Insertion of Norbornadiene into the Aryl–palladium Bond; Synthesis, Structure and Dynamics of Intramolecular η^2-Arene Palladium Species

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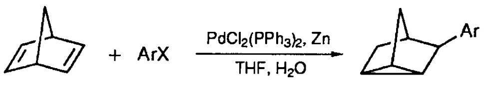
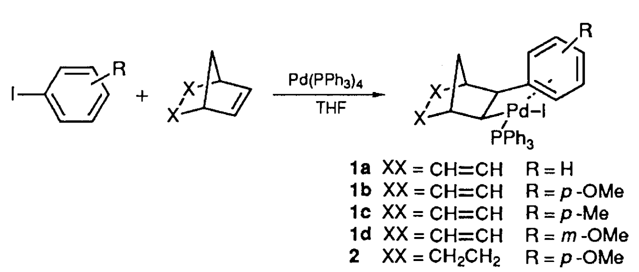
A series of fluxional intramolecular η^2-bound arene complexes, $(C_7H_8Ar)PdI(PPh_3)$, **1a–1d**, and **2** may be isolated from the catalytic reactions of norbornadiene (or norbornene) with aryl iodides in the presence of Zn and $PdCl_2(PPh_3)_2$ (eqn. 1) and their structures have been determined by X-ray crystallography and NMR spectroscopy.

It is well-known that η^2-bound arene complexes are intermediates in the C–H bond activation of arene systems.[1] However, owing to the inherent stability of aromatic compounds, few stable η^2-bound arene complexes have been isolated and characterised.[2–6] Of the η^2-bound arene species reported, most are intermolecularly coordinated.[2,3,4] To the best of our knowledge, there are only two known examples $(PhHCPz'_2)Mo(CO)_3$,[5] and $(PhPPz'_2)W(CO)_3$,[6] where Pz′ = 3,5-dimethylpyrazol-1-yl, which consist of weak intramolecular η^2-arene bonds. Recently, we reported a palladium-catalysed synthesis of aryl-substituted nortricyclenes from the reaction of aryl halides with norbornadiene (eqn. 1).[7]

In the attempt to characterise the catalytic intermediates, we isolated a class of norbornenylpalladium complexes. In



(1)



Scheme 1

spite of the rich chemistry on the C–H bond activation by palladium complexes,[8] these complexes are the only examples of stable η^2-bound palladium arene species to date.

Treatment of $PdIAr(PPh_3)_2$ with an excess of norbornadiene (10 equiv.) at 50 °C for 3 h affords a product with the stoichiometry $(C_7H_8Ar)PdI(PPh_3)$ **1** as a yellow solid in *ca.* 80% yield. The same complex may also be isolated from the reaction of $Pd(PPh_3)_4$ with norbornadiene and aryl iodide (Scheme 1) or from the catalytic reaction shown in eqn. 1. Compound **1** is quantitatively converted to 3-arylnortricyclene in the presence of Zn and ZnX_2 indicating that the palladium complex is a catalytic intermediate for eqn. (1).

The structure of **1a** has been determined by X-ray crystallography.† An ORTEP diagram accompanied by selected bond distances and angles is shown in Fig. 1. The results demonstrate that the phenyl group and the palladium metal are *cis* and *exo* to the norbornenyl group. In addition, the phenyl ring attached to the norbornenyl group is weakly bound to the palladium centre in an η^2 fashion. From Fig. 1, it is clear that the complex is square-planar with PPh_3, I^-, and norbornenyl groups as the other three ligands. Owing to the η^2 interaction which leads to partial loss of aromaticity, an alternating long–short pattern of the C–C bond length in the rest of the phenyl ring is seen. (However, the difference in the C–C bond lengths is small in the present structure compared to the values found in $Ni[P(C_6H_{11})_3]_2(1,2\text{-}\eta^2\text{-}C_{14}H_{10})$, where $C_{14}H_{10}$ = anthracene).[4] The distances from the metal to the two η^2 bound carbons C(24) and C(19) are 2.430(5) and 2.591(6) Å, respectively, which are approximately 0.3–0.4 Å longer than a normal η^2 alkene–palladium bond.[9,10] Although this bonding is weak as shown by the present X-ray data, the addition of excess ligands such as PPh_3, 1,2-bis(diphenylphosphino)ethane and pyridine to the tetrahydrofuran (THF) solution of **1** does not lead to observed substitution of the η^2-bond by any of these ligands. Moreoever, these compounds are air and thermally stable; *e.g.* **1b** survives at 60 °C in THF for 24 h without detectable decomposition. Presumably, the rigid *cis* arrangement of the phenyl ring and the palladium metal on the norbornenyl group protects the η^2 interaction from being replaced by other ligand–metal bonding.

