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Preliminary Communication

Palladium-assisted formation of carbon–carbon bonds
Part 2.* Stoichiometric synthesis of spirocyclic compounds. X-ray structure of a π-allylic palladium intermediate

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Abstract

Stoichiometric reactions of arylpalladium compounds with alkynes give spirocyclic organic and organometallic compounds. The compound bis{κ^2-C-O-(2,3,4-trimethoxy-6-acetylphenyl)}di(μ-chloro)dipalladium(II) reacts with diphenylacetylene or ethyl 3-phenylpropiolate giving 6-acetyl-1,2,3,4-tetraphenyl-9,10-dimethoxy-spiro[4.5]1,3,6,9-decatetraen-8-one and 6-acetyl-1,3-dicarboxyethyl-2,4-diphenyl-9,10-dimethoxy-spiro[4,5]1,3,6,9-decatetraen-8-one, respectively. A π-allylpalladium complex, η^3-{6-acetyl-1,2,3,4-tetraphenyl-8,9,10-trimethoxy-spiro[4,5]1,3,9-decatrien-6-enyl}(2,2'-bipyridine)palladium(II) trifluoromethylsulfonate solvated, with one molecule of 1,2-dichloroethane, has also been isolated and its structure determined by X-ray diffraction studies.

Key words: Crystal structures; Palladium complexes; Allylic ligand complexes

The spiro framework is an important subunit in a vast number of natural products, which can be made by multistep organic syntheses [1]. A few transition metal catalyzed preparations of this type of compound have been described, involving palladium [2–4] or nickel [1] catalysts.

Numerous reactions are known that involve carbon–carbon bond formation mediated by palladium compounds in catalytic or stoichiometric processes, and they often facilitate the selective synthesis of a large variety of organic molecules [5]. In particular, reactions of cyclopalladated complexes with alkynes have proved very useful. Insertion of one, two or three alkynes leads to palladium complexes, usually isolable, which, after demetallation, give different organic compounds (heterocycles, alkenes, etc.) [6]. As far we are aware only two types of reactions have afforded spirocyclic compounds [7]. High chemoselectivity and yields are observed in some cases (see Scheme 1). However, unsymmetric acetylenes give spirocyclic compounds with low regioselectivity or yield [7b]. We wish to communicate some preliminary results about reactions of **1** (see Scheme 2) with alkynes, affording highly functionalized spirocyclic compounds with good yields and high selectivity.

3,4,5-Trimethoxyacetophenone cannot be palladated but it is possible to mercuriate it. Starting from this mercurial it is possible to prepare complex **1** (see Scheme 2) [8]. The reaction of the cyclopallated complex **1** with diphenylacetylene in dichloromethane, at room temperature, gives metallic palladium and the spirocyclic compound **2a**†. The structure proposed for **2a** is based on NOE studies and on the structure of a derivative of an intermediate in this reaction (see below). A noteworthy feature of this process is the demethylation of the trimethoxy substituent located *para* to the position originally occupied by the palladium atom, giving a keto group.

When the reaction is carried out at low temperature (−10 °C) an intermediate **A** can be isolated. The same compound precipitates in acetone at room temperature; however, due to its instability we were unable to characterize it. Nevertheless, **A** reacts with 2,2'-bipyridine (bpy) and $Tl(CF_3SO_3)$ to give the cationic derivative **3**†† (see Scheme 2). The structure of **3**·$C_2H_4Cl_2$ was

*For Part 1 see ref. 12.

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†Yield 65%. M.p. 159–161 °C. *Anal.* Calc. for $C_{38}H_{30}O_4$: C, 82.89; H, 5.49. Found: C, 82.57, H, 5.45%. IR, ν(C=O): 1687, 1644 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.14–7.07, 6.98–6.92 (m, 20H, Ph), 6.73 (s, 1H, C_6H), 4.03 (s, 3H, MeO), 3.44 (s, 3H, MeO), 2.10 (s, 3H, MeCO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 197.2 (MeCO), 184.1 (C=O), 167.1, 149.6, 149.0, 141.3, 141.2, 135.1, 134.4, 133.7, 129.9, 128.9, 128.1, 127.8, 127.4, 127.1, 68.8 (quaternary sp^3 C), 61.4 (MeO), 60.5 (MeO), 28.7 (*Me*CO). MS (*m/e*): 550 (M^+, 63.6%), 105 ($PhCO^+$, 100%).

