] and [$PtCl_2$(**2d**)$_2$] have been determined, the latter as its dichloromethane solvate. The structures show that in these complexes, the ligands adopt *gga* type conformations as do all analogous tri-*o*-tolyl- and tri-*o*-isopropylphenylphosphines in square-planar and octahedral complexes. The variable-temperature NMR behaviour of the complexes shows that they are fluxional due to restricted As–C bond rotation. The rate of the fluxionality is more rapid than in the analogous phosphine complexes and this is associated with longer As–C and As–M bonds allowing more free movement. The catalytic activity of the palladium complexes of the arsines and their phosphine analogues for the reaction of 4-bromoacetophenone and *n*-butyl acrylate has been screened. The results show that the arsines are generally superior to the phosphines as ligands for this catalysis. Tri(*o*-isopropylphenyl)phosphine and tri(*o*-isopropylphenyl)arsine are superior to tri-*o*-tolylphosphine as ligands for this Heck reaction and a *p*-methoxy substituent improves the arsine catalyst but not the phosphine catalyst. The phosphine catalysts are superior to the arsine catalysts for the reaction of 4-chloroacetophenone and *n*-butyl acrylate. These observations are discussed in the context of ligand stereoelectronic effects, as measured by the Tolman electronic parameter, $\nu_{CO}$ of the [NiL(CO)$_3$] {L = $AsAr_3$ or $PAr_3$}.

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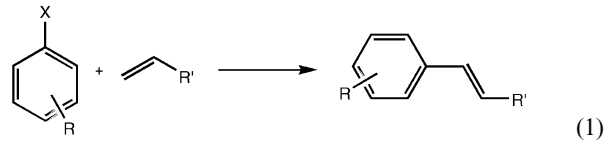
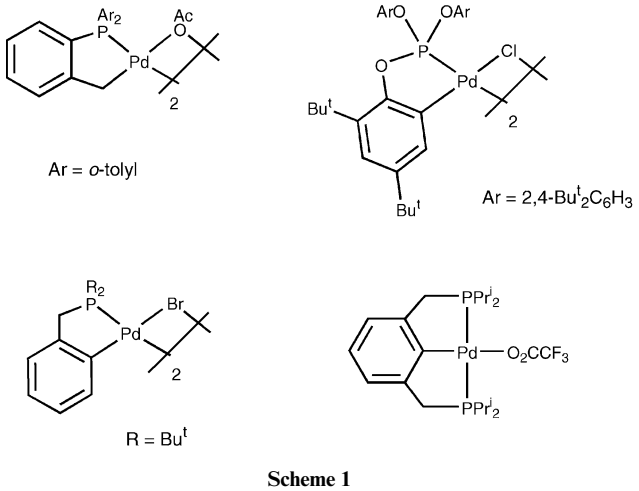
## Introduction

Heck olefination[1] (eqn. (1)) is an important C–C bond-forming reaction, made particularly useful by its functional group tolerance.[2] The palladacycle catalyst derived from tri-*o*-tolylphosphine (**1a**) was shown by Herrmann and Beller[3] to be an outstandingly active catalyst precursor and significantly, the turnover rates with chloroarenes were of commercial potential;[4] several applications in the fine chemicals industry were recently reviewed.[2] Subsequently, the groups of Milstein,[5] Bedford[6] and Cole-Hamilton[7] have shown that the cyclopalladates in Scheme 1 are all excellent catalyst precursors for Heck olefination.




(1)




**Scheme 1**

In order to probe ligand stereoelectronic effects in the catalysis of Heck olefination, we have investigated the catalytic activity of the palladium complexes of the series of phosphines **1b–d**. In view of the success of arsine ligands in the catalysis of another C–C bond-forming reaction, Stille coupling,[8] we made the triarylarsines **2a–d** and report here rare examples of arsine-based Heck catalysts.[9]

## Results and discussion

The ligands **1a–d** and **2a** were made by modifications of literature methods.[10,11] The new arsines **2a–d** have been made by treatment of $AsCl_3$ with the appropriate Grignard reagent (see Experimental section). Ligands **1b–d** and **2a–d** were designed to probe stereoelectronic effects in Heck catalysis.

### Platinum(II) and palladium(II) chemistry

We recently reported[11] the coordination chemistry of the phosphines **1a–d** with platinum(II) and palladium(II). The complexes of the arsine analogues **2a–d** have been characterised principally by $^1$H NMR, IR and mass spectrometry. They are more difficult to characterise than their phosphine analogues because of the absence of an NMR probe with the simplicity and analytical precision of $^{31}$P. From the similarity of the $^1$H NMR and IR spectra of the complexes of **1a–d** and **2a–d**, it seems reasonable to conclude that the structures are generally similar but there are differences and these are presumably associated with the increased M–As and C–As bond lengths and hence smaller cone angles (see below).

The reactions of [$PtCl_2$(NCBu$^t$)$_2$] or [$PdCl_2$(NCPh)$_2$] in refluxing toluene with 2 equiv. of **2a** or **2b** gave precipitated products very slowly, and low yields were obtained unless the reflux was continued for several days. The IR spectra (in the 200–400 cm$^{-1}$ region) were consistent with them being predominantly the *trans*-complexes **3–4a,b** and the crystal structure of **4a** has been determined (see below). The $^1$H NMR spectra for all the

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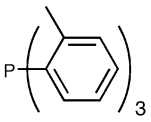
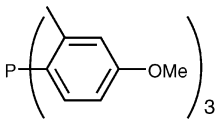
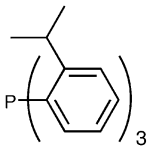


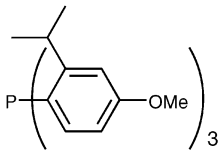

**1a**



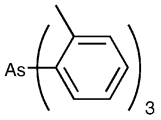

**1b**



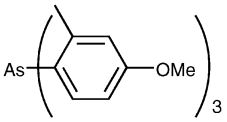

**1c**



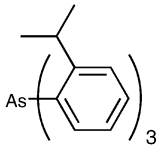

**1d**



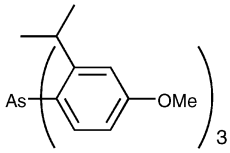

**2a**




**2b**

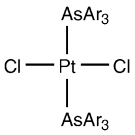


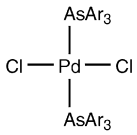

**2c**




**2d**

mononuclear complexes **3–4a,b** at +23 °C show broad signals in the $\delta$ 2.2–2.4 region for the tolyl-$CH_3$ groups indicating fluxionality due to restricted C–As bond rotation (see below). These signals are less broad than for the corresponding phosphine analogues (*e.g.* $w_{1/2}$ for the $CH_3$ signal for *trans*-[$PtCl_2$(**2b**)$_2$] and *trans*-[$PtCl_2$(**1b**)$_2$][11] were 16 and 90 Hz, respectively) consistent with C–As rotation being more rapid than C–P rotation.

