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Synthesis of mono-, di- and tripalladated 1,3,5-benzenetristyryl complexes. CO insertion to give a dipalladated indenone†

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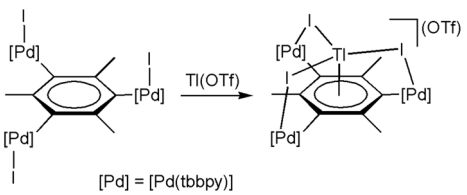
The tribrominated arenes 1,3,5-C_6(*E*-CH=CHAr)$_3$Br$_3$ (Ar = Ph, (**I**), *p*-To (**I′**)), add oxidatively to [Pd(dba)$_2$] ([Pd$_2$(dba)$_3$]·dba) in the presence of two equivalents of a phosphine (PPh_3 or PMe_2Ph) to form the mono-palladated complexes *trans*-[Pd{C_6(*E*-CH=CHAr)$_3$Br$_2$}Br(L)$_2$] (Ar = Ph, L = PPh_3 (**1a**), Ar = *p*-To, L = PPh_3 (**1a′**), Ar = Ph, L = PMe_2Ph (**1b**)), while the reaction in a 1 : 2 : 4 arene : Pd : PMe_2Ph molar ratio affords the dipalladated complex [{*trans*-PdBr(PMe_2Ph)$_2$}$_2${μ$_2$-C_6(*E*-CH=CHPh)$_3$Br}] (**2b**). Both **I** and **I′** add oxidatively to 3 equivalents of [Pd(dba)$_2$] in the presence of the chelating N-donor ligand tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) to form the tripalladated complexes [{PdBr(tmeda)}$_3${μ$_3$-C_6(*E*-CH=CHAr)$_3$}] (Ar = Ph, (**3c**), *p*-To (**3c′**)). Complex **3c** reacts with PMe_3 to form [{*trans*-PdBr(PMe_3)$_2$}$_3${μ$_3$-C_6(*E*-CH=CHPh)$_3$}] (**3d**). Compound **3c** also reacts with CO to give the novel dipalladated indenone [2-Ph-4,6-{PdBr(tmeda)}$_2$-5,7-(*E*-CH=CHPh)$_2$-inden-1-one] (**4**). The crystal structures of **1a′** and **1b** were determined by X-ray diffraction studies.

Introduction

Arylpalladium complexes continue to be a subject of great interest because they are involved in many palladium-catalysed carbon–carbon and carbon–heteroatom bond-forming reactions.[1–17] Consequently, there are many publications related to their synthesis, characterization, and reactivity.[18–36] In particular, the presence of organic substituents *ortho* to the Pd atom has been shown to provide a very rich and varied chemistry, because they frequently participate in the reactivity of these complexes, resulting in interesting new structures and the formation of novel and potentially useful organic compounds.[20–29,33,34,37,38] Some time ago, we started to explore the possibility of extending this chemistry to di-[25,26] and tripalladated[39–41] benzene derivatives, *ortho*-substituted at each Pd(II) centre. Thus, in 2001 some of us reported the first tripalladated benzene derivative, resulting from the 3-fold oxidative addition of 1,3,5-triiodomesitylene to 3 equivalents of [Pd(dba)$_2$].[39] This complex was shown to act as a metallaligand towards Tl(I) (Scheme 1).[41] We later reported tripalladated derivatives of 1,3,5-triformylbenzene.[40] Since then, there have been (to the best of our knowledge) no further reports in this area, despite the structural and chemical interest of these complexes. In fact, most of the reports involving polymetalated derivatives of benzene with general formula $C_6R_{6-n}M_n$ (*n* = 3–6) involve main-group elements, mainly Hg,[42–46] Li,[44,46–49] Mg,[44] Ge,[50,51] and Sn.[44,46,52–56] There are also reports of transition metal derivatives, which mostly involve metal clusters with face-capping arene ligands coordinated to three metal atoms, such as Co,[57] Ru,[58,59] Rh,[60,61] and Os.[58,61–63] Murahashi and co-workers have reported several sandwich-type complexes with Pd_3 to Pd_5 clusters bridging two hydrocarbon rings.[64–68] However, for σ-bonded polymetalated derivatives of benzene, the only examples with Pd are those reported by our group,[39–41] plus the 3-fold cyclopalladation of a 1,3,5-



Scheme 1 The first tripalladated benzene derivative, acting as a metallaligand towards Tl(I).

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†Electronic supplementary information (ESI) available: NMR data for complexes **1–4** and arenes **I**, **I′** (table, comments and spectra), X-ray crystallographic data, structure refinements and CIF files for complexes **1a′** and **1b**. CCDC 2195995 and 2195996. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3dt00091e

tris(di-2-pyridylamino)benzene ring.[69] There is also a report of a tripalladated arylamine and a tetrapalladated pyrene, obtained by mechanochemical solvent-free oxidative addition of aryl halides to a Pd(0) complex.[70] Regarding other transition metals, only one trimetalated benzene with Mn, 1,3,5-C_6H_3[Mn$(CO)_5$]$_3$,[71–73] and two further examples with Fe, 1,3,5-C_6H_3[Fe$(\eta^5$-Cp$)(CO)_2$]$_3$ [71–74] and 1,3,5-C_6H_3[Fe$(\eta^5$-C_5H_4Me$)(CO)_2$]$_3$,[75] have been reported so far.

In view of the lack of progress in this area, we have resumed our research[39–41] on polypalladated benzene derivatives and now report the synthesis of mono-, di- and tripalladated 1,3,5-benzenetristyryl complexes, a set of compounds with a great potential as a branch point in the area of metalladendrimer chemistry.[76] Their chemistry towards unsaturated molecules is also potentially promising, as it could lead to the Pd-mediated synthesis of organic polycyclic compounds. We have started to investigate this chemistry, and we report here the formation of a novel dipalladated indenone, as a result of a CO insertion into one of the aryl–Pd bonds, followed by a depalladation reaction.

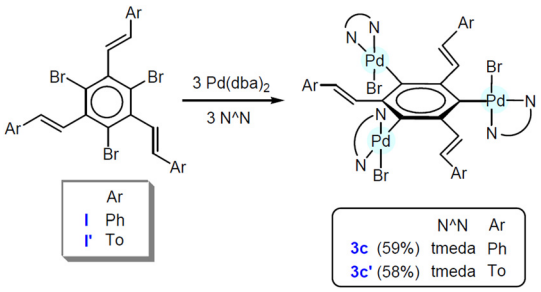
Results and discussion

Synthesis of the complexes

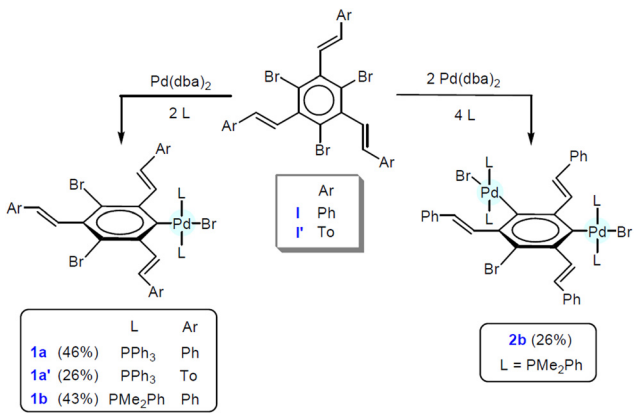
For the synthesis of the new 1,3,5-benzenetristyryl Pd(II) complexes, we have used oxidative addition reactions of the starting tribrominated arenes 1,3,5-C_6(*E*-CH=CHAr)$_3$Br$_3$ (Ar = Ph, (**I**), *p*-tolyl (**I′**)), to 1, 2 or 3 equivalents of [Pd(dba)$_2$] ([Pd$_2$(dba)$_3$]·dba),[77,78] in the presence of phosphine ligands (PPh_3 or PMe_2Ph, Scheme 2) or a chelating N-donor ligand (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, Scheme 3).[19]

