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The first example of a doubly orthometallated aryl bis(phosphinite) ligand

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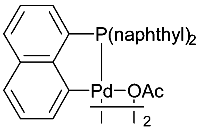
The reaction of 2-methylresorcinolbis(diphenyl)phosphinite with Pd(TFA)$_2$ gives a dimeric tetranuclear complex which contains two of the ligands, each di-ortho-palladated; the X-ray structure of the complex has been determined and its reactivity briefly examined.

Orthometallated P-donor ligands have recently attracted attention due to the high activity they show as catalysts in carbon–carbon bond formation. Shaw and co-workers demonstrated that the palladated naphthyl phosphine complexes **1** and **2** could be used as catalysts in the Heck reaction,[1] while Gibson, Cole-Hamilton and co-workers showed that the orthometallated benzyl phosphine-containing complexes **3** could be used in the Heck and Suzuki coupling of aryl bromides and even activated aryl chlorides.[2] Our interest has been in the synthesis of orthopalladated complexes of more π-acidic ligands such as triaryl phosphite and aryl phosphinites. We have found that catalysts of the type **4** show extremely high activity in the coupling reactions of aryl bromides,[3] while tricyclohexylphosphine adducts of **4** and **5** can be used to excellent effect in the Suzuki and Stille couplings of aryl chlorides.[4] High catalytic activity is not limited to κ^2-*P*,*C* complexes but is also seen for κ^3-*P*,*C*,*P*-pincer complexes. This was initially shown by Milstein and co-workers when they reported that the complexes **6** and **7** show good activity in the Heck coupling of aryl iodides.[5] Later Shibasaki and co-workers showed that complex **8a** shows even better activity.[6] We found that the *P*,*C*,*P*-bis(phosphinite) pincer complexes **8b** and **c** give very good activity in the Suzuki coupling of aryl bromides and can even be used to couple activated aryl chlorides.[7] The more electron rich analogue **8d** was shown by Morales-Morales and co-workers to be an active catalyst for the Heck couling of aryl chlorides.[8]



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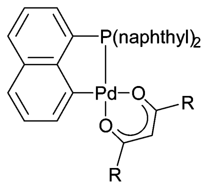
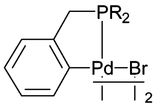
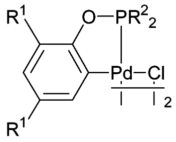


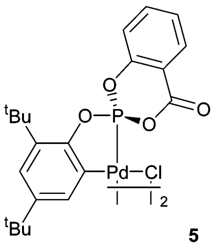
2: R = Me, CF$_3$



3: R = Ph; ^{t}Bu



4a: R^1 = ^{t}Bu; R^2 = OC$_6$H$_3$-2,4-^{t}Bu$_2$
b: R^1 = H; R^2 = Ph
c: R^1 = ^{t}Bu; R^2 = Ph
d: R^1 = ^{t}Bu, R^2 = ^{i}Pr



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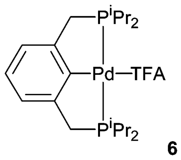

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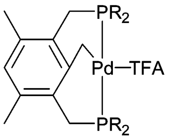
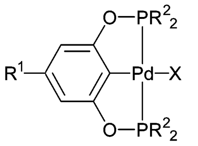