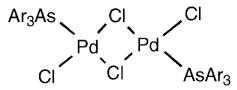



| | | | |
|---|---|---|---|
| **3a** | $AsAr_3$ = **2a** | **4a** | $AsAr_3$ = **2a** |
| **3b** | $AsAr_3$ = **2b** | **4b** | $AsAr_3$ = **2b** |
| **3c** | $AsAr_3$ = **2c** | **4d** | $AsAr_3$ = **2d** |
| **3d** | $AsAr_3$ = **2d** | | |

The reactions of [$PtCl_2$(NCBu$^t$)$_2$] or [$PdCl_2$(NCPh)$_2$] with the bulky arsines **2c** and **2d** were problematic. Impure products were obtained contaminated with solvent, metal starting materials and/or ligand. When [$PtCl_2$(NCBu$^t$)$_2$] is treated with 2 equiv. of **2c** and **2d** the *trans* mononuclear complexes **3c** and **3d** are the main products as identified on the basis of $^1$H NMR and IR spectroscopy (see Experimental section). The crystal structure of **3d** has been determined (see below). The reaction of **2c** with [$PdCl_2$(NCPh)$_2$] gave the binuclear species **5c** (see Experimental section for the data). The product of the reaction of **2d** with [$PdCl_2$(NCPh)$_2$] depends on the stoichiometry. Thus the reaction of [$PdCl_2$(NCPh)$_2$] with 2 equiv. of **2d** gave the mononuclear *trans* species **4d** ($\nu$(PdCl) 347 cm$^{-1}$) whereas with 1 equiv. of **2d**, the IR spectrum ($\nu$(PdCl) 352, 293, 257 cm$^{-1}$) of the product is consistent with the binuclear species **5d**.

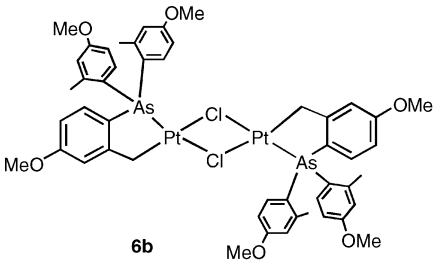
The $^1$H NMR spectrum of **5c** is sharp at −20 °C, showing inequivalent $CHMe_2$ peaks and high-frequency aromatic C–H signals in a similar pattern to its phosphine analogue (see Experimental section for the data).[11] However, at +23 °C, the $^1$H NMR spectrum for **5c** shows much coalescence of signals and is reminiscent of the spectrum of its phosphine analogue at 100 °C. This indicates that the rotameric fluxionality in the arsine complex is a significantly lower energy process than for its phosphine analogue; the estimated $\Delta G^{\ddagger}$ from coalescence temperatures is *ca.* 62 kJ mol$^{-1}$ for **5c** compared to *ca.* 78 kJ mol$^{-1}$ in the phosphine analogue.[11] The longer M–As and C–As bond lengths would be expected to allow less restricted rotation.



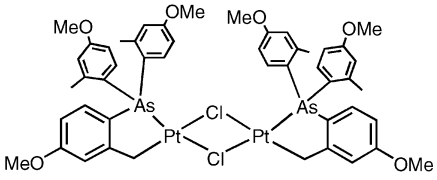

**5c** $AsAr_3$ = **2c**

**5d** $AsAr_3$ = **2d**

Treatment of [$PtCl_2$(NCBu$^t$)$_2$] with 1 equiv. of **2b** in refluxing toluene gave a product assigned to the isomeric binuclear cyclometallated species **6b** and **6b′** on the basis of the characteristic $^1$H NMR signals for the Pt–C$H_2$ at $\delta$ 3.47 and 3.43 (ratio 1 : 1) which have broad $^{195}$Pt satellites ($^2J$(PtH) 102 Hz). There are no previous reports of cyclometallation of tri-*o*-tolylarsine but cyclometallated trimesitylarsine complexes are known.[12]




**6b**




**6b'**

## X-Ray crystal structures

Molecules of *trans*-[$PdCl_2$(**2a**)$_2$] (**4a**) have crystallographic $C_i$ symmetry (see Fig. 1 and Table 1 which lists selected bond lengths and angles). The average As–C bond length is 1.94 Å, with an average C–As–C bond angle of 104.4° and a Pd–As bond length of 2.43 Å. Ligand **2a** has a cone angle of 175° in this structure. The average Pd–As–C bond angle is 114.2°. As can be seen in Fig. 1, two of the rings are close to a *gauche* (*g*) conformation, the other ring (C1–C7) is in the *anti* (*a*) conformation; the Pd–As(1)–C–C(Me) torsion angles are −70.0, −54.1 and 173.3°, *i.e.* $g^-g^-a$ conformation. The *gga* conformation is observed in all square-planar or octahedral metal complexes of tri-*o*-tolylphosphine.[11] The rotamer of **4a** observed in the crystal is the *meso* form. We have shown[11] that there are two rotamers possible in this class of complex (denoted

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**Table 1** Selected bond lengths (Å) and angles (°) for *trans*-[$PdCl_2$(**2a**)$_2$] (**4a**)

| | | | |
|---|---|---|---|
| Pd(1)–Cl(1) | 2.3034(11) | As(1)–C(8) | 1.944(5) |
| Pd(1)–As(1) | 2.4303(5) | As(1)–C(15) | 1.947(4) |
| As(1)–C(1) | 1.941(4) | | |
| | | | |
| Cl(1)–Pd(1)–Cl(1A)[a] | 180.00 | C(1)–As(1)–C(15) | 103.92(18) |
| Cl(1)–Pd(1)–As(1) | 88.37(3) | C(8)–As(1)–C(15) | 106.86(19) |
| Cl(1A)–Pd(1)–As(1) | 91.63(3) | C(1)–As(1)–Pd(1) | 116.94(13) |
| As(1)–Pd(1)–As(1A) | 180.00 | C(8)–As(1)–Pd(1) | 116.35(12) |
| C(1)–As(1)–C(8) | 102.32(18) | C(15)–As(1)–Pd(1) | 109.31(13) |

[a] Inversion symmetry generated atoms (2 − *x*, −*y*, −*z*) are designated by suffix A.

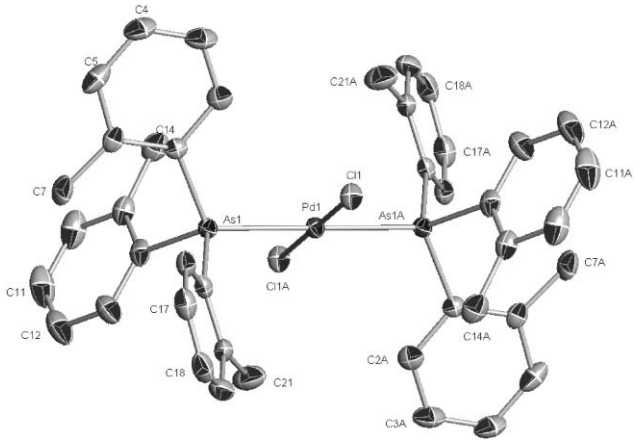



**Fig. 1** Structure of *trans*-[$PdCl_2$(**2a**)$_2$] (**4a**). Hydrogen atoms are omitted for clarity. Atoms suffixed A are related by symmetry (2 − *x*, −*y*, −*z*).


**Fig. 2** Schematic views along the L–M–L axis of the two proposed *meso* forms of complexes of the type *trans*-[$MCl_2(L)_2$] where L = **1a–d** or **2a–d**; the spheres represent the *ortho* substituents.[11]

*meso*-**A** and *meso*-**B** and illustrated in Fig. 2); the form present in crystals of **4a** is *meso*-**A**. The shortest Pd–H distance in the structure is 3.25 Å and involves a methyl C–H on one of the *gauche* tolyl groups.

