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Triarylation of η^6-dihydronaphthalene-$Cr(CO)_3$ complexes

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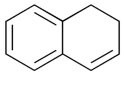
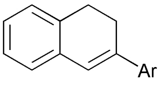
Received (in Cambridge, UK) 26th September 2002, Accepted 1st November 2002
First published as an Advance Article on the web 20th November 2002

With ease, η^6-dihydronaphthalene tricarbonylchromium(0) complexes undergo a triple arylation with concomitant ring closure, when submitted to Heck reactions under 'Jeffery conditions'.

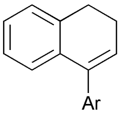
Palladium catalysed carbon–carbon bond formation, where additional ligands such as triphenylphosphine are not added to stabilize the metal, have been used extensively in recent times. These reactions that are usually run under so-called 'Jeffery conditions'[1] had been used initially in Heck-transformations, but have subsequently been introduced to other C–C coupling reactions.[2] In certain cases the outcome of the reactions under Jeffery conditions is different from that of the reactions where $Pd(PPh_3)_4$ has been used as catalyst. Thus, it is known that under Jeffery conditions, Heck-reactions of dihydronaphthalenes, *e.g.* **1**, favour the introduction of the aryl substituent in the β-position (linear product, **2**),[3] while in Heck reactions under more traditional catalysis with $Pd(PPh_3)_4$ or with external addition of the phosphine ligand to the metal the branched product **3** is favoured, especially in the presence of an excess of alkene.



1



2
linear product

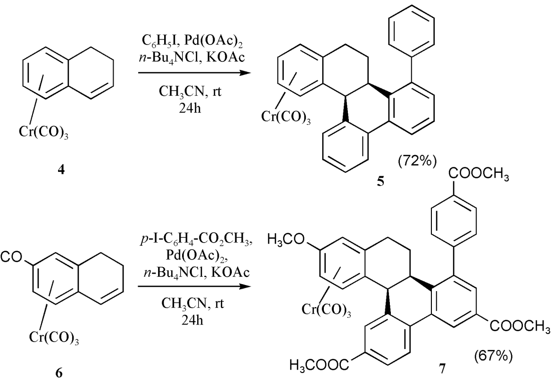


3
branched product

In neither case does the dihydronaphthalene **1** as a trisubstituted olefin undergo the Heck reaction with ease and usually the yields are poor. Undoubtedly one of the inherent problems in the transformation of these systems is the geometrically predetermined difficulty of Pd–H elimination. While a number of pathways are possible for this elimination such as α-elimination with the formation of a Pd-carbene with a subsequent 1,2-hydride shift or an inversion of the Pd-adduct before elimination, in many cases a formal *trans*-elimination of Pd–H is necessitated.[4] Evidently, this causes problems in both the dihydronaphthalenes[3] and the indene-adducts,[5] formed in the initial step of the Heck reaction of dihydronaphthalenes and indenes, respectively, a step, which is *cis*-stereospecific.[6]