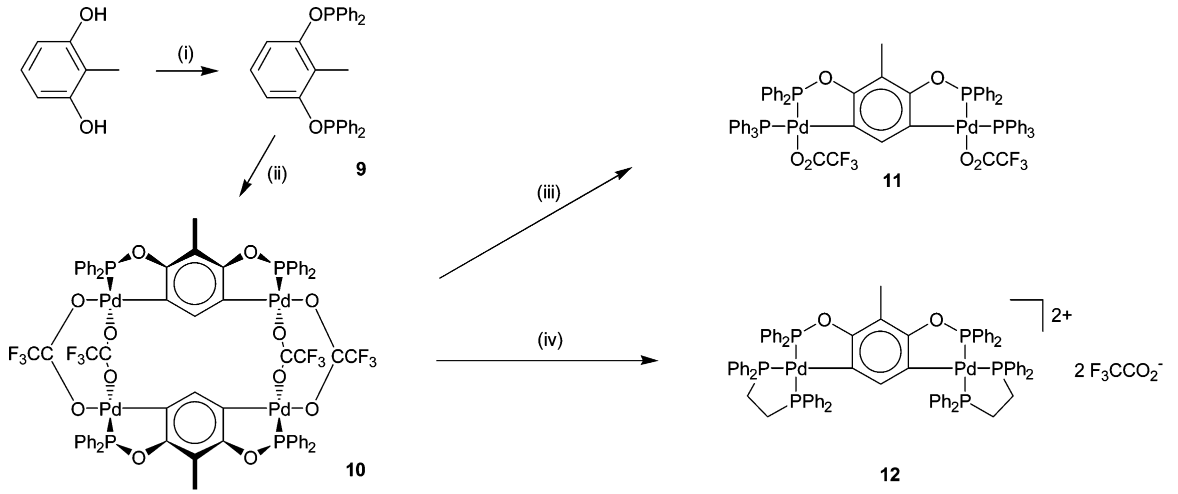
7a: R = ^{i}Pr
b: R = ^{t}Bu



8a: R^1 = H; R^2 = C$_6$H$_4$-4-OMe; X = I
b: R^1 = H; R^2 = Ph; X = TFA
c: R^1 = Me; R^2 = Ph; X = TFA
d: R^1 = H; R^2 = ^{i}Pr; X = Cl

Given the attention paid to the generation and exploitation of such orthopalladated structural types, we were interested to see whether the introduction of a 2-methyl group into a resorcinol bis(phosphinite) ligand and subsequent reaction with an appropriate palladium source would lead to a carbometallation, and whether this would be an orthometallation of the aryl ring or the C–H activation of the 2-methyl group. While the second process is in principle more difficult than the first, it may be facilitated by the fact that strong chelation of the bisphosphine ligand would effectively pre-organise the transition state for C–H activation.

The ligand 2-methylresorcinolbis(diphenyl)phosphinite, **9**, was prepared in 90% yield by the reaction of 2-methylresorcinol with 2 equivalents of chlorodiphenylphosphine in the presence of triethylamine in toluene at reflux temperature (Scheme 1).† The ^{31}P-{^{1}H} NMR spectrum of **9** shows a singlet at δ 111.7 ppm, essentially identical to those obtained for the related free resorcinol bis(phosphinite) ligands used in the synthesis of complexes **8b** and **c**.[7] When ligand **9** is reacted with one equivalent of palladium trifluoroacetate in THF at room temperature, the ^{31}P-{^{1}H} NMR spectrum of the product shows it to be a complex mixture of species. However when the reaction is repeated using a 2 : 1 palladium : ligand ratio then one major species, complex **10**, is observed in the crude reaction mixture with a singlet in the ^{31}P-{^{1}H} NMR spectrum at δ 149.3 ppm.‡ In addition there are small amounts (<10%) of additional phosphorus-containing complexes with peaks in the range δ 146.9–150.1 ppm. The close similarity of the ^{31}P data for the impurities with that of complex **10** suggest they may be oligomeric complexes related to **10**. Similar polymeric species with bridging chlorides are formed on double orthopalladation of *N*,*N*,*N*′,*N*′-tetraethylbenzene-1,3-bis(methylamine).[9] Complex **10** was obtained microanalytically pure by passing it through a plug of silica (CH$_2$Cl$_2$ eluent) followed by recrystallisation. A re-examination of the ^{31}P-{^{1}H) NMR spectrum of



Scheme 1 Conditions: (i) 2 $ClPPh_2$, excess Et_3N, toluene, Δ, 18 h. (ii) $Pd(TFA)_2$, THF, r.t., 18 h. (iii) PPh_3, CH_2Cl_2, r.t., 18 h. (iv) dppe, CH_2Cl_2, r.t., 18 h.

the reaction performed in a 1 : 1 ratio of palladium to ligand shows that complex **10** is one of the main compounds in the product mixture. The ^{31}P NMR data indicate that both phosphorus donors are in an identical environment and that they are both coordinated to palladium. The upfield shift of *ca.* 40 ppm compared to the free ligand is typical for an orthopalladated phosphinite ligand.[10] The ^1H NMR shows a singlet for the methyl group at δ 2.18 ppm and, while the shift is not particularly informative, the integration implies that all three protons are present and the lack of multiplicity due to coupling to the ^{31}P nuclei indicates that the carbon is not metallated. By contrast the protons on the metallated sp^3-methylene carbon in the complexes **7** are seen as triplets coupling to the equivalent phosphorus donors.[10] Integration of the aromatic region indicates the presence of only one residual proton on the resorcinol ring. The ^{13}C-$\{^1H\}$ NMR spectrum of **10** confirms the presence of a methyl rather than a metallated methylene with a singlet seen at δ 12.3 ppm, however due to poor solubility, many of the quaternary carbons could not be identified. The ^{19}F NMR spectrum shows two singlets of equal intensity at δ −74.8 and −75.7 ppm. This implies that there are two distinct types of TFA (trifluoroacetate) ligand.