Fig. 3 shows the structure of *trans*-[$PtCl_2$(**2d**)$_2$] (**3d**) determined in crystals of its dichloromethane solvate. Table 2 lists selected bond lengths and angles in **3d**. The two arsine ligands are not symmetry related in this case and the complex has approximate $C_2$ symmetry. The average As–C bond length is 1.96 Å with an average C–As–C bond angle of 104.2°, and an average Pt–As–C bond angle of 114.6°. The cone angle of **2d** is 191° in this structure. The isopropyl groups adopt an orientation that has the tertiary hydrogen eclipsed to the aromatic ring and towards the arsenic atom, presumably thereby minimising steric interactions of the methyl groups. This orientation is the same as that adopted in all known analogous *ortho*-isopropylarylphosphine ligands.[11]

The aryl groups of both arsine ligands in this structure adopt $g^+g^+a$ conformations; Pt–As–C–C(Pr$^i$) torsion angles are 67.3, 63.8 and 176.1° at As(1) and 62.6, 64.9 and 178.4° at As(2). As with the *meso* form, there are two rotamers possible (*rac*-**A** and *rac*-**B** as illustrated in Fig. 4);[11] the form present in crystals of **3d** is *rac*-**A**. The As–C and As–M distances in **4a** and **3d** are approximately 0.12 Å longer than the P–C and M–P bonds in their phosphine analogues and the cone angles are correspondingly reduced by *ca.* 5°.

**Table 2** Selected bond lengths (Å) and angles (°) for *trans*-[$PtCl_2$(**2d**)$_2$] (**3d**)

| | | | |
|---|---|---|---|
| Pt(1)–Cl(1) | 2.292(2) | As(1)–C(21) | 1.962(7) |
| Pt(1)–Cl(2) | 2.3218(19) | As(1)–C(11) | 1.941(7) |
| Pt(1)–As(2) | 2.4262(9) | As(2)–C(31) | 1.964(7) |
| Pt(1)–As(1) | 2.4306(10) | As(2)–C(41) | 1.967(8) |
| As(1)–C(1) | 1.949(7) | As(2)–C(51) | 1.966(7) |
| | | | |
| Cl(1)–Pt(1)–Cl(2) | 179.52(7) | C(31)–As(2)–Pt(1) | 115.2(2) |
| Cl(1)–Pt(1)–As(2) | 91.94(5) | C(41)–As(2)–Pt(1) | 106.71(19) |
| Cl(2)–Pt(1)–As(2) | 87.83(5) | C(51)–As(2)–Pt(1) | 120.7(2) |
| Cl(1)–Pt(1)–As(1) | 92.20(5) | C(11)–As(1)–C(1) | 105.9(3) |
| Cl(2)–Pt(1)–As(1) | 88.05(5) | C(11)–As(1)–C(21) | 101.9(3) |
| As(2)–Pt(1)–As(1) | 175.31(3) | C(1)–As(1)–C(21) | 104.4(3) |
| C(1)–As(1)–Pt(1) | 109.06(19) | C(31)–As(2)–C(51) | 101.4(3) |
| C(11)–As(1)–Pt(1) | 113.3(2) | C(31)–As(2)–C(41) | 104.8(3) |
| C(21)–As(1)–Pt(1) | 121.0(2) | C(51)–As(2)–C(41) | 106.9(3) |

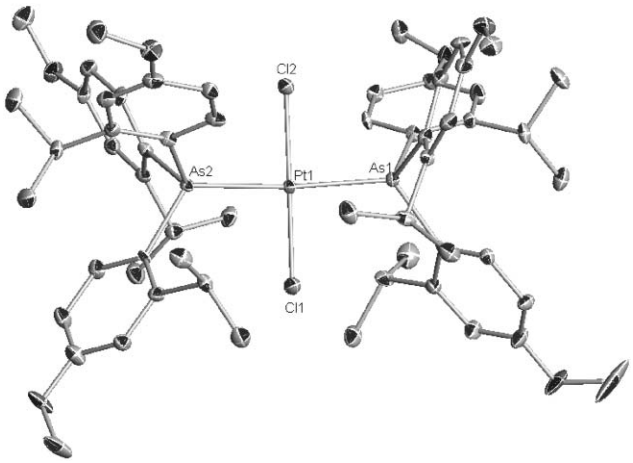



**Fig. 3** Structure of *trans*-[$PtCl_2$(**2d**)$_2$] (**3d**). Hydrogen atoms have been omitted for clarity.

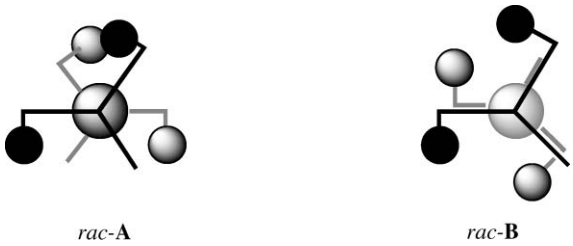
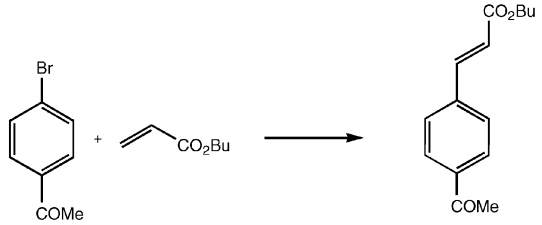



**Fig. 4** Schematic views along the L–M–L axis of the two proposed *rac* forms of complexes of the type *trans*-[$MCl_2(L)_2$] where L = **1a–d** or **2a–d**; the spheres represent the *ortho* substituents.[11]

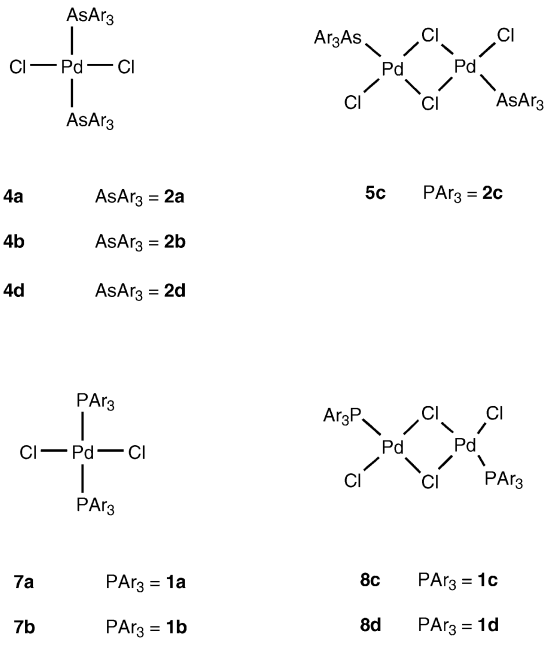
## Heck catalysis

Palladium complexes of **1a–d** and **2a–d** were screened using high-throughput apparatus for the Heck reaction shown in eqn. (2).




(2)

The catalysts were either the pre-formed palladium complexes shown in Scheme 2 or [$Pd(OAc)_2$]/ligand mixtures.




