Convenient Synthesis of Spiro Compounds by the Insertion of Alkynes into the Pd–C Bond of Cyclopalladated 2-Benzylpyridine

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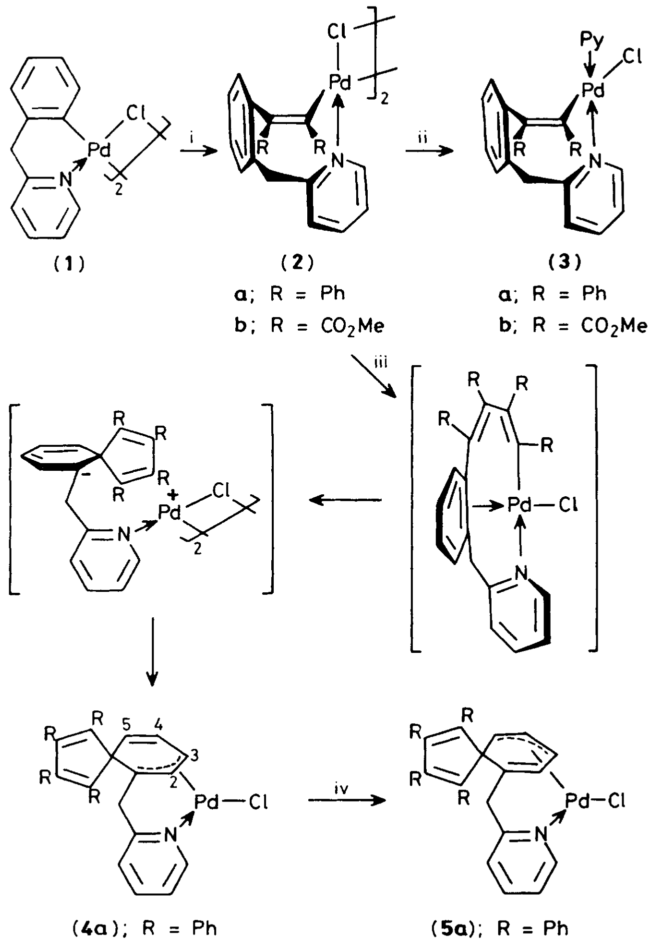
Insertion of one alkyne molecule into the Pd–C bond of *ortho*-palladated 2-benzylpyridine affords an eight-membered organometallic ring; the further insertion of a second alkyne leads to the quantitative formation of an unexpected spiro-compound which has been characterized by an *X*-ray diffraction study.

It is now well established that cyclopalladated tertiary amines are useful starting materials for the formation of carbon–carbon bonds *via* the insertion of various reagents into their Pd–C bonds.[1] In this respect we have already shown that substituted alkynes readily insert into such bonds.[2] The complexes studied so far contained the more common five-membered metallocyclic rings and we therefore considered it to be of interest to investigate the behaviour of the rarer six-membered metallocycles, for instance those compounds obtained by the cyclometallation of 2-benzylpyridine.[3]

Treating a solution of compound (**1**) (see Scheme 1) in CH_2Cl_2 with diphenylacetylene or dimethylacetylene dicar-



Py = pyridine

Scheme 1. *Reagents and conditions*: i, RC≡CR, CH_2Cl_2, 4 h; ii, Py, CH_2Cl_2; iii, PhC≡CPh, CH_2Cl_2, reflux, 18 h; iv, PhCl, reflux, 15 min.

boxylate (1 equiv.) affords quantitative yields of (**2a**) and (**2b**) respectively.† Analyses and ^{1}H n.m.r. data indicate that each compound is a dimer, existing as a mixture of *cis*- and *trans*-isomers. Cleavage of the chloride bridges with pyridine leads to compounds (**3a**) and (**3b**), each consisting of only one isomeric form, with the pyridine most probably located *trans* to the N atom of the 2-benzylpyridine. These results strongly indicate that the insertion of the alkyne has resulted in the formation of an eight-membered ring in which the N and the σ-bonded carbon atoms of the organic group are bonded to the metal in a *cis*-arrangement. This is in marked contrast to observations on the eight-membered ring system formed by the insertion of two molecules of hexafluorobut-2-yne or diphenylacetylene into *ortho*-metallated triphenylphosphine compounds.[4,5] In these expanded rings the phosphorus and the carbon atoms were found to be *trans* to each other on the metal centre.

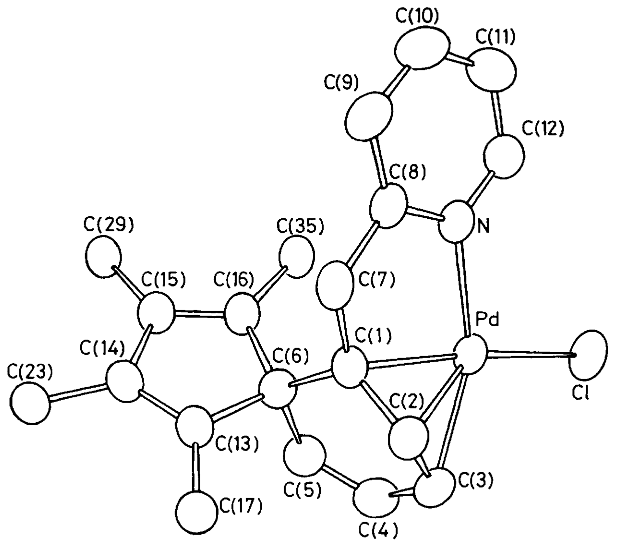


Figure 1. Molecular structure of compound (**4a**) (the hydrogen atoms and the phenyl groups of the cyclopentadiene unit are omitted for clarity). Bond lengths: Pd–N 2.137(2), Pd–C(1) 2.100(2), Pd–C(2) 2.047(2), Pd–C(3) 2.146(2), C(1)–C(2) 1.420(3), C(2)–C(3) 1.409(3), C(4)–C(5) 1.326(3), C(1)–C(6) 1.523(3), C(6)–C(16) 1.511(3) Å; angles: Cl–Pd–N 104.59(5), Cl–Pd–C(1) 172.06(6), N–Pd–C(3) 148.81(9), C(1)–Pd–N 82.02(7), C(1)–C(2)–C(3) 114.8(2), C(1)–C(6)–C(5) 112.5(2), C(13)–C(6)–C(16) 102.2(2)°.