Taken together the spectroscopic data suggest that the ligand has been doubly orthometallated by two equivalent palladium centres (Scheme 1). This suggestion is confirmed unequivocally by a single crystal X-ray structure determination.§ The molecular structure of complex **10** is shown in Fig. 1. As can be seen each ligand has two palladium centres bonded through both a P-donor ligand and the ortho-carbon. The molecule is a tetranuclear dimeric complex in which half the dimer contains one-dipalladated bisphosphinite ligand. The two halves of the dimer are held together by μ^2-TFA ligands, giving a 'hinge-like' structure. In addition there is a twist away from the conformation in which the methyl groups would be eclipsed, giving a C_2-axis which renders the complex chiral.

To the best of our knowledge this is a unique example of a di-orthometallated P-donor ligand. Indeed there are very few reports of structurally characterised di-orthometallated aryl ligands supported by any donor groups. Those that exist tend to be based on *N*,*N*,*N′*,*N′*-tetraalkylbenzene-1,3-bis(methylamine)—C_6H_4-1,3-$(CH_2NR_2)_2$—and related *N*-donor ligands.[9,11]

Complex **10** reacts with 1 equivalent of triphenylphosphine per palladium in dichloromethane at room temperature to give the complex **11** (Scheme 1). The ^{31}P-$\{^1H\}$ NMR spectrum consists of two doublets at δ 154.5 and 18.8 ppm corresponding to the phosphinite and phosphine donors respectively. Only one of the three potential isomers is formed, namely that with the PPh_3 ligands *cis* to the phosphinite donors and thus *trans* to the palladated carbon, as evidenced by the magnitude of the $^2J_{PP}$ coupling (28.4 Hz). This is in contrast with similar reactions with doubly orthopalladated and -platinated *N*,*N*,*N′*,*N′*-tetraethylbenzene-1,3-bis(methylamine) complexes which give adducts with PPh_3 *cis* to the metallated carbon.[9,11a]

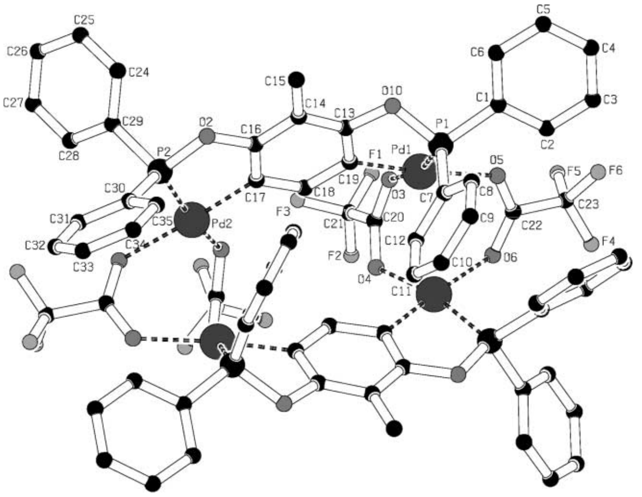


Fig. 1 Molecular structure of complex **10**·$2CHCl_3$. Selected interatomic lengths (Å) and angles (°): Pd1–C19 1.996(3), Pd2–C17 1.992(3), Pd1–P1 2.1756(9), Pd2–P2 2.1690(9), Pd1–O3^i 2.141(2), Pd2–O4 2.145(2), Pd1–O5^i 2.149(2), Pd2–O6 2.151(2), Pd1 ··· Pd2^i 3.2190(3), P1–Pd1–C19 77.28(9), P2–Pd2–C17 80.44(10), C19–Pd1–O3^i 95.06(11), C17–Pd2–O4 96.33(11), O3^i–Pd1–O5^i 87.23(9), O4–Pd2–O6 88.15(9), P1–Pd1–O5^i 99.53(7), P2–Pd2–O6 95.09(7), C19–Pd1–O5^i 175.02(11), C17–Pd2–O6 175.49(11), P1–Pd1–O3^i 165.66(7), P2–Pd2–O4 165.07(7).