**Scheme 2** Pre-formed palladium complexes screened for catalysis.

The products were analysed by gas chromatography (GC) which showed that a single alkene product was formed in each case. Duplicate experiments were carried out for each catalyst run to ensure reproducibility. The pre-formed catalysts generally exhibited higher activity than the corresponding *in situ* catalyst but the trends in the results were similar. For simplicity, only the results for the pre-formed catalysts are given in Table 3 and presented graphically in Fig. 5. Herrmann has previously reported[13] that the same catalytic performance was obtained with palladium acetate or palladium halide complexes and we have also observed similar results with **1a**/$Pd(OAc)_2$ and **7a** for the reaction in eqn. (2).

The following are apparent from Table 3 and Fig. 5:

1. $AsPh_3$ (entry 2) gives a superior catalyst to $PPh_3$ (entry 1).
2. The catalyst derived from **1a** gives a more active catalyst (entry 3) than the arsine analogue **2a** (entry 4).
3. The presence of the *para*-methoxy group in ligands **1b** and **2b** has the effect of reducing the activity of the phosphine catalyst **7b** but of improving the activity of the arsine catalyst **4b** significantly (entries 5 and 6).
4. Replacement of the *ortho*-methyl group with an *ortho*-isopropyl group improves the activity of the catalysts derived from phosphine **1c** and arsine **2c** (entries 7 and 8).

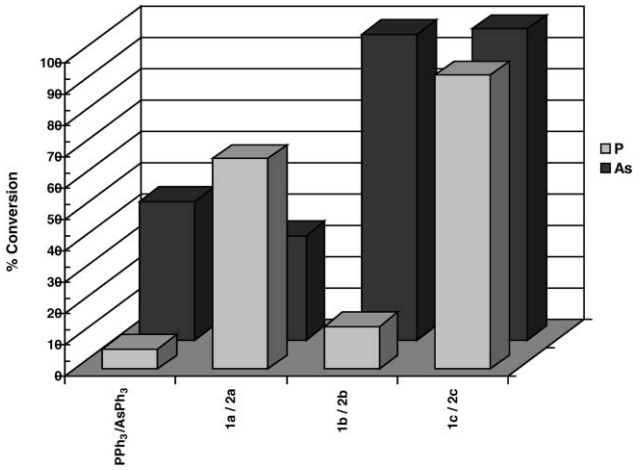



**Fig. 5** Conversions in the Heck reaction shown in eqn. (2) with catalysts derived from phosphines **1** and arsines **2** under the conditions given in Table 3.

We concluded from these observations that triarylarsines can be at least as effective as triarylphosphines as ligands for the Heck reaction. In addition *ortho*-isopropyl and *para*-methoxy substituents were beneficial for the performance of the triarylarsine catalysts. It was therefore of interest to investigate whether the effects of these substituents was cumulative and therefore ligands **1d** and **2d** were screened.

In a Schlenk tube, a mixture of *n*-butyl acrylate and 4-bromoacetophenone was heated to 100 °C and then 0.5 mol% of the palladium complexes of **1a**, **1d** and **2d** (*i.e.* **7a**, **8d** and **4d**, respectively) were added and the reaction (eqn. (2)) was monitored by GC over 90 min; the results are plotted in Fig. 6.

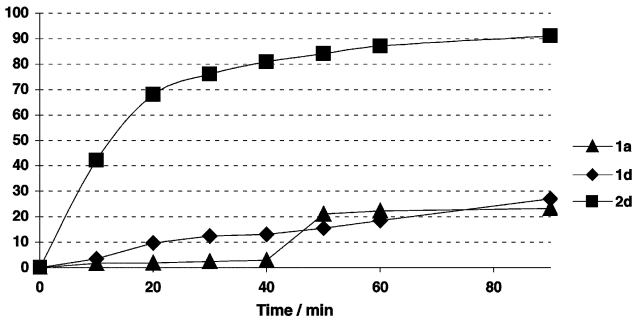



**Fig. 6** Conversions in the Heck reaction shown in eqn. (2) as a function of time with catalysts derived from phosphines **1a**, **1d** and arsine **2d** under the conditions given in Table 3.

**Table 3** Catalysis results

| Entry | Catalyst | Ligand | mol% Pd | Reaction eqn. | Time/h | Temp/°C | Conv. (%) | TON |
|---|---|---|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2/PPh_3$ | $PPh_3$ | 0.5 | 2 | 16 | 100 | 7 | 13 |
| 2 | $Pd(OAc)_2/AsPh_3$ | $AsPh_3$ | 0.5 | 2 | 16 | 100 | 45 | 89 |
| 3 | **7a** | **1a** | 0.5 | 2 | 16 | 100 | 67 | 130 |
| 4 | **4a** | **2a** | 0.5 | 2 | 16 | 100 | 34 | 68 |
| 5 | **7b** | **1b** | 0.5 | 2 | 16 | 100 | 13 | 26 |
| 6 | **4b** | **2b** | 0.5 | 2 | 16 | 100 | 98 | 196 |
| 7 | **8c** | **1c** | 0.5 | 2 | 16 | 100 | 94 | 188 |
| 8 | **5c** | **2c** | 0.5 | 2 | 16 | 100 | 99 | 200 |
| 9 | **7a** | **1a** | 0.0001 | 2 | 24 | 100 | 1 | 12200 |
| 10 | **8d** | **1d** | 0.0001 | 2 | 24 | 100 | 6 | 64200 |
| 11 | **4d** | **2d** | 0.0001 | 2 | 24 | 100 | 43 | 431000 |
| 12 | **7a** | **1a** | 0.1 | 3 | 21 | 140 | 10 | 100 |
| 13 | **4a** | **2a** | 0.1 | 3 | 21 | 140 | 1 | 8 |
| 14 | **4b** | **2b** | 0.1 | 3 | 21 | 140 | 4 | 40 |
| 15 | **8c** | **1c** | 0.1 | 3 | 21 | 140 | 12 | 125 |
| 16 | **5c** | **2c** | 0.1 | 3 | 21 | 140 | 9 | 85 |
| 17 | **8d** | **1d** | 0.1 | 3 | 21 | 140 | 13 | 133 |
| 18 | **4d** | **2d** | 0.1 | 3 | 21 | 140 | 7 | 68 |

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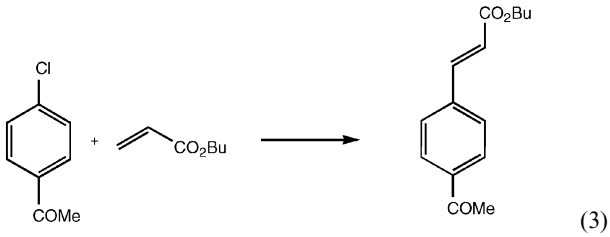
Under these conditions, complexes derived from **1a** and **1d** performed similarly but the arsine system derived from **2d** greatly outperformed the phosphines. In another experiment, much lower levels ($10^{-3}$ mol%) of the catalysts were added and the reactions run for 24 h to determine turnover numbers. Under these conditions (see Table 3, entries 9–11), the arsine system **2d** achieves a TON of 431 000 which is over 6 times that of the phosphine analogue **1d** and 35 times that of **1a**.