††Yield 18% with respect to **1**. M.p. 194 °C (dec.). Λ_M (in acetone) = 120 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{50}H_{41}N_2F_3O_7PdS$: C, 61.45; H, 4.23; N, 2.87. Found: C, 62.74, H; 4.57; N, 3.45%. Our efforts to improve these analytical data have failed because of tenacious solvents (as seen by NMR and in the crystal structure determination). IR, ν(C=O): 1671, 1626 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.5–6.3 (several multiplets, 29H, bpy, 4 Ph, C_6H), 4.04 (s, 3H, MeO), 3.80 (s, 3H, MeO), 3.70 (s, 3H, MeO), 2.39 (s, 3H, MeCO).

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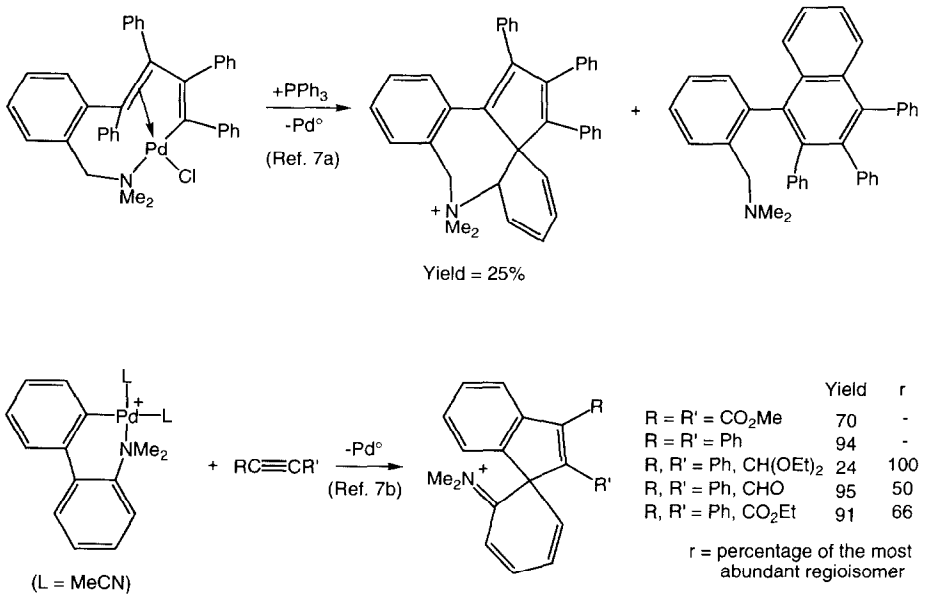
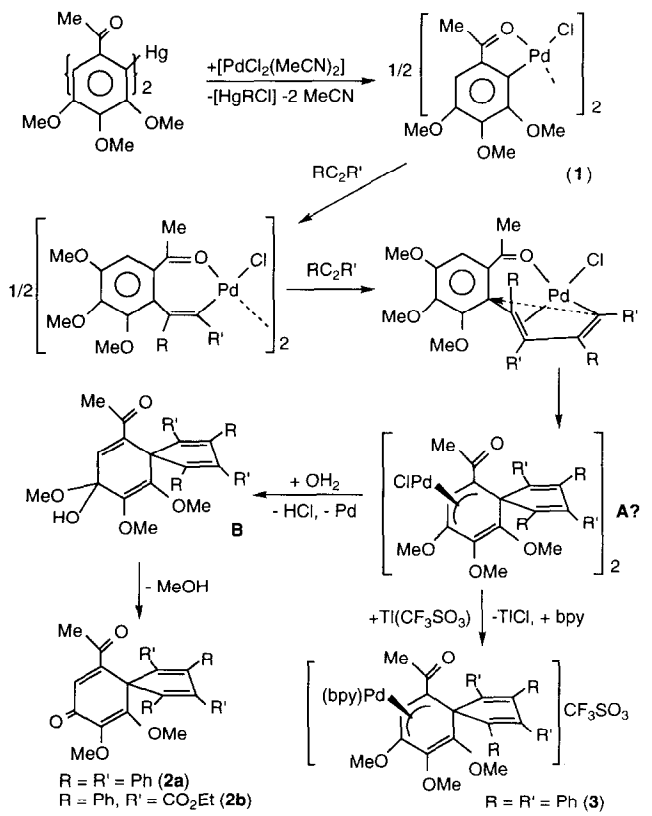


Scheme 1.