Reaction with phosphines. 2,4,6-Tribromo-1,3,5-tris-(*E*-styryl)benzene (1,3,5-C_6(*E*-CH=CHPh)$_3$Br$_3$, **I**, Scheme 2) adds oxidatively to one equivalent of [Pd(dba)$_2$] in the presence of two equivalents of phosphine (PPh_3 or PMe_2Ph) to form *trans*-[Pd{C_6(*E*-CH=CHPh)$_3$Br$_2$}Br(L)$_2$] (L = PPh_3 (**1a**), PMe_2Ph (**1b**)). Similar reactions with a 1 : 2 : 4 arene : Pd : phosphine molar ratio only afford a dipalladated complex, [{*trans*-PdBr$(PMe_2Ph)_2$}$_2${μ_2-C_6(*E*-CH=CHPh)$_3$Br}] (**2b**), with PMe_2Ph, as the reaction with PPh_3 again gives complex **1a**. Our previous work had shown that the trihaloarenes 1,3,5-$C_6Me_3I_3$ [39] and 1,3,5-C_6(CHO)$_3$Br$_3$ [40] also form dipalladated Pd(II) complexes only with the more basic and less sterically demanding phosphine PMe_2Ph, and not with PPh_3, so this seems to be a general trend. Also similarly to those arenes,[39,40] the 3-fold oxidative addition of **I** to [Pd(dba)$_2$] in the presence of any of the phosphine ligands (PPh_3, PMe_2Ph, or PMe_3) was unsuccessful. The related arene 1,3,5-C_6(*E*-CH=CHTo)$_3$Br$_3$ (To = *p*-tolyl, **I′**) reacts with [Pd(dba)$_2$] and PPh_3 in a 1 : 1 : 2 ratio to give a monopalladated complex **1a′** (Scheme 2), which was characterized by X-ray crystallography, as was **1b** (Fig. 1 and 2). Oxidative addition reactions of **I′** in the presence of PMe_2Ph or PMe_3 were not investigated.

Reactions with tmeda. The arene **I** reacts with [Pd(dba)$_2$] and the chelating N-donor ligand tmeda to form the tripalladated complex [{PdBr(tmeda)}$_3${μ_3-C_6(*E*-CH=CHPh)$_3$}] (**3c**,



Scheme 3 Oxidative addition reactions of **I**, **I′** to [Pd(dba)$_2$] in the presence of tmeda, to form the tripalladated complexes **3c**, **3c′**.



Scheme 2 Oxidative addition reactions of **I**, **I′** to [Pd(dba)$_2$] in the presence of phosphines, to form mono- (**1a**, **1a′**, **1b**) and dipalladated (**2b**) complexes.

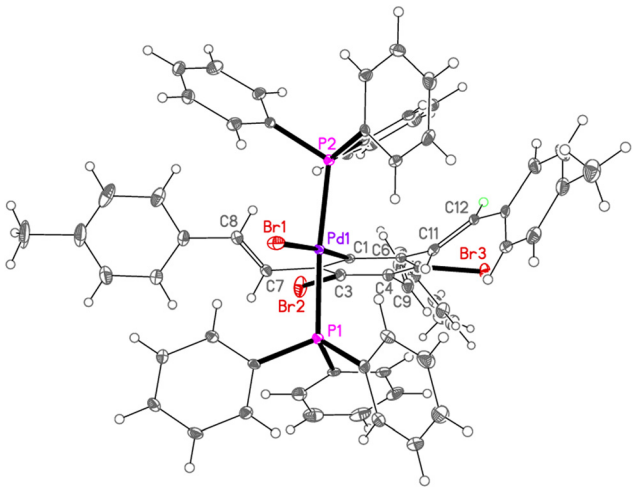


Fig. 1 Thermal ellipsoid plot (50% probability level) of **1b**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) = 2.010(3), Pd–P(1) = 2.3138 (9), Pd(1)–P(2) = 2.3116(9), Pd(1)–Br(1) = 2.5180(4), Br(2)–C(3) = 1.916(3), Br(2)–C(5) = 1.916(3), C(1)–Pd(1)–P(1) = 89.85(8), C(1)–Pd(1)–P(2) = 90.17(8), P(2)–Pd(1)–P(1) = 177.54(3), C(1)–Pd(1)–Br(1) = 177.05(9), P(1)–Pd(1)–Br(1) = 90.00(2), P(2)–Pd(1)–Br(1) = 90.10(2).

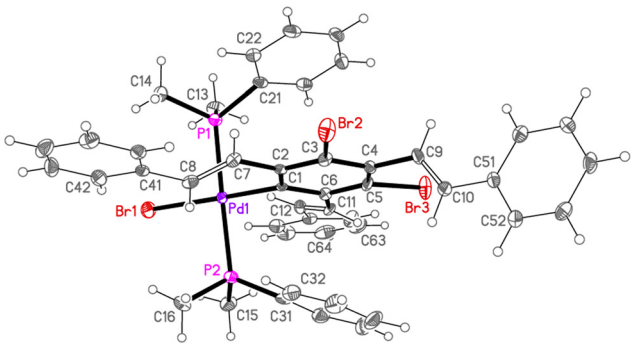
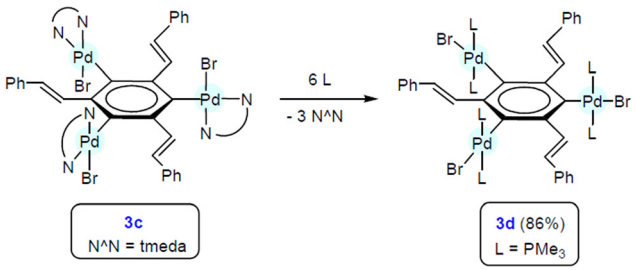


Fig. 2 Thermal ellipsoid plot (30% probability level) of **1a′**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) = 2.022(2), Pd–P(1) = 2.3334 (6), Pd(1)–P(2) = 2.3680(6), Pd(1)–Br(1) = 2.5201(3), Br(2)–C(3) = 1.915(2), Br(2)–C(5) = 1.919(2), C(1)–Pd(1)–P(1) = 87.39(6), C(1)–Pd(1)–P(2) = 91.05(6), P(1)–Pd(1)–P(2) = 174.70(2), C(1)–Pd(1)–Br(1) = 176.24(6), P(1)–Pd(1)–Br(1) = 88.987(18), P(2)–Pd(1)–Br(1) = 92.648(18).