When treated with an excess of diphenylacetylene in refluxing CH_2Cl_2 (**2a**) quantitatively affords compound (**4a**) which has been shown by analytical data to contain two alkyne units per Pd atom. The ^{1}H n.m.r. spectrum shows that four aromatic protons of the 2-benzylpyridine ligand have been dramatically shifted to high field suggesting significant changes in the bonding mode of this unit. In order to determine unambiguously the geometry of this new molecule, an *X*-ray diffraction study was carried out.‡ The structure of (**4a**) is shown in Figure 1 together with relevant bond lengths and angles. The most interesting feature is the presence of a spiro [4,5]-decatetraenyl moiety. Thus, through the addition of two alkyne units to (**1**), the carbon atom C(6) which was previously σ-bonded to Pd has become a spiro carbon linking a cyclopentadiene and a hexadienyl ring. This new ligand is bonded to Pd through the η^3-hexadienyl unit and the N atom of the pyridine ring.

The formation of this somewhat unexpected compound can be rationalized according to Scheme 1 which shows a probable intermediate in the formation of (**4a**). We have shown

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† All compounds give satisfactory elemental analyses. Selected n.m.r. data (*J* in Hz) $\delta(CDCl_3)$, (**2a**) ^{1}H: 4.62—4.03 (m, 2H, CH_2, $^2J_{A,B}$ 15.9); (**2b**) ^{1}H: 4.33—3.98 (m, 2H, CH_2, $^2J_{A,B}$ 16.3) and 3.83—3.59 (m, 6H, CO_2Me); (**3a**) ^{1}H: 4.61 and 4.18 (2d, 2H, CH_2, $^2J_{A,B}$ 16.1 Hz); (**3b**) ^{1}H: 4.40 and 4.19 (2d, 2H, CH_2, $^2J_{A,B}$ 16.8), 3.71 (s, 3H, CO_2Me), and 3.60 (s, 3H, CO_2Me); (**4a**) ^{1}H: 6.08 (dd, H^4, $^3J_{4,3}$ 5.5, $^3J_{4,5}$ 9.1), 5.99 (d, H^2, $^2J_{2,3}$ 6.0), 5.68 (d, H^5), 4.65 (td, H^3), 3.60 and 3.49 (2d, 2H, CH_2, $^2J_{A,B}$ 16.7); ^{13}C: 124.78 and 121.77 (C-4 or C-5), 102.78 (C-2), 72.68 (C-6), 59.04 (C-3), and 43.40 (CH_2); (**5a**) ^{1}H: 6.10 (dd, H^4, $^3J_{4,3}$ 5.6, $^3J_{4,5}$ 9.0), 5.81 (d, H^2, $J_{2,3}$ 5.9), 5.35 (d, H^5), 4.86 (t, H^3), 3.26 and 3.06 (2d, 2H, $^2J_{A,B}$ 16.0); ^{13}C: 101.45 (C-4), 66.04 (C-6), 59.9 (C-3), and 43.40 (CH_2).

‡ *Crystal data*: $C_{40}H_{30}ClNPd$, $M = 666$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.222(8)$, $b = 16.066(5)$, $c = 9.204(2)$ A, $\alpha = 98.44(2)$, $\beta = 94.27(4)$, $\gamma = 71.41(5)°$, $U = 1555.1$ Å^3, $Z = 2$, $D_c = 1.42$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 7.03$ cm^{-1}, $F(000) = 680$. The structure was solved by direct methods and refined by full-matrix least-squares methods. 5188 independent reflections for which $I > \sigma(I)$ were collected on an Enraf-Nonius CAD-4 diffractometer in the range $1 < \theta < 27°$. They were refined to conventional values of $R = 0.031$ and $R_w = 0.043$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Labaratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

previously that the insertion of two alkyne units into the Pd–C bonds of related compounds produced 9-membered rings in which a butadienyl unit is η^3-bonded to the Pd atom.[2a] Molecular models suggest that this bonding mode would not be possible in a 10-membered ring. They suggest instead that the Pd atom in such a hypothetical molecule would interact with a C=C bond of the benzyl ring rather than with that of the adjacent butadiene moiety. We believe that this situation could be responsible for the instability of the molecule leading to the heterolytic cleavage of its Pd–C bond producing therefore a carbanion and a cationic Pd centre. The spiro union could subsequently be obtained by ring closure of the butadiene fragment on C(6) leaving a negative charge on C(1), the hexadienyl unit thus formed rapidly becoming η^3-co-ordinated to the Pd atom.

Compound (**4a**) can be quantitatively transformed into the new compound (**5a**) by heating in refluxing chlorobenzene. We suggest, on the basis of ^{1}H and ^{13}C n.m.r. data, that (**5a**) is an isomer of (**4a**) in which the C(1)—C(6) ring is η^3-bonded to the Pd atom *via* the C(3), C(4), and C(5) carbon atoms.

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