Bis(1-methoxynaphthalene-8-*C,O*)palladium(II). A Reactive Palladocyclic Compound with Labile O to Pd Donor Bonds

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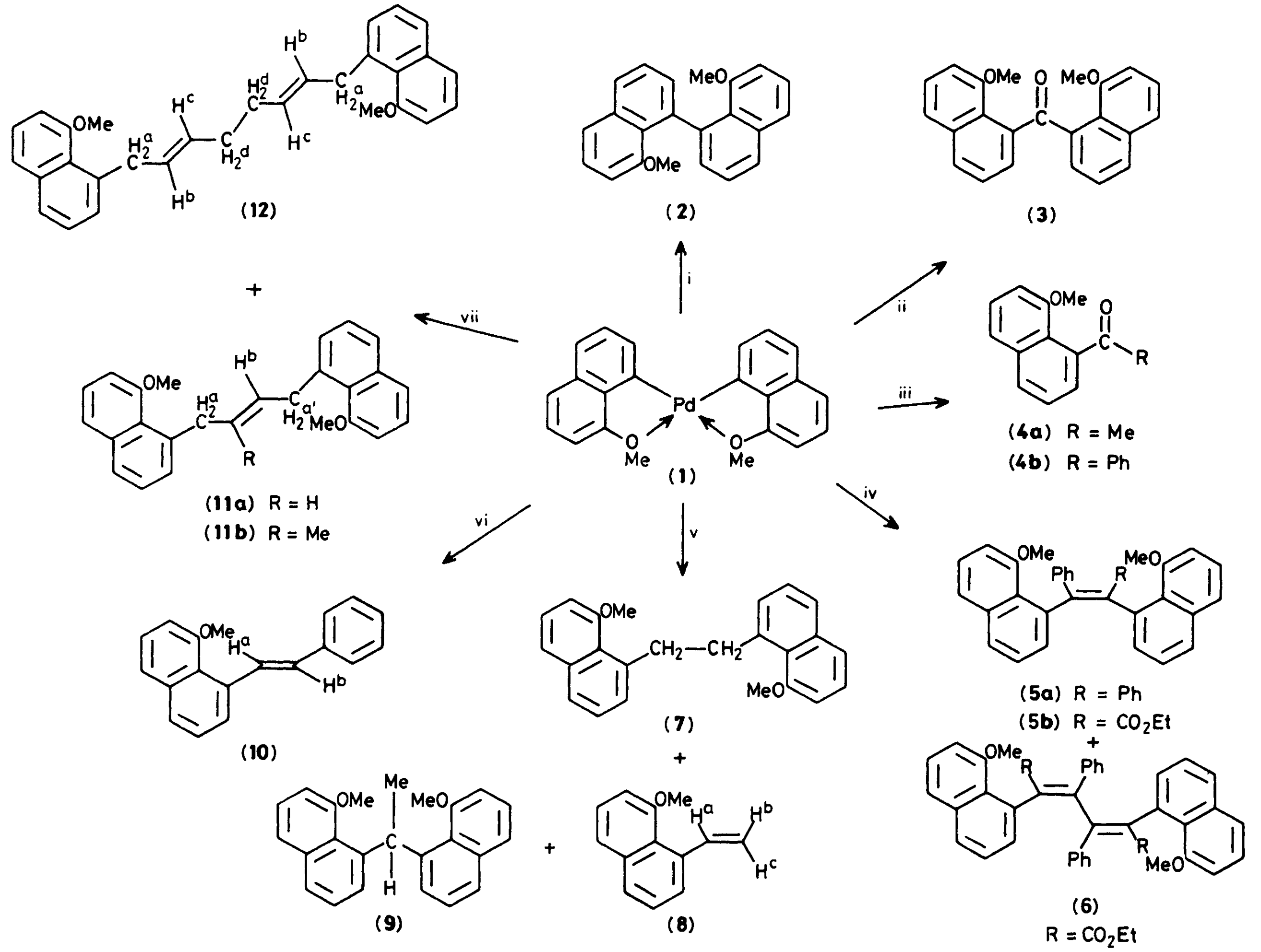
Bis(1-methoxynaphthalene-8-*C,O*)palladium(II) reacts stoicheiometrically with both nucleophiles and electrophiles to afford organic compounds *via* selective carbon–carbon bond formation.

We have recently described the synthesis of 1-methoxynaphthalene-8-*C* palladium complexes in which the oxygen atom is internally co-ordinated to the metal atom.[1] It was shown that this Pd–O bond is rather labile and therefore we expected these compounds to be more reactive than related compounds derived from the internal metallation of tertiary amines.[2—5] We show herein that the symmetrical compound bis(1-methoxynaphthalene-8-*C,O*)palladium(II) (**1**) displays, as anticipated, an enhanced reactivity of its Pd–C bonds compared with these compounds since it reacts readily with a large variety of reagents.