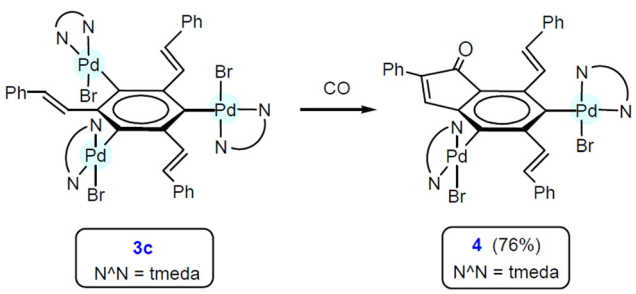
Scheme 4 Ligand displacement reaction on **3c**.

Scheme 3), even if substoichiometric amounts of Pd and tmeda are used (1 : 1 : 1 or 1 : 2 : 2 arene : Pd : tmeda ratio, instead of the required 1 : 3 : 3 ratio, which, nonetheless, results in a cleaner reaction). A similar tripalladated complex, [{PdBr(tmeda)}$_3${μ_3-C$_6$(*E*-CH=CHTo)$_3$}] (**3c′**), can be isolated from the reaction of 1,3,5-C$_6$(*E*-CH=CHTo)$_3$Br$_3$ (**I′**) with [Pd(dba)$_2$] and tmeda, although **3c′** forms alongside minor amounts of another complex, presumably a lower nuclearity analogue. Curiously, we have found that a substoichiometric arene : Pd : tmeda ratio (such as 1 : 2 : 2) increases the yield of **3c′**, which was purified by TLC (see Experimental). Our previous work[39,40] had shown that similar reactions with the arene 1,3,5-C$_6$Me$_3$I$_3$ [39] also afforded tripalladated complexes [{PdI(N^N)}$_3$(μ_3-C$_6$Me$_3$)] (N^N = bpy, tbbpy), even with substoichiometric arene : Pd : N^N ratios, while the oxidative addition of 1,3,5-C$_6$(CHO)$_3$Br$_3$ [40] to [Pd(dba)$_2$] in the presence of N^N ligands afforded mixtures of mono-, di- or tripalladated complexes (depending on the stoichiometric reactant ratio), from which the separate complexes could be isolated and characterized (with N^N = bpy the solubility was very low, and only a monopalladated complex was isolated, while with N^N = tmeda and tbbpy the mono-, di- and tripalladated complexes could be separated by TLC and fully characterized). Clearly, the strong electron-withdrawing character of the formyl groups in 1,3,5-C$_6$(CHO)$_3$Br$_3$ did not favour the successive oxidative additions,[40] allowing a certain degree of selectivity in the palladation of the arene, in contrast to 1,3,5-C$_6$Me$_3$I$_3$,[39] and the arenes **I** and **I′** described here.

Reactions of **I** and **I′** with [Pd(dba)$_2$] in the presence of other chelating N^N ligands such as tbbpy (4,4′-di-*tert*-butyl-2,2′-bipyridine) or bpy (2,2′-bipyridine), or a chelating phosphine ligand, dppe, resulted in mixtures of compounds, which could not be characterized.

Reactions with complex 3c. The tripalladated complex [{PdBr(tmeda)}$_3${μ_3-C$_6$(*E*-CH=CHPh)$_3$}] (**3c**) reacts with excess PMe$_3$ (1 : 12 ratio) at 50 °C to form [{*trans*-PdBr(PMe$_3$)$_2$}$_3${μ_3-C$_6$(*E*-CH=CHPh)$_3$}] (**3d**, Scheme 4), which could not be prepared by direct oxidative addition (see above). This reactivity is also consistent with previous observations,[39,40] showing that the failure to obtain tripalladated complexes by oxidative addition in the presence of PMe$_3$ is probably the result of kinetic, and not thermodynamic, effects. A similar ligand displacement reaction with **3c′** was not pursued.

We have started to explore the reactivity of **3c** towards unsaturated organic molecules, which could potentially insert into the C–Pd bonds, resulting in novel polynuclear complexes or polycyclic organic compounds (see the Introduction). Frequently, this reactivity is promoted by TlOTf, but when **3c** was reacted with alkynes (RC≡CR, R = Me, Ph, COOMe) in the presence of TlOTf, the product was the same as in the reaction with TlOTf alone, and was presumably a complex between **3c** and TlOTf, similar to that shown in Scheme 1 (Introduction),[41] but which we have not been able to characterize fully. Reactions of **3c** with alkynes in the absence of TlOTf yielded only the starting material, and the use of AgClO$_4$ instead of TlOTf resulted in mixtures of compounds, which could not be characterized. Reactions of **3c** with XyNC also failed to yield a major characterizable product, but when **3c** was reacted with CO, the dipalladated indenone, [2-Ph-4,6-{PdBr(tmeda)}$_2$-5,7-(*E*-CH=CHPh)$_2$-inden-1-one] (**4**, Scheme 5), formed as a major product, which was purified from the minor impurities by preparative TLC and isolated with a very good yield (76%). Complex **4** is the result of the insertion of CO into only one of the three aryl–Pd(II) bonds in **3c**, followed by depalladation in that position, and has been fully characterized by NMR. No further CO insertions into the two remaining aryl–Pd(II) bonds (to form a *C*3-symmetric tri-indenone derivative) were achieved, even if the reaction was carried out in excess CO and



Scheme 5 CO insertion in **3c** to form the dipalladated indenone **4**.

heating at 60 °C (see Experimental). Attempts to further react **4**, once isolated, with CO have also been unsuccessful. Thus, the formation of the first indenone ring seems to deactivate the complex towards successive insertions. Although the palladium-catalyzed synthesis of indenones by annulation of alkynes and CO with *ortho*-functionalized arenes has been described before,[79–82] in those reports the intermediate *ortho*-alkenylarylpalladium complexes were not isolated. Moreover, this is the first time that such a CO insertion reaction is carried out in a polypalladated complex, thus affording a dipalladated indenone, a type of dinuclear Pd(II) complex that has not been described before. The reactivity of the PMe_3 complex **3d** towards CO was not similar to that of **3c** and provided no clean result. Complex **3c′** was not considered a suitable starting material for this research, because of the difficulties related to its purification (see above). The reactivity of the mono- and dipalladated complexes **1a**, **1a′**, **1b** and **2b** towards unsaturated molecules has not been investigated so far.

