

Palladium-catalyzed electrochemical carbonylation of alkynes, under very mild conditions

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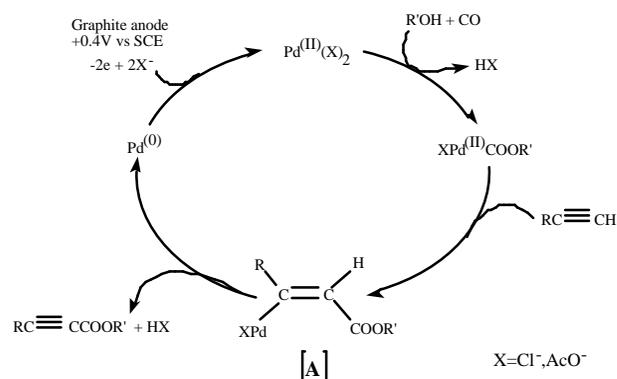
Palladium(II)-catalyzed carbonylation of terminal alkynes in methanol gives methyl acetylenecarboxylates. These reactions are carried out using PdCl₂ as catalyst and stoichiometric amounts of CuCl₂ as reoxidant.¹ However, from a synthetic and environmental point of view, it is important to develop a halogen-free and copper-free reoxidant system. Recently, Sakurai *et al* reported a new oxidation system, Pd(OAc)₂/chlorohydroquinone/molybdovanadophosphate (NPMoV), to render the reaction catalytic in palladium(II).² However, a high pressure of carbon monoxide and dioxygen are still required.

Herein we report a new procedure for the electrochemical synthesis of methyl acetylenecarboxylates from alkynes, under mild conditions, using a palladium complex as catalyst, carbon monoxide (p CO=1 atm) and methanol at room temperature. The process is outlined in the following reaction:



The reaction proceeds under atmospheric pressure of carbon monoxide at 25°C in a CH₃CN/CH₃OH solvent in the presence of bases (NaOAc or NEt₃) using a catalytic amount of a palladium(II) complex regenerated by oxidation of an intermediate Pd(0) complex at the anode. The results for the electrolyses using various palladium(II) complexes show that the reaction efficiently proceeded under atmospheric pressure of carbon monoxide with all the catalyst systems taken into account (77-95% current efficiency). The following general procedure was used: the electrolysis was carried out on a solution of alkyne (1 mmol) in 0.03 dm³ of CH₃CN/CH₃OH (7:3) containing *n*-Bu₄NBF₄ (0.2 mol dm⁻³) as supporting electrolyte, in the presence of palladium catalyst (0.1 mmol) and NaOAc or NEt₃ (2 mmol), under 1 atm of CO, at +0.4 V vs SCE, at 25°C. A graphite electrode, of apparent area 3 cm², was used as the working electrode. The counter-electrode was a Pt wire and the reference was a saturated calomel electrode (SCE). At the end of the electrolyses, yields were calculated by GC analysis of crude reaction mixtures by comparison with authentic samples of standards. Methyl acetylenecarboxylates were obtained with fair good yields (53-87%).

As proposed by Heck, for the carbonylation of olefins and acetylenes, the electrocarbonylation of terminal alkynes is considered to proceed via a similar mechanism (see Scheme).³



Because of the *syn* addition of L₂(OAc)PdCOOR' on the alkyne, the formation of HPd(OAc)(PPh₃)₂ by a β-hydride *syn* elimination is impossible. The reaction is considered to proceed by the elimination of H⁺ in the β position in complex [A], induced by the base.⁴ NEt₃ is probably more efficient than AcO⁻ in this reaction. The Pd(0) is then generated in higher concentrations from complex [A] in the presence of NEt₃ and can be reoxidized to Pd(II) at the anode. Moreover, when acetate was used as base, acetic acid is formed from complex [A] concomitantly with the Pd(0) complex. We have reported that Pd(0) undergoes oxidative addition with acetic acid to form a cationic palladium(II) hydride.⁵



Under such conditions the Pd(0) complex generated from [A] would be partially stored under the form of HPd(II)(PPh₃)₂⁺, a reaction which is in competition with its reoxidation at the anode.

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References.

1. Tsuji, J.; Takahashi, M.; Takahashi, T. *Tetrahedron Lett.*, **1980**, *21*, 849-850.
2. Sakurai, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.*, **1999**, *40*, 1701-1704.
3. Heck, R. F. *J. Am. Chem. Soc.*, **1972**, *94*, 2712-2719.
4. Negishi, E. *Acc. Chem. Res.*, **1982**, *15*, 340-348.
5. Amatore, C.; Jutand, A.; Meyer, G.; Carelli, I.; Chiarotto, I. *Eur. J. Inorg. Chem.* **2000**, *8*, 1855-1859.