The reactions of (**1**) are summarized in Scheme 1. Although



Scheme 1. *Reagents and conditions:* i, CO, (2 atm), 100% yield; ii, $Co_2(CO)_8$ (2 equiv.), 10 min, 59%; iii, RCOCl, 5 min; (**4a**) 49%, (**4b**) 40%; iv, PhC≡CPh, 110 °C, 16 h; (**5a**) 52%; $PhC{\equiv}CCO_2Et$, 3 days; (**5b**) 66%, (**6**) traces; v, ethylene (2 atm), 10 min, 70 °C; (**7**) 9%, (**8**) 24%, (**9**) 33%, 1-methoxynaphthalene 24%; ethylene (2 atm), 1 h, 0 °C; (**7**) 57%, (**8**) 10%, (**9**) 20%, 1-methoxynaphthalene 10%; vi, styrene, 24 h; (**10**) 31%, 1-methoxynaphthalene, 31%; vii, butadiene 10 min; (**11a**) 30%, (**12**) 46%; isoprene, 24 h; (**11b**) 48%. All reactions were carried out in toluene at room temperature unless otherwise stated. Yields were determined by ^1H n.m.r. spectroscopy. The yield of (**2**) in reactions ii—vii is the difference between 100% and the sum of the other products of each reaction.†

compound (**1**) is stable in the solid state, it decomposes slowly in solution affording (**2**) and metallic palladium.[1] Moreover, in the presence of other reagents the decomposition of (**1**) [to give (**2**)] is often accelerated so that the amount of (**2**) which is formed along with the other products is sometimes larger than would be expected from the known stability of (**1**). With carbon monoxide for instance (**1**) is instantaneously and quantitatively converted into (**2**) and no incorporation of CO can be detected in the product. However, when a metal carbonyl is used as a source of CO one obtains a good yield of the symmetrical diaryl ketone (**3**). In order to explain the difference between these reactions one might suggest that the latter reaction goes *via* the formation of a heterobimetallic intermediate as has been postulated for the synthesis of benzophenone from mercury(II) aryl compounds and cobalt carbonyl.[6] Acyl chlorides react with (**1**) to give unsymmetrical ketones (**4**), a result that is similar to that described previously for cyclopalladated amines.[4] It is however important to point out that here the reactions are almost instantaneous and proceed under very mild conditions.

No stable organometallic intermediate could be isolated from the reaction of (**1**) with diphenylacetylene to give (**5a**) or phenyl ethyl propiolate giving (**5b**) and traces of (**6**) contrary to what was found for related compounds having nitrogen as