Structure of the complexes

The ^{1}H, ^{13}C and ^{31}P NMR data of complexes **1–4** agree with the structures proposed in Scheme 2–5 (see Table 1 in the ESI† for a comparative assignment). The 16 Hz value for the $^3J_{HH}$ coupling constant between the alkenyl protons confirms the *E* geometry for all the complexes. The tripalladated complexes **3c** and **3c′** show a 1 : 2 pattern for all the NMR resonances, as one of the [PdBr(N^N)] groups is oriented in the opposite direction to the other two with respect to the aryl plane (the rotation around the Pd–C bonds is hindered). The mono- (**1a**, **1a′**, **1b**) and dipalladated (**2b**) phosphine complexes also show a 1 : 2 pattern in the ^{1}H and ^{13}C-NMR spectra, as a result of the substitution pattern around the aryl ring. In contrast, the tripalladated PMe_3 complex **3d** shows a single set of resonances, both in the ^{1}H and in the ^{13}C spectra, as this molecule has a 3-fold axis perpendicular to the aryl plane.

The phosphine complexes, **1a**, **1a′**, **1b**, **2b** and **3d**, have an all-*trans* geometry and thus they have a symmetry plane in the aryl ring and show a single ^{31}P resonance. As usual, the ^{31}P chemical shift decreases in the order PPh_3 (δ *ca.* 21 ppm for **1a,a′**) > PMe_2Ph (δ −9.9 ppm for **1b** and −12.4 ppm for **2b**) > PMe_3 (δ −19.2 ppm for **3d**).[39,40]

The ^{13}C NMR resonances of complexes **1–4** were fully assigned with the help of 2D NMR experiments (see Table 1 in the ESI†). The highest chemical shifts correspond to the aryl carbon atoms directly bonded to Pd: *ca.* 152 ppm for the tmeda complexes and slightly higher (161–165 ppm) for the phosphine complexes, as is usual.[19,40,83] The aryl carbon atoms bonded to the alkenyl substituents appear in the range 136–146 ppm, similar to the starting arenes **I**, **I′** (139.6 ppm), with the highest chemical shifts when this carbon is *ortho* to two [$PdBrL_2$] moieties (L = phosphine, complexes **2b** and **3d**). The C–Br carbon atoms resonate at lower frequencies, 122–126 ppm (similar to 124 ppm in **I**, **I′**). See the ESI† for a more detailed discussion of the NMR data.

The crystal and molecular structures of the monopalladated complexes **1a′** (Fig. 1) and **1b** (Fig. 2) were determined by X-ray diffraction studies (Table 1 in ESI†). The structures show somewhat distorted square planar coordination around the Pd atoms. R.m.s. deviations from the best plane through Pd and the four donor atoms are 0.056 Å for complex **1a′** and 0.021 Å for **1b**. The Pd–C bond distances are 2.022(2) Å for **1a′** and 2.010(3) Å for **1b**, similar to the value found for the related complex *trans*-[Pd{C_6(CHO)$_3$Br$_2$}Br(PPh_3)$_2$] (2.0163(15) Å).[40] The Pd–P (2.3426(4) Å and 2.3279(4) Å) distances in that complex[40] are also similar to those found in **1a′** (2.3334(6) Å, 2.3680(6) Å) and **1b** (2.3138(9) Å, 2.3116(9) Å). In contrast, the Pd–Br distance, 2.4865(2) Å,[40] is slightly shorter than in **1a′** (2.5201(3) Å) and **1b** (2.5180(4) Å), an indication that the 1,3,5-benzenetristyryl ring has a larger *trans* influence than the 1,3,5-benzenetricarboxaldehyde. The styryl substituents of the central aromatic ring C1–6 of the tristyrylbenzene moieties are differently disposed in the two structures; for **1a′** all the styryl double bonds point to the same side of the ring, whereas for **1b**, C7=C8 and C9=C10 point in the opposite direction to C11=C12 [*cf.* (a) torsion angles C1–C2–C7–C8, C3–C4–C9–C10 and C5–C6–C11–C12, which are 51.5, 61.9 and 48.7° for **1a′**, but 29.8, 91.9 and −156.3° for **1b** and (b) interplanar angles to the central ring: C41–46 72°, C51–56 29°, C61–66 79° for **1a′** but 3°, 84°, 9° for **1b**]. The bromine atom Br1 of **1b** lies appreciably outside the ring plane (by 0.36 Å, in the opposite direction to the styryl groups).

Experimental

The starting arenes, *trans*-1,3,5-C_6(*E*-CH=CHAr)$_3$Br$_3$, (Ar = Ph, (**I**), *p*-Tol (**I′**)) were prepared by a 3-fold HWE (Horner–Wadsworth–Emmons) reaction on the phosphonate 2,4,6-tribromo-1,3,5-tris(diethoxyphosphorylmethyl)benzene,[84] which, in turn, was prepared from 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)benzene[85] by reaction with $P(OEt)_3$. See ESI† for a depiction of the synthetic route. The conditions for the HWE were analogous to those described in the literature for related, non-brominated aromatic phosphonates.[86]

Nuclear magnetic resonance (NMR) spectra (^{1}H, ^{13}C and ^{31}P) were recorded on 400 MHz and 600 MHz Bruker Avance spectrometers at room temperature. Chemical shifts are given in ppm (δ) relative to TMS (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). Infrared spectra were recorded on a PerkinElmer 16F-PC-FT spectrometer with Nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. All experiments were conducted under N_2 atmosphere using Schlenk techniques. CH_2Cl_2 was distilled before use. "[Pd(dba)$_2$]"[77,78] was prepared according to literature procedures. Tmeda (Fluka), bpy (Fluka), PPh_3 (Fluka), PMe_2Ph (Aldrich) and PMe_3 (Aldrich) were used as received.

Synthesis of *trans*-1,3,5-C_6(*E*-CH=CHPh)$_3$Br$_3$ (I)

2,4,6-Tribromo-1,3,5-tris(diethoxyphosphorylmethyl)benzene (1.53 g, 2.00 mmol) and benzaldehyde (0.61 mL, 6.00 mmol)

were mixed in THF (20 mL) under N_2. KO^{t}Bu (673 mg, 6.00 mmol) was added in small portions and the mixture was stirred for 3 h at RT. On hydrolysis with water (70 mL) a thick white precipitate formed, and the suspension was further stirred for 30 min. After centrifugation the precipitate was separated by decantation and washed with water (2 × 50 mL) and EtOH (2 × 5 mL). Finally, filtration yielded 2,4,6-tribromo-1,3,5-tristyrylbenzene as colourless feathery crystals. Yield: 1.12 g (90%). Mp: 226–228 °C. IR: no relevant signals. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.56 (d, 6H, *o*-H Ph, $^3J_{HH}$ = 7 Hz), 7.40 (t, 6H, *m*-H Ph, $^3J_{HH}$ = 8 Hz), 7.32 (t, 3H, *p*-H Ph, $^3J_{HH}$ = 8 Hz), 7.00 (AB, 3H, α-CH, $^3J_{HH}$ = 16 Hz), 6.79 (AB, 3H, β-CH, $^3J_{HH}$ = 16 Hz). **^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$):** δ 139.6 (3C, C-alkenyl), 136.8 (3C, β-CH═), 136.5 (3C, i-C Ph), 129.0 (6C, *m*-CH Ph), 128.63 and 128.59 (3C each, α-CH═ and *p*-CH Ph), 127.0 (6C, *o*-CH Ph), 124.1 (3C, C–Br). Anal. Calcd for $C_{30}H_{21}Br_3$: C, 58.00; H, 3.41. Found: C, 57.81; H, 3.35.