One great advantage of the **1a**/Pd system is that it catalyses the Heck olefination of chloroarenes.[4] We therefore screened the phosphine and arsine complexes for catalysis of 4-chlorobenzophenone with *n*-butyl acrylate (eqn. (3)). The results are given in Table 3 (entries 12–18) and shown in Fig. 7. It can be seen that, in general the phosphine systems are superior to the analogous arsine systems. The *ortho*-isopropyl group improves the performance of both phosphine and arsine-based catalysts.




(3)

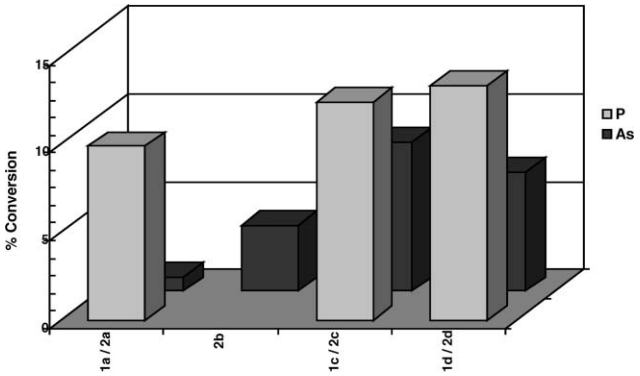



**Fig. 7** Conversions in the Heck reaction shown in eqn. (3) with catalysts derived from phosphines **1** and arsines **2** under the conditions given in Table 3.

The paucity of catalysis data on arsine complexes is partly due to the perceived disadvantage of arsines in terms of toxicity. Moreover, early hydrogenation[14] and hydroformylation[15] studies indicated that for these reactions, triphenylarsine–rhodium catalysts were inferior to triphenylphosphine-rhodium catalysts. However there are several examples of C–C coupling reactions where arsine complexes give more active or selective catalysts.[8,9,16] We have demonstrated here for the Heck reaction that triarylarsine catalysts can perform as well as or better than the analogous, very active triarylphosphine catalysts.

To compare the bonding properties of **1a–d** with **2a–d**, the ligands were reacted with an excess of [Ni(CO)$_4$] and the IR spectra of the resulting [NiL(CO)$_3$] complexes were obtained to determine the frequency of the $A_1$ stretching mode (*i.e.* the Tolman electronic parameter[17]). The results are given in Table 4. It is clear that the $\nu$(CO) values for the arsines are consistently higher than for the analogous phosphines, consistent with arsines being poorer σ-donors/better π-acceptors.

The catalyst performance in terms of yields from the chloroarene Heck reaction (eqn. (3)) is plotted against the Tolman electronic parameter in Fig. 8. There appears to be a general correlation: the better the σ-donor, the higher the yield which is consistent with oxidative addition of the chloroarene being rate determining. The results for the bromoarene reaction (eqn. (2)) show no simple correlation which implies that more complex ligand stereoelectronic effects determine the rate.

**Table 4** IR and $^{31}$P NMR data for the [Ni(CO)$_3$L] complexes in $CH_2Cl_2$

| L | $\nu_{CO}$ | $\delta_P$ |
|---|---|---|
| $PPh_3$ | 2068.9 | 42.9 |
| **1a** | 2066.4 | 29.4 |
| **1b** | 2063.9 | 49.4 |
| **1c** | 2064.8 | 31.9 |
| **1d** | 2062.7 | 76.6 |
| $AsPh_3$ | 2071.9 | |
| **2a** | 2069.6 | |
| **2b** | 2067.7 | |
| **2c** | 2064.9 | |
| **2d** | 2064.4 | |

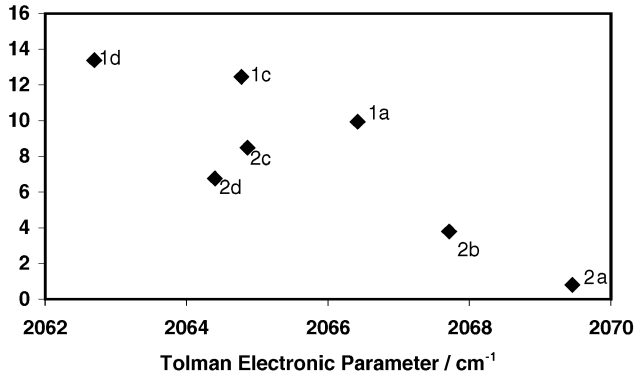
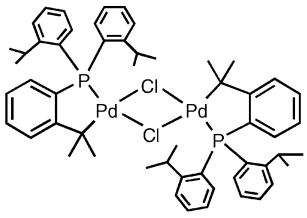



**Fig. 8** Conversions in the Heck reaction shown in eqn. (2) with catalysts derived from phosphines **1** and arsines **2** as a function of Tolman electronic parameter.

Herrmann *et al.*[13] have suggested that the Heck catalysts derived from **1a** involve cyclopalladates. In an attempt to shed light on the Pd species that may be present under the conditions we used for the catalysis, the reactions of dipalladium complex **8c** under the catalysis conditions were investigated. Complex **8c** dissolved in hot *N*,*N*-dimethylacetamide to give a clear orange solution. This was then treated with 10 equiv. of $Na_2CO_3$ and heated further to give a cloudy brown solution. The $^{31}$P NMR spectrum of this solution showed several species were present including **8c** and dissociated ligand **1c**; the most intense (70%) signal at $\delta$ −26.7 corresponded to a new species which we have also observed upon treatment of **8c** with various bases ($Cs_2CO_3$, $NEt_3$, KOBu$^t$) in THF or $CDCl_3$ and upon treatment of **8c** with $AgBF_4$ in MeCN followed by $NEt_3$. It is tempting to assign this signal to the cyclopalladated complex **9c**, the platinum analogue of which we have previously identified.[11] However several attempts to isolate this species have been unsuccessful because it decomposes upon concentration of its solutions.




**9c**

The mechanism of Heck olefination catalysed by palladacycles has been widely discussed. Pd(0)/Pd(II) (with or without rupture of the Pd–C bond[18]) and Pd(II)/Pd(IV)[19] cycles have been presented with the suggestion that the high activity of the metallacycles can be rationalised in terms of the electron richness of the intermediates leading to rapid oxidative addition of the ArX. It has also been postulated[20] that colloidal or nanocluster Pd particles are involved and the metallacycle provides a source of palladium particles at the temperatures of the reactions. Others have shown[21] that when metallic palladium is used as

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a catalyst, it is leached during Heck reactions to give soluble palladium(II) species in solution.

The beneficial effect of the *o*-isopropyl group on the phosphine and arsine catalysts may be a result of the steric protection offered by the *o*-isopropyl substituents thermally stabilising the catalysts or leading to production of more active palladium nanoparticles.