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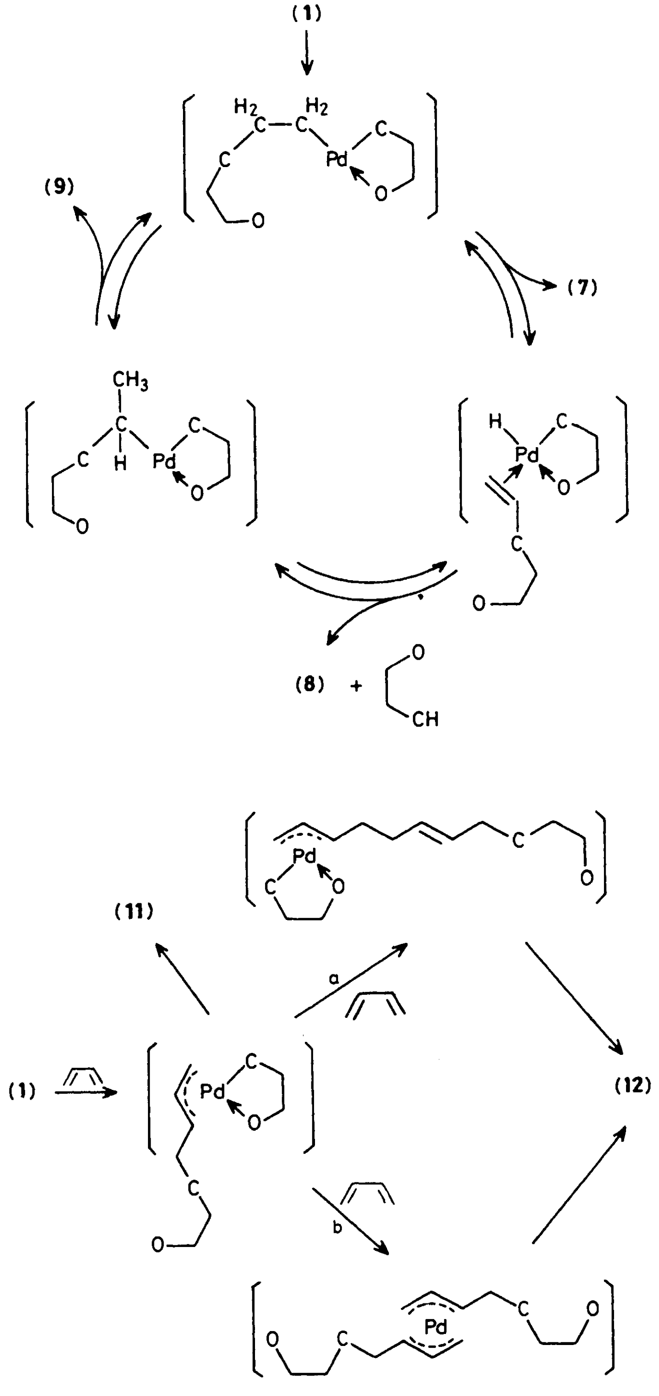
† Selected ^1H n.m.r. spectroscopic data: (δ, $CDCl_3$, coupling constants in Hz), (**3**) 3.82 (OMe); (**4a**) and (**4b**) 3.46 (OMe); (**5a**) 3.76 (OMe); (**5b**) 3.92 (q, CH_2), 3.90 and 3.80 (OMe), 0.86 (t, CMe); (**6**) 3.72 (OMe), 0.60 (t, CMe); (**7**) 4.02 (CH_2), 3.66 (OMe); (**8**) 7.84 [dd, H^a, $J(H^aH^b)$ 10.8, $J(H^aH^c)$ 17.2], 5.4 [dd, H^b, $J(H^bH^c)$ 2.0], 5.20 (dd, H^c), 3.93 (OMe); (**9**) 7.00 [q, CH, J(HH) 6.9], 3.57 (OMe), 1.72 (d, CMe); (**10**) 8.34 and 6.74 [d, H^a and H^b, $J(H^aH^b)$ 16.0], 3.94 (OMe); (**11a**) 5.74 (m, H^b), 3.99 [d, H^a, $J(H^aH^b)$ 4.7], 3.72 (OMe); (**11b**) 5.12 [t, H^b, $J(H^bH^{a'})$ 3.0], 3.98 (H^a), 3.97 (d, $H^{a'}$), 3.57 and 3.56 (OMe), 1.77 (Me); (**12**) 5.66 [m, H^b, $J(H^bH^c)$ 15.2], 5.46 (m, H^c), 3.97 [d, H^a, $J(H^aH^b)$ 6.4], 3.88 (OMe), 2.02 (m, H^d). The products have been characterised by their ^1H n.m.r. and mass spectra. Compounds (**2**), (**3**), (**4**), (**5a**), (**7**), and (**12**) have been isolated and gave satisfactory elemental analysis.



Scheme 2. Proposed intermediates for the reactions of (**1**) with ethylene and butadiene.

the donor atom.[5] This behaviour can be explained by the poorer donor ability of the oxygen atom towards Pd. It is thus likely that the insertion of one or two alkynes into the Pd–C bond of (**1**) is rapidly followed by reductive elimination affording (**5**) and (**6**) respectively.

Whereas the product of the reaction of (**1**) with styrene to give (**10**) resembles that observed with cyclopalladated amines, *viz. trans*-stilbene derivatives,[3] to our knowledge no reaction has yet been reported between these compounds and ethylene or butadiene. With ethylene three products are obtained, the composition of the mixture being strongly dependent on the temperature of the reaction. The formation of these compounds (**7**)—(**9**) is rationalized in Scheme 2 showing likely intermediates which are able to give the products by reductive elimination processes (**7**) and (**9**), or deco-ordination of the substituted alkene (**8**). Butadiene also inserts into a Pd–C bond of (**1**). Since it has been shown that 'Ar–Pd–Cl' gives a π-allyl–Pd dimer with chloride bridges on reaction with butadiene,[7] the mechanism that we propose for the formation of (**11**) and (**12**) is as shown in Scheme 2. The formation of (**12**) is based on a recent report by Goliaszewski and Schwartz[8] in which they reported that bis(π-allyl)Pd(II) compounds are stable complexes because strong reducing agents are necessary to induce the reductive elimination reaction to afford C–C coupled products. Since no such reductant is present in our reaction we prefer path a for the formation of (**12**).

This study has shown that the reactivity of this palladocyclic species is much greater than that of the related cyclopalladated amines. Indeed it is comparable with that of the as yet uncharacterized 'ArPdCl' intermediates[9] which have been found in many organic reactions.

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