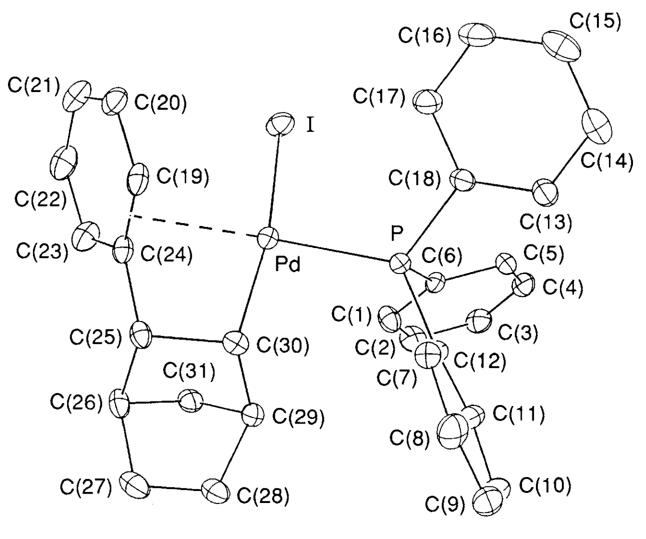


Fig. 1 ORTEP drawing of $(C_7H_8Ph)Pd(PPh_3)I$ **1a** showing the atom-labelling scheme. Selected bond distances (Å) and angles (°): I–Pd 2.728(1), Pd–P 2.254(2), Pd–C(30) 2.052(6), Pd–C(24) 2.430(5), Pd–C(19) 2.591(6), C(19)–C(24) 1.392(10), C(19)–C(20) 1.377(11), C(20)–C(21) 1.364(12), C(21)–C(22) 1.387(13), C(22)–C(23) 1.362(12), C(23)–C(24) 1.394(10); I–Pd–P 96.2(1), I–Pd–C(19) 97.5(2), I–Pd–C(24) 105.4(1), I–Pd–C(30) 164.3(2), P–Pd–C(19) 144.6(2), P–Pd–C(24) 158.3(2), P–Pd–C(30) 92.2(2), C(19)–Pd–C(30) 82.2(2), C(24)–Pd–C(30) 66.3(2), C(20)–C(19)–C(24) 121.7(7), C(19)–C(20)–C(21) 119.5(8), C(20)–C(21)–C(22) 120.0(8), C(21)–C(22)–C(23) 120.4(8), C(22)–C(23)–C(24) 120.9(7), C(19)–C(24)–C(23) 117.5(6), C(19)–C(24)–C(25) 119.0(6).

The NMR spectra of **1** are temperature-dependent. Using **1b** as the example, at 25 °C in CD_2Cl_2, in addition to resonances due to coordinated PPh_3 and norbornenyl group, a doublet at δ 98.07 and singlets at δ 117.03 and 163.69 for the *ipso, meta* and *para* carbons, respectively, of the *p*-anisyl ring were observed in the $^{13}C\{^1H\}$ NMR spectra of the complex. The *ortho*-carbon signal was missing at this temperature. However, lowering the temperature to −40 °C led to the observation of six well-defined signals at δ 96.99(d), 115.58, 116.90, 126.84, 134.07 and 162.92 for the anisyl ring. This low-temperature-limit spectrum is in agreement with an η^2-coordination which splits the ring into six different carbons. The observed doublet at δ 98.07 is due to the coupling with phosphorus and is assigned as the signal of the *ipso* carbon. Three carbons in the norbornenyl group, C(30), C(29) and C(28) (see Fig. 1) were also found to couple with the phosphorus atom with coupling constants of 14.3, 4.2 and 8.6 Hz, respectively. An upfield shift of 37 ppm for the doublet at δ 98.07 relative to the corresponding signal of 3-*p*-anisylnortricyclene was observed. However, a slight downfield shift of the coordinated *ortho* carbon (δ 134.07) relative to that (δ 128.81) in 3-*p*-anisylnortricyclene was found. The results as well as those from the X-ray data show that the η^2 interaction