Synthesis of *trans*-1,3,5-C$_6$(*E*-CH═CH(*p*-Tol))$_3$Br$_3$ (I′)

2,4,6-Tribromo-1,3,5-tris(diethoxyphosphorylmethyl)benzene (3.62 g, 4.73 mmol) and *p*-tolylaldehyde (1.69, 14.2 mmol) were mixed in THF (60 mL) under N_2. KO^{t}Bu (1.59 g, 14.2 mmol) was added in small portions and the mixture was stirred for 6 h at RT. On hydrolysis with water (200 mL) a thick white precipitate formed, and the suspension was further stirred for 30 min. After centrifugation the precipitate was separated by decantation and washed with water (2 × 50 mL) and EtOH (2 × 5 mL). Finally, filtration yielded 2,4,6-tribromo-1,3,5-tris-(*E*-2-(*p*-tolyl)ethenyl)benzene as an off-white solid. Yield: 1.75 g (56%). Mp: 185–187 °C. IR: no relevant signals. **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.43 (AA′BB′, 6H, *o*-H Tol, $^3J_{HH}$ = 8 Hz), 7.17 (AA′BB′, 6H, *m*-H Tol, $^3J_{HH}$ = 8 Hz), 6.93 (AB, 3H, α-CH, $^3J_{HH}$ = 16 Hz), 6.75 (AB, 3H, β-CH, $^3J_{HH}$ = 16 Hz), 2.36 (s, 9H, CH_3). **^{13}C{^{1}H} NMR (150.9 MHz, CDCl$_3$):** δ 139.6 (3C, C-alkenyl), 138.5 (3C, *p-C* Tol), 136.7 (3C, β-CH═), 133.8 (3C, i-C Tol), 129.6 (6C, *m*-CH Tol), 127.8 (3C, α-CH═), 126.9 (6C, *o*-CH Tol), 124.0 (3C, C–Br), 21.5 (3C, Me). Anal. Calcd for $C_{33}H_{27}Br_3$: C, 59.76; H, 4.10. Found: C, 59.77; H, 3.94.

Synthesis of *trans*-[Pd{C$_6$(*E*-CH═CHPh)$_3$Br$_2$}Br(PPh$_3$)$_2$] (1a)

[Pd(dba)$_2$] (277 mg, 0.48 mmol), PPh_3 (252 mg, 0.96 mmol) and C$_6$(*E*-CH═CHPh)$_3$Br$_3$ (300 mg, 0.48 mmol) were mixed under N_2 atmosphere in dry degassed toluene (20 mL). The mixture was stirred at 50 °C for 5 h until the dark red colour of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then evaporated to dryness and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (20 mL) was added and a solid formed, which was filtered off, thoroughly washed with Et_2O and dried *in vacuo* to give **1a** as a pale yellow solid. Yield: 278 mg (46%). Mp: 223–225 °C (dec). IR: no relevant signals. **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.53 (d, 2H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.40–7.26 (several m, 9H, *m*,*p*-H), 7.40–7.26 (very broad, 18H, *o*,*p*-H PPh_3), 7.24 (AB, 2H, α-CH═, $^3J_{HH}$ = 16 Hz), 7.19 (d, 4H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.13 (very broad, 12H, *m*-H PPh_3), 6.77 (AB, 1H, α-CH═, $^3J_{HH}$ = 16 Hz), 6.59 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 6.47 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz). **^{13}C{^{1}H} NMR (150.9 MHz, CDCl$_3$):** δ 165.4 (m, 1C, C1–Pd), 140.4 (t, 2C, C2-alkenyl, $^3J_{PC}$ = 3 Hz), 137.5 (s, 2C, i-C To), 137.2 (s, 1C, i-C To), 136.1 (t, 1C, C4-alkenyl, $^5J_{PC}$ = 1 Hz), 135.1 (s, 1C, β-CH═), 134.3 (s, 2C, β-CH═), 131.2 (t, 2C, α-CH═, $^4J_{PC}$ = 2 Hz), 130.9 (vt, 6C, i-C PPh_3, $^1J_{PC}$ + $^3J_{PC}$ = 46 Hz), 130.6 (s, 1C, α-CH═), 130.7 (very broad, 12C, *o*-CH PPh_3), 128.9 (s, 2C, *m*-CH To), 128.8 (s, 4C, *m*-CH To), 128.0 (s, 1C, *p*-CH To), 128.0 (very broad, 12C, *m*-CH PPh_3), 127.9 (s, 2C, *p*-CH To), 127.0 (s, 4C, *o*-CH To), 126.7 (s, 2C, *o*-CH To), 122.3 (s, 2C, C3–Br) (resonance for *p*-CH PPh_3 not observed). **^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$):** δ 20.7 (s). Anal. Calcd for $C_{66}H_{51}Br_3P_2Pd$: C, 63.31; H, 4.11. Found: C, 63.48; H, 4.49.

Synthesis of *trans*-[Pd{C$_6$(*E*-CH═CHTo)$_3$Br$_2$}Br(PPh$_3$)$_2$] (1a′)

[Pd(dba)$_2$] (132 mg, 0.23 mmol), PPh_3 (121 mg, 0.46 mmol) and C$_6$(*E*-CH═CHTo)$_3$Br$_3$ (150 mg, 0.23 mmol) were mixed under N_2 atmosphere in dry degassed toluene (15 mL). The mixture was heated at 60 °C for 3.5 h until the dark red colour of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then evaporated to dryness and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. A mixture of Et_2O (5 mL) and hexane (15 mL) was added and a solid formed, which was filtered off, washed with boiling hexane (2 × 10 mL) and dried *in vacuo* to give **1a′** as a pale yellow solid. Yield: 101 mg, 34%. Single crystals of **1a′** were obtained by slow diffusion of hexane into an Et_2O solution of **1a′**. Yield: 77 mg, 26% Mp: 248–250 °C. IR: no relevant signals. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.7–7.0 (very broad, 30H, PPh_3), 7.43–7.07 (several m, 14H, *o*,*m*-H Ph, α-CH═), 6.72 (AB, 1H, α-CH═, $^3J_{HH}$ = 16 Hz), 6.54 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 6.42 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz), 2.46 (s, 6H, Me To), 2.37 (s, 3H, Me To). **^{13}C{^{1}H} NMR (100.8 MHz, CDCl$_3$):** δ 164.9 (m, 1C, C1–Pd), 140.4 (t, 2C, C2-alkenyl, $^3J_{PC}$ = 3 Hz), 137.9 (s, 1C, *p*-C Ph), 137.7 (s, 2C, *p*-C Ph), 136.2 (t, 1C, C4-alkenyl, $^3J_{PC}$ = 1 Hz), 134.9 (s, 1C, β-CH═), 134.7 (s, 2C, i-C Ph), 134.4 (s, 1C, i-C Ph), 134.2 (s, 2C, β-CH═), 131.0 (vt, 6C, i-C PPh_3, $^1J_{PC}$ + $^3J_{PC}$ = 46 Hz), 130.3 (very broad, 12C, *o*-CH PPh_3), 130.2 (t, 2C, α-CH═, $^3J_{PC}$ = 2 Hz), 129.7 (s, 1C, α-CH═), 129.5 (s, 2C, *m*-CH Ph), 129.4 (s, 4C, *m*-CH Ph), 127.9 (very broad, 12C, *m*-CH PPh_3), 127.0 (s, 4C, *o*-CH Ph), 126.6 (s, 2C, *o*-CH Ph), 122.2 (s, 2C, C3–Br), 21.6 (s, 2C, Me To), 21.5 (s, 1C, Me To). **^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$):** δ 20.7 (s). Anal. Calcd for $C_{69}H_{57}Br_3P_2Pd$: C, 64.03; H, 4.44. Found: C, 64.04; H, 4.20.