Scheme 2.

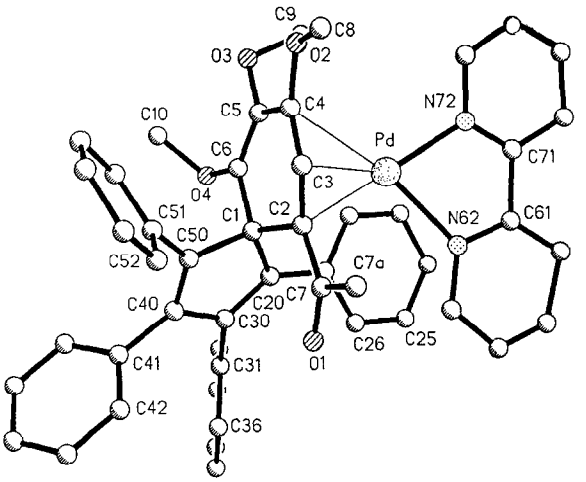


Fig. 1. The cation of complex **3** in the crystal. Only one orientation of the disordered bipyridyl group is shown, and H atoms are omitted. Selected bond lengths (Å) and angles (°): Pd–C(2) 2.097(8), Pd–C(3) 2.100(8), Pd–C(4) 2.385(8), C(1)–C(6) 1.545(10), C(1)–C(2) 1.555(11), C(2)–C(3) 1.426(11), C(3)–C(4) 1.409(11), C(4)–C(5) 1.451(12), C(5)–C(6) 1.322(11); C(6)–C(1)–C(2) 111.4(6), C(3)–C(2)–C(1) 116.9(7), C(4)–C(3)–C(2) 116.9(7), C(3)–C(4)–C(5) 121.2(7), C(6)–C(5)–C(4), 120.7(7), C(5)–C(6)–C(1) 122.6(7).

determined by X-ray diffraction studies (Fig. 1). The structure and reactivity of **3** are similar to those found in the products of reactions between *ortho*-palladated 2-benzylpyridine complexes and acetylenes which decompose to metallic palladium together with other undetermined organic products [9].

A pathway for the formation of **2a** is outlined in Scheme 2, in which the successive insertion of two alkynes into the palladium–carbon bond of **1** would give a palladacycle having 9 atoms in the ring. Intermediates with one and two inserted alkynes such as those depicted in Scheme 2, with nitrogen donors in the *ortho* position, have been isolated [6,10]. The doubly inserted species would undergo a ring contraction, leading to a spirocyclic junction at the formerly pal-

ladium-bonded arylic carbon, and the $PdCl^+$ moiety would migrate to occupy the other *ortho* position to the acetyl substituent. This species could be the unstable compound **A**.

Formation of the keto group and depalladation are assumed to occur through reaction of **A** with adventitious water, leading to intermediate **B**, which would decompose to give **2a**. In fact, when the reaction is carried out using freshly distilled dichloromethane, slow decomposition is initially observed but rapidly stops. The resulting solution remains unaltered but addition of water gives **2a**.

The X-ray structure determination (Fig. 1) confirms the allylic nature of the ligand in complex **3***. The coordination of the palladium atom to the allyl moiety is markedly unsymmetric, with Pd–C2 2.097(8), Pd–C3 2.100(8) and Pd–C4 2.385(8) Å. Since the allylic ligand is crystallographically well-resolved, this is probably a genuine effect, although its cause is not obvious (there are no other short contacts to Pd). The ring atoms C1,4,5,6 are coplanar within ±0.03 Å, consistent with the formulation of C5=C6 as a double bond; C3 lies only 0.1 Å out of the plane.