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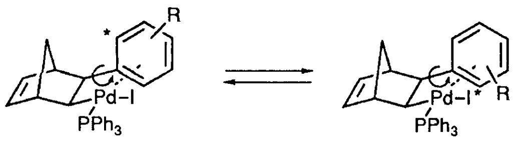
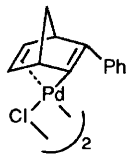
† *Crystal data* for **1**: $Pd(C_7H_8Ph)I(PPh_3)\cdot 0.5(CH_3OH)$, M = 678.8, monoclinic, space group $P2_1/n$, Z = 4, a = 11.881(4), b = 18.771(6), c = 12.189(3) Å, β = 93.34(2)°, an orange single crystal of dimension 0.44 × 0.20 × 0.18 mm was selected for X-ray analysis. Siemens R3m/V diffractometer, graphite-monochromated Mo-Kα radiation; θ/2θ scan technique. Cell parameters from least-squares procedures on 18 reflections ($9.33 < 2\theta < 21.71°$). Systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. A total of 5412 reflections measured up to $2\theta = 50°$ and in the range $-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 22$, $0 \leqslant l \leqslant 14$. No significant variation in intensities of three standards monitored every 50 reflections. Scan width of 1.00° + Kα-separation and scan speed 2.93–14.65° min^{-1}. 2948 unique structure amplitudes with $I \geqslant 3.0\,\sigma(I)$ were corrected for absorption, Lorentz and polarization effects. Corrections for absorption were based on φ scans of a few suitable reflections with x values close to 90° (T_{max}, T_{min} = 0.941, 0.886; μ = 18.78 cm^{-1}). The structure was solved by direct methods and refined by full-matrix least squares analysis based on F values. All the non-hydrogen atoms were refined with anisotropic temperature factors. All the hydrogen atoms of the molecule were located on difference map. The hydrogen atoms of the solvent MeOH were calculated. At convergence R = 0.0319, R_w = 0.0308, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $\sigma^2(F)$ based on counting statistics, $(\Delta/\sigma)_{max}$ = 0.001, s = 1.07, $(\Delta\rho)_{max}$ = 0.56, $(\Delta\rho)_{min}$ = −0.46 eÅ^{-3}. Scattering factors were taken from *International Tables for X-ray crystallography* (1974). All calculations were performed on a DEC Micro VAXII computer system using the SHELXTL-Plus programs (Sheldrick 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2



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is unsymmetrical with the bonding of *ipso* carbon to Pd metal much stronger than that of the *ortho* carbon. Similar fluxional behaviour in the ^{1}H NMR spectra of **1b** was also observed. At 25 °C, the complex exhibits two doublets at δ 7.88 and 7.08 for the *ortho* and *meta* protons, respectively, of the anisyl ring. The low-temperature-limit spectrum is reached at -40 °C and each doublet is split into two sets of doublets at δ 7.06, 7.12, and 7.68, 8.01 respectively. Complexes **1a**, **1c**, **1d** and **2** also exhibit characteristic doublets at δ 109.29, 105.81, 112.31 and 91.37 respectively for the *ipso* carbons and their NMR spectra are also temperature-dependent indicating that these complexes are similar to **1b** in structure and NMR properties.

These reversible spectral changes are consistent with a facile rotation process of the anisyl ring about the C–C bond connecting the aryl and the norbornenyl group as indicated in Scheme 2. At 40 °C this process is rapid on the NMR time scale, making the two *ortho* and the two *meta* carbons or hydrogens equivalent. At low temperature (-40 °C), the process is slow and the spectral patterns are consistent with a structure identical to that observed in the solid state.

Complexes **1** and **2** are also likely catalytic intermediates for a number of palladium-catalysed reactions involving norbornadiene or norbornene as the substrates,[11] although the detailed pathways for these catalytic reactions have not been wholly explored. The *exo–exo* geometry of **1** is quite surprising in view of the fact that only the *endo–endo* structures such as **3** have been observed to yield nortricyclyl derivatives.[9,12] It should be interesting to see how complex **1** may be transformed to the nortricyclene products. The results of the investigation on this aspect will be reported shortly.

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