Synthesis of *trans*-[Pd{C$_6$(*E*-CH═CHPh)$_3$Br$_2$}Br(PMe$_2$Ph)$_2$] (1b)

[Pd(dba)$_2$] (92 mg, 0.16 mmol), PMe_2Ph (45 μL, 0.32 mmol) and C$_6$(*E*-CH═CHPh)$_3$Br$_3$ (99 mg, 0.16 mmol) were mixed under N_2 atmosphere in dry degassed toluene (20 mL). The mixture was stirred at 50 °C for 16 h until the dark red colour of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then evaporated to dryness and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (10 mL) was added and a clear solution was

obtained, to which cold hexane (10 mL) was added. A solid formed, which was filtered off, washed with a small amount of cold Et_2O (2 mL) and dried *in vacuo* to give **1b** as a beige solid. Single crystals of **1b** were grown by slow diffusion of hexane into an Et_2O solution of **1b**. Yield: 69 mg (43%). Mp: 220–222 °C. IR: no relevant signals. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.13 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 7.55 (d, 2H, *o*-H Ph, $^3J_{HH}$ = 7 Hz), 7.46 (AB, 2H, α-CH═, $^3J_{HH}$ = 16 Hz), 7.43–7.38 (m, 6H, *o*,*m*-H Ph), 7.35 (t, 4H, *m*-H Ph), 7.33–7.26 (m, 7H, *o*-H PPh + *p*-H Ph), 7.21 (t, 2H, *p*-H PPh, $^3J_{HH}$ = 7 Hz), 7.13 (t, 4H, *m*-H PPh, $^3J_{HH}$ = 7 Hz), 6.87 (AB, 1H, α-CH═, $^3J_{HH}$ = 16 Hz), 6.54 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz), 1.61 (vt, 12H, PMe, $^2J_{PH}$ + $^4J_{PH}$ = 7 Hz). **^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$):** δ 161.8 (t, 1C, C1–Pd, $^2J_{PC}$ = 2 Hz), 139.8 (t, 2C, C2-alkenyl, $^3J_{PC}$ = 2 Hz), 137.4 (s, 2C, i-C Ph), 137.1 (s, 1C, i-C Ph), 135.6 (t, 1C, C4-alkenyl, $^5J_{PC}$ = 1 Hz), 135.5 (s, 1C, β-CH═), 133.8 (vt, 2C, i-C PMe_2*Ph*, $^1J_{PC}$ + $^3J_{PC}$ = 45 Hz), 132.7 (t, 2C, α-CH═, $^4J_{PC}$ = 1 Hz), 131.8 (t, 2C, β-CH═, $^5J_{PC}$ = 2 Hz), 130.5 (vt, 4C, *o*-CH PMe_2*Ph*, $^2J_{PC}$ + $^4J_{PC}$ = 10 Hz), 130.2 (s, 1C, α-CH═), 129.6 (s, 2C, *p*-CH PMe_2*Ph*), 129.1 (s, 4C, *m*-CH Ph), 128.9 (s, 2C, *m*-CH Ph), 128.1 (s, 1C, *p*-CH Ph), 128.02 (s, 2C, *p*-CH Ph), 127.99 (vt, 4C, *m*-CH PMe_2*Ph*, $^3J_{PC}$ + $^5J_{PC}$ = 9 Hz), 126.8 (s, 4C, *o*-CH Ph), 126.7 (s, 2C, *o*-CH Ph), 123.7 (s, 2C, C3–Br), 14.0 (vt, 4C, PMe, $^1J_{PC}$ + $^3J_{PC}$ = 31 Hz). **^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$):** δ −9.9 (s). Anal. Calcd for $C_{46}H_{43}Br_3P_2Pd$: C, 55.03; H, 4.32. Found: C, 54.67; H, 4.43.

Synthesis of [{*trans*-PdBr(PMe_2Ph)$_2$}$_2${μ$_2$-C$_6$(*E*-CH═CHPh)$_3$Br}] (2b)

$[Pd(dba)_2]$ (737 mg, 1.28 mmol), PMe_2Ph (364 μL, 2.56 mmol) and C_6(*E*-CH═CHPh)$_3Br_3$ (398 mg, 0.64 mmol) were mixed under N_2 atmosphere in dry degassed toluene (20 mL). The mixture was heated at 50 °C for 16 h until the dark red colour of $[Pd(dba)_2]$ was no longer observed. The brownish suspension was then evaporated to dryness and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (5 mL) was added and a clear solution was obtained to which cold hexane (10 mL) was added. A solid formed, which was filtered off, washed with a small amount of cold Et_2O (2 mL) and dried *in vacuo* to give **2b** as a beige solid. Yield: 234 mg (26%). Mp: 206–208 °C. IR: no relevant signals. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.46 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz), 8.26 (AB, 1H, α-CH═, $^3J_{HH}$ = 16 Hz), 8.12 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 7.81 (AB, 2H, α-CH═, $^3J_{HH}$ = 16 Hz), 7.66–7.60 (m, 8H, Ph), 7.4–6.9 (several m, 27H, Ph), 1.48 and 1.27 (vt, 12H each, PMe, $^2J_{PH}$ + $^4J_{PH}$ = 7 Hz). **^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$):** δ 160.7 (m, 2C, C1–Pd), 146.0 (m*, 1C, C2-alkenyl), 138.2 (m, 2C, C3-alkenyl), 137.8 (s, 2C, i-C Ph), 137.6 (s, 1C, i-C Ph), 137.4 (m, 1C, α-CH═), 134.7 (vt, 4C, i-C PMe_2*Ph*, $^1J_{PC}$ + $^3J_{PC}$ = 44 Hz), 134.0 (m, 2C, β-CH═), 131.7 (vt, 8C, *o*-CH PMe_2*Ph*, $^2J_{PC}$ + $^4J_{PC}$ = 12 Hz), 130.5 (m, 2C, α-CH═), 129.9 (s, 5C, β-CH═ + *p*-CH PMe_2*Ph*), 129.0 (s, 4C, *m*-CH Ph), 128.5 (s, 2C, *m*-CH Ph), 128.4 (vt, 8C, *m*-CH PMe_2*Ph*, $^3J_{PC}$ + $^5J_{PC}$ = 10 Hz), 127.6 (s, 2C, *p*-CH Ph), 127.0 (s, 1C, *p*-CH Ph), 126.74 (s, 2C, *o*-CH Ph), 126.70 (s, 4C, *o*-CH Ph), 126.3 (s, 1C, C4–Br), 15.8 (vt, 4C, PMe_2Ph, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz), 13.3 (vt, 4C, PMe_2Ph, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz). **^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$):** δ −12.4 (s). Anal. Calcd for $C_{62}H_{65}Br_3P_4Pd_2$: C, 53.70; H, 4.72. Found: C, 53.88; H, 4.80.