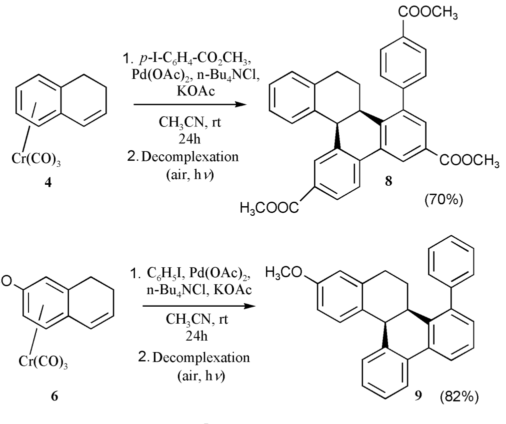
When dihydronaphthalene tricarbonylchromium(0) complexes are subjected to Heck reactions under 'Jeffery' conditions, neither branched nor linear mono-adducts are formed, but rather a third pathway asserts itself and a triarylation of the alkene occurs to give compounds **5** and **7**–**9** (Schemes 1 and 2). Triarylations of this general nature have been described almost exclusively for norbonene derived systems,[7,8] which possess a strained olefinic bond and which are less sterically exacting than the dihydronaphthalenes due to their rigid geometry. Earlier, for these systems also a bisarylation had been observed.[9] Heck reactions under Jeffery conditions of the dihydronaphthalenes themselves lead to poor turn-overs. Thus, after 24 h, uncomplexed **4** with iodobenzene gives only 10% of the product, uncomplexed **5**, where most of the starting material is left unreacted. In comparison, the corresponding dihydronaphthalene chromiumtricarbonyl(0) complex **4**, which can be prepared by the usual methods[10] gives the stable and isolable complex **5** in 72% yield after 24 h. Alternatively, **5** can be decomplexed within 2 h by exposure to light in an aerated solvent. Exclusively one isomer is formed in the Heck reaction in all of the cases examined, the general structure of which has been determined by ^1H NMR spectroscopy[11] and the regio- and relative stereochemistry of which have been ascertained by X-ray crystal structural analysis of decomplexed products **8** and **9** (Scheme 2). Thus, the *para*-substituent on the aryl halide does not affect the regiochemistry of the formed product.

DOI: 10.1039/b209494k



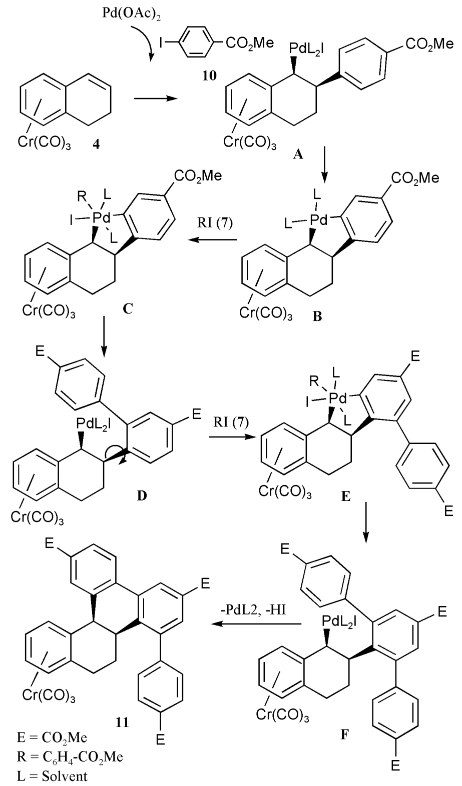
Scheme 1

The mechanism of the reaction is thought to run *via* palladacycles and is depicted in Scheme 3. Although the active species of the Pd-catalyst in Heck-type reactions under Jeffery conditions is still under discussion, where mechanisms involving the formation of Pd-nanoparticles[12] have been favored, it can be suggested that the initial reaction of the Pd-catalyst with the aryl halide will lead to either $[RPdL_2I]$ or [RPdLOAcI], where L is a solvent molecule. *cis*-Addition of the Pd-complex to **1** occurs. Whereas it has been pointed out that the Pd moiety usually acts as the nucleophilic partner in the addition, it is deemed that the destabilisation of the benzylic cation due to the strongly electron withdrawing character of the chromium tricarbonyl moiety counterbalances the electrophilicity of the olefinic β-carbon. Of importance, as there is no immediate



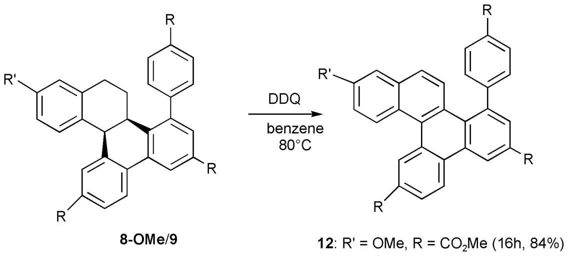
Scheme 2

possibility for the species to undergo *syn*-elimination, is the difficulty of the subsequent Pd–H *trans*-elimination. This allows Pd to undergo a C–H insertion at the *ortho*-position of the added aryl group, thus creating the first metallacycle (**B**) of the reaction cycle. This is opened by addition of a second arylpalladium iodide to **C**. The sequence repeats with the addition of a third arylpalladium iodide (Scheme 3).