## Conclusion

The coordination chemistry of the bulky arsines **2a–d** has been compared with that of the analogous phosphines **1a–d**. From the NMR studies, the greater As–C and As–M bond lengths make As–C/M–As rotation more rapid than the P–C/M–P rotation in analogous compounds. The X-ray crystallography and IR studies reveal that the arsines are less bulky and poorer σ-donors or better π-acceptors than the analogous phosphines. For the Heck olefinations involving bromoarene substrates, the catalysts derived from the palladium–arsine complexes were generally more active than the analogous phosphine derived catalyst; the bulky arsine **2d** yielded a particularly efficient catalyst and illustrated once again the activating effect an *ortho*-isopropyl group can have on catalyst performance.[11]

## Experimental

Unless otherwise stated, all work was carried out under a dry nitrogen atmosphere, using standard Schlenk-line techniques. Dry $N_2$-saturated solvents were collected from a Grubbs system[22] in flame and vacuum dried glassware. Dry dimethylacetamide (DMA) for the Heck olefination reactions was purchased from Aldrich. 4-Bromo-3-isopropylanisole,[23] triarylphosphines **1b–d**,[11] tri(*o*-tolyl)arsine (**2a**),[10] $[PtCl_2(NC^tBu)_2]$[24] and $[PdCl_2(NCPh)_2]$[25] were prepared by literature methods. Tri(*o*-tolyl)phosphine (**1a**) was purchased from Strem and all other starting materials were purchased from Aldrich. NMR spectra were measured on a Jeol Eclipse 300, Jeol Eclipse 400 or Jeol GX 400. Unless otherwise stated $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded at 300, 100 and 121 MHz, respectively, at room temperature. Mass spectra were recorded on a MD800 or a Fisons VG Quattro positive electrospray mass spectrometer. Infrared spectra were recorded on a Perkin Elmer Spectrum 1 Spectrometer as Nujol mulls between polythene plates for the Pt and Pd complexes and as $CH_2Cl_2$ solutions for the $[NiL(CO)_3]$ species. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. GC analysis was done with the help of Graham Henderson at Johnson Matthey using a Perkin Elemer Autosystem XL GC with a CP-SIL-5 column.

### Tri(*p*-methoxy-*o*-tolyl)arsine (2b)

4-Bromo-3-methylanisole (17.69 g, 88 mmol) was added to Mg turnings (3.20 g, 132 mmol) in THF (50 $cm^3$) over 5 min. The mixture was heated at reflux for 3 h until the Mg turnings had disappeared. The grey solution was cooled in an acetone/ice bath before the dropwise addition of $AsCl_3$ (5.27 g, 29 mmol) over 10 min. The reaction was stirred overnight and then distilled water (95 $cm^3$) was added and the mixture stirred for 30 min. The mixture was then extracted with $Et_2O$ (3 × 50 $cm^3$) and the ethereal extracts combined and dried over $Na_2SO_4$. The solution was filtered and the solvents were removed *in vacuo* to yield a brown solid, which was digested with methanol (2 × 50 $cm^3$). The solvent was removed *in vacuo* and $CH_2Cl_2$ (2 × 50 $cm^3$) was added to precipitate the MgClBr salts, which were filtered off. The solvent was then evaporated *in vacuo* from the filtrate to give a white solid, which was digested with methanol to give the product **2b** as a fine white powder (8.35 g, 19.00 mmol, 65%). Elemental analysis (%): found (calc.): C, 65.15 (65.75); H, 6.47 (6.20); MS (CI) *m/z*: 438 ($M^+$); $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 6.71 (1H, d, $^3J$ = 3.5 Hz), 6.59 (1H, d, $^4J$ = 8.3 Hz), 6.52 (1H, dd, $J$ = 2.9, 8.3 Hz), 3.68 (3H, s), 2.27 (3H, s); $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 160.6 (s), 144.3 (s), 134.8 (s), 129.1 (s), 116.1 (s), 112.0 (s), 55.4 (s), 22.2 (s).

### Tri(*o*-isopropylphenyl)arsine (2c)

1-Bromo-2-isopropylbenzene (12.50 g, 63 mmol) was added to Mg turnings (1.53 g, 63 mmol) in THF (60 $cm^3$) over 5 min. The mixture was heated at reflux for 1 h until the Mg turnings had disappeared. The grey solution was then allowed to cool to room temperature before the dropwise addition of $AsCl_3$ (3.80 g, 21 mmol) in THF (50 $cm^3$) at −78 °C over 30 min. The reaction was stirred overnight and then distilled water (50 $cm^3$) and saturated $NH_4Cl$ solution (30 $cm^3$) were added and the mixture stirred for 30 min. The mixture was then extracted with $Et_2O$ (2 × 50 $cm^3$) and the ethereal extracts combined and dried over $Na_2SO_4$. The solvents were removed *in vacuo* to yield a viscous brown oil, which was digested with methanol (60 $cm^3$) for 48 h to leave a white precipitate. The supernatant methanol was then removed with a cannula before the powder was washed with cold methanol (2 × 20 $cm^3$) and the product dried *in vacuo*, $CH_2Cl_2$ (2 × 50 $cm^3$) was added to precipitate the MgClBr salts, which were filtered off, The solvent was then evaporated *in vacuo* from the flitrate to give the product **2c** as a fine white powder (2.25 g, 5.20 mmol, 25%). MS (CI) *m/z*: 432 ($M^+$); $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.25 (2H, m), 6.95 (1H, m), 6.75 (1H, d), 3.36 (1H, septet), 1.07 (6H, d); $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 153.5 (s), 138.1 (s), 134.5 (s), 129.3 (s), 126.5 (s), 125.7 (s), 33.2 (s), 24.1 (s).

### Tri(*o*-isopropyl-*p*-methoxy)arsine (2d)

4-Bromo-3-isopropylanisole (9.01 g, 39 mmol) was added to Mg turnings (1.00 g, 41 mmol) in THF (5 $cm^3$) over 5 min. The mixture was heated at reflux for 2 h. The black solution was then allowed to cool to room temperature and filtered to remove excess Mg, before the dropwise addition of $AsCl_3$ (1.87 g, 10.3 mmol) in THF (20 $cm^3$). The reaction was stirred overnight and then an aqueous $NH_4Cl$ solution (2 M, 100 $cm^3$) was added and the mixture stirred for 30 min. The mixture was then extracted with $Et_2O$ (3 × 30 $cm^3$) and the ethereal extracts combined and dried over $Na_2SO_4$. The solvents were removed *in vacuo* to yield a brown solid, which was digested with methanol (50 $cm^3$) to leave a white precipitate. The supernatant methanol was then removed with a cannula before the powder was washed with cold methanol (2 × 20 $cm^3$) and the product dried *in vacuo* to give the product **2d** as a white powder (2.21 g, 4.23 mmol, 41%). Elemental analysis (%): found (calc.): C, 68.53 (68.95); H, 7.77 (7.52); MS (CI) *m/z*: 522 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.81 (1H, d), 6.73 (1H, d), 6.55 (1H, dd), 3.83 (s, 3H), 3.35 (septet, 1H), 1.05 (d, 6H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 160.3 (s), 154.6 (s), 135.4 (s), 127.9 (s), 111.5 (s), 111.1 (s), 55.0 (s), 32.8 (s), 24.0 (s).

### *trans*-$[PtCl_2(2a)_2]$ (3a)

Arsine **2a** (0.121 g, 0.347 mmol) and $[PtCl_2(NCBu^t)_2]$ (0.075 g, 0.174 mmol) were dissolved in toluene (5 $cm^3$) and heated at 85 °C for 15 h to give a green–yellow precipitate. The solution was allowed to cool to room temperature before removal of the solvent by cannula. The resulting solid was then dissolved in $CH_2Cl_2$ and filtered through a pad of Florisil to give a yellow solution. The solvent was reduced and hexane was added to induce precipitation. The solution was filtered off and the remaining solid was washed with cold toluene (2 × 1 $cm^3$) before drying *in vacuo* to give **3a** as a pale yellow powder (0.050 g, 0.048 mmol, 28%). Elemental analysis (%) for **3a**·$CH_2Cl_2$ (presence of solvent confirmed by $^1H$ NMR): found (calc.): C, 48.74 (49.30); H, 4.00 (4.23); MS (FAB) *m/z* 890 ($M^+ - 2Cl$); IR: $\nu$(Pt–Cl) 343 $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.71 (1H, br s), 7.32 (1H, dt), 7.13 (2H, m), 2.25 (3H, br s).