Synthesis of [{PdBr(tmeda)}$_3${μ$_3$-C$_6$(*E*-CH═CHPh)$_3$}] (3c)

$[Pd(dba)_2]$ (576 mg, 1.00 mmol), tmeda (150 μL, 1.00 mmol) and C_6(*E*-CH═CHPh)$_3Br_3$ (205 mg, 0.33 mmol) were mixed under N_2 atmosphere in dry degassed toluene (30 mL). The mixture was heated at 65 °C for 2.5 h until the dark red colour of $[Pd(dba)_2]$ was no longer observed. The dark green suspension was then concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 (40 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (20 mL) was added and a solid formed, which was filtered off, thoroughly washed with Et_2O and dried *in vacuo* to give **3c** as a yellow solid. Yield: 252 mg (59%). Mp: 209–210 °C (dec). IR: no relevant signals. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 9.63 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz), 9.25 (AB, 2H, α-CH═, $^3J_{HH}$ = 16 Hz), 9.23 (AB, 1H, α-CH═, $^3J_{HH}$ = 16 Hz), 8.85 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 7.80 (d, 4H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.71 (d, 2H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.34 (t, 4H, *m*-H Ph, $^3J_{HH}$ = 8 Hz), 7.30 (t, 2H, *m*-H Ph, $^3J_{HH}$ = 8 Hz), 7.18 (t, 2H, *p*-H Ph, $^3J_{HH}$ = 7 Hz), 7.11 (t, 1H, *p*-H Ph, $^3J_{HH}$ = 7 Hz), 2.73, 2.61, 2.54, 2.33, 2.27 and 2.20 (s, 6H each, Me), 2.6–2.2 (several m, 12H, CH_2). **^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$):** δ 152.1 (2C, C3–Pd), 151.7 (1C, C1–Pd), 141.4 (2C, *C*2-alkenyl), 141.2 (1C, i-*C* Ph), 140.52 (1C, *C*4-alkenyl), 140.49 (2C, i-C Ph), 138.9 (1C, α-CH═), 137.7 (2C, α-CH═), 128.8 (4C, *m*-CH Ph), 128.7 (2C, *m*-CH Ph), 128.3 (2C, β-CH═), 126.12 (2C, *o*-CH Ph), 126.08 (4C, *o*-CH Ph), 125.9 (2C, *p*-CH Ph), 125.6 (1C, *p*-CH Ph), 125.2 (1C, β-CH═), 63.2 (1C, CH_2), 63.0 (2C, CH_2), 58.32 (2C, CH_2), 58.26 (1C, CH_2), 51.7 (4C, Me), 51.0, 49.2, 48.55 and 48.50 (2C each, Me). Anal. Calcd for $C_{48}H_{69}Br_3N_6Pd_3$: C, 44.72; H, 5.40; N, 6.52. Found: C, 44.40; H, 5.43; N, 6.31.

Synthesis of [{PdBr(tmeda)}$_3${μ$_3$-C$_6$(*E*-CH═CHTo)$_3$}] (3c′)

$[Pd(dba)_2]$ (173 mg, 0.30 mmol), tmeda (45 μL, 0.30 mmol) and C_6(*E*-CH═CHTo)$_3Br_3$ (100 mg, 0.15 mmol) were mixed under N_2 atmosphere in dry degassed toluene (15 mL). The mixture was heated at 70 °C for 1.5 h until the dark red colour of $[Pd(dba)_2]$ was no longer observed. The dark green suspension was then concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (15 mL) was added and a solid formed, which was filtered off and thoroughly washed with Et_2O. This solid was purified by a preparative TLC on silica gel using a mixture of acetone/hexane (1 : 1.25) as eluent. The yellow band with R_f = 0.6 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and addition of Et_2O (15 mL) precipitated a solid, which was filtered off, thoroughly washed with Et_2O and dried *in vacuo* to give **3c′** as a yellow solid. Yield: 77 mg, 58%. Mp: 210–212 °C (dec). IR: no relevant signals. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.57 (AB, 1H, β-CH═, $^3J_{HH}$ = 16 Hz), 9.20 (AB, 2H, α-CH═, $^3J_{HH}$ = 16 Hz), 9.16 (AB,

1H, α-CH═, $^3J_{HH}$ = 16 Hz), 8.82 (AB, 2H, β-CH═, $^3J_{HH}$ = 16 Hz), 7.71 (d, 4H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.62 (d, 2H, *o*-H Ph, $^3J_{HH}$ = 8 Hz), 7.18–7.10 (m, 6H, *m*-H Ph), 2.73, 2.62 and 2.54 (s, 6H each, Me tmeda), 2.36 (s, 9H, Me To), 2.34, 2.32 and 2.26 (s, 6H each, Me tmeda), 2.75–2.15 (several m, 12H, CH_2). **$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$):** δ 151.6 (2C, C3–Pd), 151.1 (1C, C1–Pd), 141.3 (2C, *C*2-alkenyl), 140.4 (1C, *C*4-alkenyl), 138.4 (1C, *p*-C To), 138.0 (1C, α-CH═), 137.7 (2C, *p*-C To), 136.6 (2C, α-CH═), 135.4 (2C, i-*C* To), 135.1 (1C, i-C Tl), 129.51 (4C, *m*-CH To), 129.45 (2C, *m*-CH To), 128.1 (2C, β-CH═), 126.0 (6C, *o*-CH To), 124.9 (1C, β-CH═), 63.1 (1C, CH_2), 63.0 (2C, CH_2), 58.25 (2C, CH_2), 58.20 (1C, CH_2), 51.7 (4C, Me tmeda), 51.0 and 49.1 (2C, Me tmeda), 48.5 (4C, Me tmeda), 21.40 (2C, Me To), 21.36 (1C, Me To). Anal. Calcd for $C_{51}H_{75}Br_3N_6Pd_3$: C, 46.02; H, 5.68; N, 6.31. Found: C, 45.97; H, 5.36; N, 6.11.