Scheme 3

The compounds gained in the above reactions can be dehydrogenated with DDQ[13] to the polycondensed aromatic compounds **12** and **13** (Scheme 4). These and some of their derivatives are highly fluorescent. The ease of dehydrogenation depends on the substituents both of the former dihydronaphthalene as well of the aryl halide used. The triarylation can also be applied successfully to molecules, where the dihydronaphthalene unit is part of a more complex structure such as in estra-1,3,5(10),6-tetraenes.



12: R' = OMe, R = CO_2Me (16h, 84%)
13: R' = OMe, R = H (5h, 92%)

Scheme 4

While the described reaction presents a quick access to multi-annelated aromatic systems, possibilities for the use of this transformation in systems of different ring size will be assessed in further studies. Undoubtedly, the application of this reaction towards other ring systems will be governed to a large extent by the geometric parameters of the first addition product, *i.e.* of analogs of **A**.

Notes and references

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11 The following experimental procedures may be seen as representative: *for complexes: for decomplexed products*: a mixture of 50 mg (0.19 mmol) 4, 21 mg (0.05 eq.) $Pd(OAc)_2$, 150 mg (0.6 mmol, 3 eq.) methyl *p*-iodobenzoate (10),. 105 mg (0.38 mmol, 2 eq.) *n*-Bu_4NCl and 46 mg (0.5 mmol, 2.5 eq.) $Pd(OAc)_2$ in acetonitrile (1 mL) was stirred under inert atmosphere for 24 h at rt. Thereafter, the solution was aerated and exposed to light. Insoluble material was fitered off and the concentrated filtrate was subjected to column chromatography on silica gel (hexane/$CHCl_3$ 1 : 1) to give **8** (70 mg, 0.14 mmol, 70%) as colorless crystals; mp 287 °C; ^1H NMR (600 MHz, $CDCl_3$): δ 8.57 (d, 1H, ^4J 1.6 Hz), 8.09 (d, 2H, ^3J 8.5 Hz), 7.99 (d, 1H, ^3J 8.2 Hz), 7.98 (d, 1H, ^3J 8.2 Hz), 7.92 (d, 1H, ^4J 1.6 Hz), 7.46 (br s, 1H), 7.42 (d, 2H, ^3J 8.5 Hz), 7.22–7.28 (m, 3H), 7.10 (br d, 1H, ^3J 7.3 Hz), 4.20 (d, 1H, ^3J 4.5 Hz), 3.97 (s, 3H, $COOCH_3$), 3.94 (s, 3H, $COOCH_3$), 3.82 (s, 3H, $COOCH_3$), 3.17 (ddd, 1H, 13.2, 4.5, 3.5 Hz), 2.58–2.66 (m, 2H), 1.69–1.75 (m, 1H), 1.60–1.64 (m, 1H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 166.9, 166.8, 166.7, 144.9, 143.9, 141.0, 138.8, 137.2, 135.8, 135.2, 133.4, 131.5, 130.9, 130.2, 129.8, 129.6, 129.5, 129.4, 129.2, 128.9, 128.5, 128.4, 127.8, 127.4, 126.4, 125.7, 124.5, 52.3, 52.2, 52.0, 42.2, 36.0, 28.3, 23.6. IR (neat): ν 2930, 2854, 1720, 1606, 1490, 1436, 1261, 1243, 1113, 870, 804, 766 cm^{-1}. MS (70 eV) *m*/*z* (%) 532 (M^+, 100), 501 (13), 399 (24), 339 (28), 104 (58). HRMS for $C_{34}H_{28}O_6$. Calc., C, 76.67; H, 5.29. Found: C, 76.10; H, 5.31%.

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