We have also tested unsymmetric alkynes such as ethyl 3-phenylpropiolate. In this case complete regioselectivity in favour of the head-to-tail alkyne insertion product is observed, since only the isomer **2b**** is detected in the crude material obtained after removal of the metallic palladium (see Scheme 2). This is another difference from other reactions between acetylenes and *ortho*-palladated compounds. Thus, while the insertion of the first molecule of an unsymmetric acetylene can be regioselective [11] or not [7b,9], the second one is rarely regioselective [11b]. We are currently investigating these reactions with other symmetric, unsymmetric and terminal alkynes, in order to extend the scope of these results.

Supplementary material

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD 40629.

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Crystal data: $3 \cdot C_2H_4Cl_2$, $C_{52}H_{45}Cl_2F_3N_2O_7PdS$, $M_r = 1076.26$, monoclinic, $P2_1/c$, $a = 23.470(5)$, $b = 11.594(3)$, $c = 17.537(4)$, Å, $\beta = 90.72(2)°$, $V = 4772(2)$ Å^3, $Z = 4$, $D_x = 1.498$ Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.61$ mm^{-1}, $F(000) = 2200$, $T = -100$ °C. *Data collection and reduction*: an orange prism 0.8×0.5×0.35 mm was mounted in inert oil (type RS3000, donated by Riedel de Haën) and transferred to the cold gas stream of the diffractometer (Siemens R3 system with LT-2 low temperature attachment). A total of 8899 intensities (8431 unique, R_{int} 0.045) was measured to 2θ 50°. Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range 20–23°. Absorption corrections were based on ψ-scans, with transmission factors 0.85–0.90. *Structure solution and refinement*: the structure was solved by the heavy-atom method and refined on F^2 using the program SHELXL-93. Early in the refinement considerable disorder became apparent (ironically not involving the solvent, which was well-resolved): the bipyridyl ligand adopts two different orientations, and the anion displays 'head-to-tail' disorder (the second orientation of both groups is distinguished by primed atom names in the Table of atomic coordinates, see 'Supplementary material'). Disordered groups and solvent C were refined isotropically, other non-H atoms anisotropically; H atom were included using a riding model. In view of the disorder problems and associated high residual electron density (2.6 e Å^{-3}) it would be unwise to overinterpret the bond lengths and angles involving the disordered groups. The weighting scheme was $w^{-1} = [\sigma^2(F_o^2) + (0.146P)^2 + 29.1P]$, with $P = (F_o^2 + 2F_c^2)/3$. The final $R_w(F^2)$ for all reflections was 0.297, with a conventional $R(F)$ of 0.088, for 577 parameters and 598 restraints; $S = 1.06$.

**Yield 76%. M.p. 97 °C. *Anal.* Calc. for $C_{32}H_{30}O_8$: C, 70.84; H, 5.52. Found: C, 70.47, H, 5.75%. IR, ν(C=O): 1720–1680 (br), 1650 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37, 7.29–7.26, 7.25–7.11 (m, 10H, Ph), 6.88 (s, 1H, C_6H), 4.04 (s, 3H, MeO), 4.0–3.8 (two overlapping quadruplets, 4H, 2 CH_2), 3.70 (s, 3H, MeO), 2.31 (s, 3H, MeCO), 0.93 (t, ^3J(HH) = 7 Hz, 3H, CH_2Me), 0.75 (t, ^3J(HH) = 7 Hz, 3H, CH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.4 (CH_3CO), 184.0 (C=O), 163.7 (*C*OOEt), 162.0 (*C*OOEt), 159.3, 158.7, 155.5, 146.1, 141.7, 140.6, 135.7, 134.8, 132.6, 129.1, 128.7, 128.2, 127.9, 127.7, 127.5, 127.4, 66.8 (quaternary sp^3 C), 61.9 (MeO), 60.7 (CH_2), 60.4 (MeO), 60.2 (CH_2), 27.8 (*Me*CO), 13.7 (CH_2Me), 13.4 (CH_2Me). MS (*m/e*): 543 ($M^+ + 1$, 2.6%), 105 ($PhCO^+$, 100%).

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