Synthesis of [{*trans*-PdBr(PMe$_3$)$_2$}$_3${μ$_3$-C$_6$(*E*-CH═CHPh)$_3$}] (3d)

3c (100 mg, 0.077 mmol) and PMe_3 (924 μL of a 1 M solution in toluene, 0.924 mmol) were mixed under N_2 atmosphere in dry degassed THF (15 mL). The mixture was heated at 50 °C for 6 h, during which the precipitation of a pale green solid was observed. The reaction mixture was then evaporated to dryness and the residue was extracted with CH_2Cl_2 (30 mL). The extract was filtered through Celite and the filtrate was evaporated to dryness *in vacuo*. Et_2O (20 mL) was added and a solid formed, which was filtered off, thoroughly washed with Et_2O and dried *in vacuo* to give **3d** as a pale green solid. Yield: 92 mg (86%). Mp: 208–209 °C (dec). IR: no relevant signals. **^1H NMR (600 MHz, $CDCl_3$):** δ 8.76 (AB, 3H, β-CH═, $^3J_{HH}$ = 16 Hz), 8.59 (AB, 3H, α-CH═, $^3J_{HH}$ = 16 Hz), 7.63 (d, 6H, *o*-H Ph, $^3J_{HH}$ = 7 Hz), 7.39 (t, 6H, *m*-H Ph, $^3J_{HH}$ = 7 Hz), 7.23 (t, 3H, *p*-H Ph, $^3J_{HH}$ = 7 Hz), 1.29 (vt, 54H, PMe_3, $^2J_{PH}$ + $^4J_{PH}$ = 7 Hz). **$^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$):** δ 162.8 (m, 3C, C1–Pd), 143.6 (m, 3C, C2-alkenyl), 139.3 (m, 3C, α-CH═), 138.4 (s, 3C, i-C Ph), 129.4 (s, 6C, *m*-CH Ph), 127.2 (s, 3C, *p*-CH Ph), 126.3 (s, 6C, *o*-CH Ph), 125.2 (m, 3C, β-CH═), 15.7 (vt, 18C, P*Me*$_3$, $^1J_{PC}$ + $^3J_{PC}$ = 30 Hz). **$^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$):** δ −19.2 (s). Anal. Calcd for $C_{48}H_{75}Br_3P_6Pd_3$: C, 41.27; H, 5.41. Found: C, 41.62; H, 5.43.

Synthesis of 2-Ph-4,6-{PdBr(tmeda)}$_2$-5,7-(*E*-CH═CHPh)$_2$-inden-1-one (4)

CO was bubbled for 5 min through a solution of complex **3c** (60 mg, 0.047 mmol) in dry degassed THF (25 mL) in a Carius tube, and the solution was then heated at 60 °C for 2 h. The dark red solution was then filtered through $MgSO_4$ and the filtrate was evaporated to dryness *in vacuo*. The residue was redissolved in the minimum amount of CH_2Cl_2 and the solution was chromatographed by preparative TLC on silica gel using a mixture of acetone/hexane (2 : 3) as eluent. The brick-red band with R_f = 0.75 was collected and extracted with acetone (30 mL). The acetone solution was concentrated to a small volume and addition of Et_2O (15 mL) precipitated a solid, which was filtered off and dried *in vacuo* to give **4** as a brick-red solid. Yield: 36 mg (76%). Mp: 208–209 °C (dec). IR: ν(CO): 1676 cm^{-1}. **^1H NMR (300 MHz, $CDCl_3$):** δ 9.54 (d, 1H, β^{II}-CH═, $^3J_{HH}$ = 16 Hz), 9.31 (d, 1H, α^{I}-CH═, $^3J_{HH}$ = 16 Hz), 8.87 (d, 1H, β^{I}-CH═, $^3J_{HH}$ = 16 Hz), 8.59 (d, 1H, α^{II}-CH═, $^3J_{HH}$ = 16 Hz), 8.28 (s, 1H, H7), 7.86–7.83 (m, 2H, *o*-H Ph^{I}), 7.83–7.80 (m, 2H, *o*-H Ph^{III}), 7.72 (d, 2H, *o*-H Ph^{II}, $^3J_{HH}$ = 7 Hz), 7.44–7.39 (m, 2H, *m*-H Ph^{I}), 7.39–7.36 (m, 2H, *m*-H Ph^{III}), 7.36–7.32 (m, 2H, *m*-H Ph^{II}), 7.30–7.27 (m, 1H, *p*-H Ph^{I}), 7.27–7.24 (m, 1H, *p*-H Ph^{III}), 7.24–7.20 (m, 1H, *p*-H Ph^{II}), 2.75–2.2 (several m's, 8H, CH_2), 2.70 (s, 9H, Me), 2.59, 2.36 and 2.31 (s, 3H each, Me), 2.63 (s, 6H, Me). **$^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$):** δ 199.8 (CO), 152.3 (C3–Pd), 151.4 (*C*2-alkenyl), 148.6 (CH7), 145.6 (C6), 145.0 (C1–Pd), 139.2 (i-C Ph^{I}), 138.8 (i-C Ph^{II}), 137.6 (α^{I}-CH═), 136.5 (*C*4-alkenyl), 133.4 (β^{II}-CH═), 133.2 (i-C Ph^{III}), 132.4 (C8), 130.9 (β^{I}-CH═), 128.9 (2C, *m*-CH Ph^{I}), 128.6 (2C, *m*-CH Ph^{II}), 128.2 (2C, *m*-CH Ph^{III}), 127.4 (2C, *o*-CH Ph^{III}), 127.3 (α^{II}-CH═), 127.1 (*p*-CH Ph^{II}), 127.0 (*p*-CH Ph^{III}), 126.8 (3C, *o*-CH Ph^{II} and *p*-CH Ph^{I}), 126.2 (2C, *o*-CH Ph^{I}), 125.1 (C5), 62.92, 62.86, 58.4 and 58.3 (CH_2), 51.8, 51.6, 51.5, 51.2, 49.1, 48.7, 48.6 and 48.3 (Me). Anal. Calcd for $C_{43}H_{52}Br_2N_4OPd_2$: C, 50.96; H, 5.17; N, 5.53. Found: C, 51.03; H, 5.56; N, 5.59. **Exact mass (ESI+ TOF):** *m*/*z* calculated for [**4**-Br]$^+$ ($C_{43}H_{52}BrN_4OPd_2$): *m*/*z*: 933.1407, found: 933.1394, Δ = 1.3 ppm.

Conclusions

We have described a novel family of mono-, di-, and tripalladated benzene derivatives, with alkenyl substituents in *ortho* position to the Pd(II) atoms. These complexes possess a great chemical potential regarding their reactivity towards organic molecules. Thus, a dipalladated indenone has been obtained by CO insertion into one of the aryl–Pd bonds of a tripalladated complex, followed by depalladation in that position. Further research in this area will be pursued.

Author contributions

Rashmi V. Shenoy: investigation and writing – original draft preparation. Peter G. Jones: X-ray crystallography and manuscript editing. José Vicente: conceptualization, methodology, project administration, funding acquisition. Eloísa Martínez-Viviente: methodology, supervision, writing – original draft preparation, reviewing and editing, visualisation.

Conflicts of interest

There are no conflicts to declare.

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