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**_trans_-[$PtCl_2(2b)_2$] (3b)**

Complex **3b** was prepared as a yellow solid (0.20 g, 0.17 mmol, 61%) in a similar fashion to **3a**. Elemental analysis (%) for **3b**·$H_2O$ (presence of solvent confirmed by $^1$H NMR): found (calc.): C, 49.63 (49.67); H, 4.94 (4.86); MS (FAB) *m/z* 1142 ($M^+$), 1105 ($M^+ - Cl$), 1070 ($M^+ - 2Cl$); IR: *ν*(Pt–Cl) 342 cm$^{-1}$; $^1$H NMR (400 MHz, $CD_2Cl_2$): *δ* 7.58 (1H, br s), 6.68 (2H, m), 3.72 (3H, s), 2.22 (3H, br s); $^{13}$C NMR ($CD_2Cl_2$): *δ* 161.7 (s), 144.8 (s), 136.0 (br s), 120.3 (s), 117.3 (s), 111.5 (s), 54.1 (s), 23.4 (s).

**_trans_-[$PtCl_2(2c)_2$] (3c)**

Complex **3c** was prepared as a pale yellow solid in a similar fashion to **3a** but satisfactory elemental analyses were not obtained. IR: *ν*(Pt–Cl) 346 cm$^{-1}$; $^1$H NMR (400 MHz, $CD_2Cl_2$): *δ* 8.65 (br), 7.65 (br), 7.53 (br), 7.30 (br), 7.14 (br), 7.08 (br), 3.50 (br), 3.20 (br), 2.37 (br), 1.80 (br), 1.45 (br), 1.18 (d), 1.07 (br), 0.92 (br), −0.15 (br), −0.20 (br).

**_trans_-[$PtCl_2(2d)_2$] (3d)**

Complex **3d** was prepared as an orange solid in a similar fashion to **3a** but satisfactory elemental analyses were not obtained. IR: *ν*(Pt–Cl) 347 cm$^{-1}$; $^1$H NMR ($CDCl_3$): *δ* 8.64 (br), 7.38 (br), 7.18 (br), 6.68 (br), 3.88 (br), 3.77 (br), 3.61 (br), 3.32 (br), 2.52 (br), 1.83 (br), 1.29 (br), 1.00 (br), −0.02 (br).

**_trans_-[$PdCl_2(2a)_2$] (4a)**

Complex **4a** was prepared as a yellow powder (0.76 g, 0.83 mmol, 91%) in a similar fashion to **3a** replacing [$PdCl_2(NCPh)_2$] for [$PtCl_2(NCBu^t)_2$]. Elemental analysis (%) for **4a**·1/3$CHCl_3$ (presence of solvent confirmed by $^1$H NMR): found (calc.): C, 55.71 (55.65); H, 4.68 (4.67); MS (FAB) *m/z* 839 ($M^+ - Cl$), 802 ($M^+ - 2Cl$); IR: *ν*(Pd–Cl) 356 cm$^{-1}$; $^1$H NMR ($CDCl_3$): *δ* 7.73 (1H, br m) 7.32 (1H, dt), 7.20 (2H, m), 2.37 (3H, br s).

**_trans_-[$PdCl_2(2b)_2$] (4b)**

Complex **4b** was prepared as an orange solid (1.31 g, 1.12 mmol, 82%) in a similar fashion to **4a**. Elemental analysis (%) for **4b**·$CHCl_3$ (presence of solvent confirmed by $^1$H NMR): found (calc.): C, 50.11 (50.15); H, 4.85 (4.72); MS (FAB) *m/z* 1020 ($M^+ - Cl$), 982 ($M^+ - 2Cl$); IR: *ν*(Pd–Cl) 340 cm$^{-1}$; $^1$H NMR ($CDCl_3$): *δ* 7.62 (1H, br), 6.73 (2H, m), 3.80 (3H, s), 2.33 (3H, br s); $^{13}$C NMR ($CD_2Cl_2$): *δ* 164.1 (s), 146.3 (s), 138.0 (br s), 126.8 (s), 119.3 (s), 113.7 (s), 57.0 (s), 27.6 (s).

**_trans_-[$PdCl_2(2d)_2$] (4d)**

Complex **4d** was prepared as an orange solid (0.40 g, 0.23 mmol, 43%) in a similar fashion to **4a**. Elemental analysis (%) for **4d**·**2d** (presence of 1 equiv. of free ligand confirmed by $^1$H NMR): found (calc.): C, 62.39 (61.95); H, 6.81 (6.76); IR: *ν*(Pd–Cl) 347 cm$^{-1}$; $^1$H NMR (400 MHz, $CD_2Cl_2$): *δ* 8.40 (br) 7.22 (br), 6.64 (br), 3.76 (br, m), 3.44 (br), 3.15 (br), 2.39 (br), 1.80 (br), 1.38 (br), 1.20 (br), 0.93 (br), −0.04 (br), −0.12 (br).

**[$PdCl_2(2c)]_2$ (5c)**

Complex **5c** was prepared as an orange solid (0.629 g, 0.48 mmol, 53%) in a similar fashion to **4a**. Elemental analysis (%) for **5c**·$C_6H_5CH_3$ (presence of solvent confirmed by $^1$H NMR): found (calc.): C, 55.51 (55.85); H, 5.91 (5.69); MS (FAB) *m/z* 1185 ($M^+ - Cl$), 1148 ($M^+ - 2Cl$); IR: *ν*(Pd–Cl) 352, 301, 264 cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$): *δ* 8.79 (br), 7.59 (br), 7.45 (br), 7.13 (m), 3.66 (br), 3.24 (br), 2.38 (br), 1.95 (br), 1.49 (br), 1.23 (br), 0.99 (br), −0.05 (br), −0.13 (br); $^1$H NMR ($CD_2Cl_2$, −20 °C): *δ* 8.83 (m), 8.71 (m), 7.65 (m), 7.44 (m), 7.15 (m), 3.61 (m), 3.37 (m), 3.19 (m), 3.00 (m), 2.53 (d), 2.30 (m), 2.20 (d), 1.95 (d), 1.51 (d), 1.45 (d), 1.25 (d), 1.20 (d), 1.17 (d), 0.98 (d), −0.01 (d), −0.06 (d), −0.11 (d), −0.20 (d).