The analogous reaction of complex **10** with 1,1′-bis(diphenylphosphino)ethane (dppe) gives the binuclear complex **12**. The best evidence for the formation of complex **12** is provided by the ^{31}P NMR spectra which consists of a doublet of doublets corresponding to the phosphite ligands at δ 149.5 ppm with couplings to the *cis* and *trans* phosphine donors of 24 and 379 Hz respectively, and two doublets of doublets at δ 51.6 and 46.0 ppm corresponding to the phosphine groups *trans* and *cis* to the phosphite respectively with a mutual $^2J_{PP_{cis}}$ of 34 Hz. In this case there is evidence for a second, minor species with similar shifts and coupling patterns in the ^{31}P NMR spectrum.¶ It is possible that this second species is a tetranuclear dimeric complex with bridging dppe ligands. Further work is ongoing to establish its identity.

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Notes and references

† Synthesis of ligand **9**: To a solution of 2-methylresorcinol, (2.5 g, 20.1 mmol) and chlorodiphenylphosphine (7.3 mL, 40.3 mmol) in toluene (40 mL) was added triethylamine (7.0 mL, 50.0 mmol) dropwise. The mixture was heated at reflux temperature for 18 h, cooled and the solvent removed under reduced pressure. The residue was extracted with THF (20 mL), the solution filtered through celite and the celite washed with THF (2 × 20 mL). The solvent was removed from the combined THF fractions to give the product as a pale yellow solid that was not purified further (8.9 g, 90%). NMR data ($CDCl_3$, 25 °C): ^1H NMR (300 MHz): δ 2.78 (s, 3H, CH_3), 6.85 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H^4 and H^6 resorcinol ring), 6.97 (t, $^3J_{HH}$ = 8.0 Hz, H^5 resorcinol ring), 7.38 (m, 12H, Ph), 7.62 (m, 8H, Ph). ^{31}P-{^1H} NMR (121 MHz): δ 111.7.

‡ A solution of palladium trifluoroacetate (1.00 g, 0.30 mmol) and ligand **9** (0.74 g, 0.15 mmol) in THF (25 mL) was stirred under an atmosphere of nitrogen for 18 h. The solvent was removed *in vacuo*, $CHCl_3$ (20 mL) added, the residue was collected on a plug of silica which was washed with $CHCl_3$ (2 × 15 mL) and the residual yellow precipitate on the silica was dissolved in and eluted with dichloromethane. The solvent was removed from the CH_2Cl_2 solution *in vacuo* and the residue was recrystallised from CH_2Cl_2/EtOH to give **10** as a yellow solid (0.92 g, 66%). Crystals suitable for X-ray analysis were grown from $CHCl_3$/EtOH. Calc. for ($C_{70}H_{48}F_{12}O_{12}P_4Pd_4$)·2$CHCl_3$: C, 41.23; H, 2.40%. Found: C, 41.0; H, 2.3%. ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 7.70–7.54 (m, 12H, Ar), 7.51–7.43 (m, 8H, Ar), 7.18–7.06 (m, 4H, Ar), 7.02–6.96 (m, 2H, Ar), 6.90–6.79 (m, 8H, Ar), 6.78–6.70 (m, 8H, Ar), 2.10–2.02 (m,6H, CH_3) ppm.

§ *Crystallographic data for* $C_{72}H_{50}Cl_6F_{12}O_{12}P_4Pd_4$: Monoclinic, space group *C*2/*c*, a = 33.4010(5), b = 14.0306(3), c = 20.3106(3) Å, β = 126.461(1)°, U = 7655.2(2) Å^3, D_c = 1.82 Mg m^{-3}, Z = 4, T = 120(2) K, yellow rod, 0.2 × 0.08 × 0.06 mm^3. Data collection was carried out using an Enraf Nonius KappaCCD area detector and SHELXS-97 and SHELXL-97[12] programs were used for structure solution and refinement. 38540 reflections collected, 8745 independent [R(int) = 0.0763] which were used in all calculations. R_1 = 0.0387 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.0905 for all data. The max. and min. residual electron densities on the final difference Fourier map were 0.883 and −0.903 e Å^{-3}, respectively. CCDC reference number 210006. See http://www.rsc.org/suppdata/dt/b3/b305136f/ for crystallographic data in CIF or other electronic format.

¶ ^{31}P-{^1H) NMR (121 MHz) of second species: δ 150.1 (dd, $^2J_{PP\mathit{trans}}$ = 371.5 Hz, $^2J_{PP\mathit{cis}}$ = 26.1 Hz, phosphite), 55.05 (dd, $^2J_{PP\mathit{trans}}$ = 371.9 Hz, $^2J_{PP\mathit{cis}}$ = 33.2 Hz, phosphine *trans* to phosphite), 43.0 (dd, $^2J_{PP\mathit{cis}}$ = 33.2 Hz, $^2j_{PP\mathit{cis}}$ = 24.2 Hz, phosphine *cis* to phosphite).

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