**[$PdCl_2(2d)]_2$ (5d)**

Complex **5d** was prepared as an orange solid (0.396 g, 0.25 mmol, 74%) in a similar fashion to **4a** except that 1 equiv. of **2d** was used rather than 2 equivs. Elemental analysis (%) for **5d**·2$CH_2Cl_2$ (presence of solvent confirmed by $^1$H NMR): found (calc.): C, 47.51 (47.44); H, 5.22 (5.27); MS (ES) *m/z* 1362 ([$Pd_2Cl_3$(**2d**)$_2$]$^+$), 665 ([$Pd_2Cl_2$(**2d**)$_2$]$^{2+}$); IR: *ν*(Pd–Cl) 352, 293, 257 cm$^{-1}$; $^1$H NMR ($CDCl_3$): *δ* 8.88 (br), 7.19 (m), 6.98 (br), 6.73 (br), 3.81 (br, m), 3.37 (br), 2.65 (br), 2.48 (br), 2.37 (br), 2.03 (br), 1.56 (br), 1.35 (br), 1.07 (br), 0.09 (br).

**[PtCl(2b − H)]$_2$ (6b)**

Arsine **2b** (0.156 g, 0.356 mmol) and [$PtCl_2(NCBu^t)_2$] (0.154 g, 0.356 mmol) were dissolved in toluene (10 cm$^3$) and heated at reflux for 22 h to give a dark brown solution. The volatiles were removed *in vacuo* and the resulting residue was re-dissolved in $CH_2Cl_2$ (20 cm$^3$). The solution was filtered through a 2 cm thick plug of Florisil which was washed through with a further 60 cm$^3$ of $CH_2Cl_2$ to give a pale yellow solution. The solvent was removed *in vacuo* to give **6b** as a pale yellow solid (0.150 g, 0.11 mmol, 63%). Elemental analysis (%): found (calc.): C, 42.75 (43.13); H, 3.86 (3.92); MS (ES) *m/z* 1298 ([$Pt_2$Cl(**2b** − H)$_2$]$^+$); IR: *ν*(Pt–Cl) 281, 248 cm$^{-1}$; $^1$H NMR ($CDCl_3$): *δ* 7.17 (m), 6.92 (m), 6.79 (d), 6.76 (d), 6.64 (m), 3.76 (s), 3.47 (s, $^2J$(Pt–H) = 102 Hz), 3.43 (s, $^2J$(Pt–H) = 102 Hz), 2.67 (s), 2.53 (s); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ* 161.88 (s), 161.85 (s), 161.56 (s), 161.49 (s), 157.79 (s), 157.73 (s), 144.04 (s), 144.00 (s), 133.73 (br s), 131.87 (s), 131.65 (s), 128.06 (s), 12.96 (s), 121.16 (v br), 117.45 (s), 117.43 (s), 112.97 (s), 112.72 (s), 111.52 (s), 111.29 (s), 111.03 (s), 110.93 (s), 55.41 (s), 55.32 (s), 23.18 (s), 23.12 (s), 14.83 (s), 14.43 (s).

**High-throughput Heck olefinations**

The pre-formed palladium complexes of ligands **1a–d** or **2a–d** (0.01 mmol) or ligands **1a–d** or **2a–d** (0.04 mmol) with [$Pd(OAc)_2$] (0.02 mmol) were added to vials containing aliquots of DMA solutions of 4-bromoacetophenone (1.0 cm$^3$, 2.0 M, 2.0 mmol) and mesitylene (0.12 g, 1.0 M, 1.0 mmol). Then a solution of *n*-butylacrylate (1.0 cm$^3$, 2.8 M, 2.8 mmol) was added and finally $Na_2CO_3$, (2.2 mmol). The vials were placed in a Baskerville "lunch-box" and purged with argon ten times to a pressure of 10 atm, before releasing the pressure to 2 atm. The "lunchbox" was then heated at 100 °C for 17 h with agitation. The products were analyzed by GC.

**Monitored Heck olefinations**

Schlenk flasks were filled with NaOAc (0.45 g, 5.5 mmol), 4-bromoacetophenone (0.925 g, 5 mmol) and *n*-butyl acrylate (1.0 cm$^3$, 7.0 mmol) and were degassed *via* freeze–pump thawing before heating to 100 °C and injection of hot (100 °C) DMA solutions (3.0 cm$^3$) of **7a**, **8d** or **4d** (0.0125 mmol). The flasks were sampled periodically (see Fig. 4) and products analysed by either NMR or GC.

**[$NiL(CO)_3$] complexes**

[$Ni(CO)_4$] was added dropwise from an inverted cylinder into a solution of *ca.* 0.1 g of ligand (**1a–d**) or (**2a–d**) in $CH_2Cl_2$ (10 cm$^3$) in a Schlenk tube. The mixture was then frozen by immersion in liquid $N_2$ before detaching the reaction vessel from the tubing connecting it to the cylinder. The solutions were allowed to warm to room temperature and left to stir for 16 h. The solvent and remaining [$Ni(CO)_4$] were evaporated off under reduced pressure into a trap containing bleach. The product was dissolved in

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**Table 5** Crystal and refinement data

| | *trans*-**4a** | *trans*-**3d**·3$CH_2Cl_2$ |
|---|---|---|
| Colour, habit | Yellow plate | Yellow block |
| Size/mm | 0.3 × 0.2 × 0.05 | 0.2 × 0.2 × 0.2 |
| Formula | $C_{42}H_{42}As_2Cl_2Pd$ | $C_{63}H_{84}As_2Cl_8O_6Pt$ |
| $M_r$ | 873.90 | 1565.83 |
| Crystal system | Monoclinic | Monoclinic |
| Space group (no.) | $P2_1/c$ (14) | $P2_1/n$ (14) |
| $a$/Å | 10.6786(18) | 14.116(3) |
| $b$/Å | 10.9964(19) | 24.806(5) |
| $c$/Å | 15.825(3) | 19.594(4) |
| $\beta$/° | 93.093(3) | 99.57(3) |
| $V$/Å$^3$ | 1855.6(5) | 6766(2) |
| $Z$ | 2 | 4 |
| $\mu$/mm$^{-1}$ | 2.443 | 3.408 |
| $T$/K | 173 | 100 |
| Reflections collected | 19130 | 47826 |
| Unique data | 4250 | 15511 |
| $R_{int}$ | 0.089 | 0.0553 |
| Final $R_1$ [$I > 2\sigma(I)$] | 0.047 | 0.0654 |
| $\Delta\rho_{max, min}$/e Å$^{-3}$ | 0.65, −0.72 | 2.70, −2.37 |

$CH_2Cl_2$ and analysed by $^{31}$P NMR and IR spectroscopy (see Table 4).

### X-Ray crystal structure analyses of 4a and 3d·3$CH_2Cl_2$

X-Ray diffraction experiments on *trans*-[$PdCl_2$(**2a**)$_2$] (**4a**) and *trans*-[$PtCl_2$(**2d**)$_2$]·3$CH_2Cl_2$ (**3d**·3$CH_2Cl_2$) were carried out at −100 °C on a Bruker SMART diffractometer using Mo-Kα X-radiation, $\lambda = 0.71073$ Å. Crystal data and refinement data are given in Table 5. Absorption corrections were based on equivalent reflections and structures refined against all $F_o^2$ data with hydrogen atoms riding in calculated positions. In **3d**·3$CH_2Cl_2$ the solvent is severely disordered and the model used, although the best that could be obtained, is not completely satisfactory given the large residual electron density features close to the solvent molecules and the presence of apparent voids of volume *ca.* 30 Å$^3$ nearby.

CCDC reference numbers 256982 and 256983

See http://www.rsc.org/suppdata/dt/b4/b417910b/ for crystallographic data in CIF or other electronic format.

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