

Microwave synthesis of bis(tetrazolato)-Pd^{II} complexes with PPh₃ and water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA). The first example of C-CN bond cleavage of propionitrile by a Pd^{II} centre.

Autorzy

J. Lasri
M. J. Fernández Rodríguez
Silva M. Fátima. C. Guedes
da
Piotr Smoleński
Maximilian N. Kopylovich
J. J. R. Fraústo da Silva
Armando J. L. Pombeiro

Rok wydania

2011

Czasopismo

Journal of Organometallic
Chemistry

Numer woluminu

696

Strony

3513-3520

DOI

10.1016/j.jorganchem.2011.07.047

Kolekcja

Naukowa

Język

Angielski

Streszczenie

[2 + 3] Cycloaddition reactions of the di(azido)-Pd^{II} complex *trans*-[Pd(N₃)₂(PPh₃)₂] (**1**) with an organonitrile RCN (**2**), under heating for 12 h, give the bis(tetrazolato) complexes *trans*-[Pd(N₄CR)₂(PPh₃)₂] (**3**) [R = Me (**3a**), Ph (**3b**), 4-ClC₆H₄ (**3c**), 4-FC₆H₄ (**3d**), 2-NC₅H₄ (**3e**), 3-NC₅H₄ (**3f**), 4-NC₅H₄ (**3g**)]. The reaction of *trans*-[Pd(N₃)₂(PPh₃)₂] (**1**) with propionitrile (**2h**) also affords, apart from *trans*-[Pd(N₄CEt)₂(PPh₃)₂] (**3h**), the unexpected mixed cyano-tetrazolato complex *trans*-[Pd(CN)(N₄CEt)(PPh₃)₂] (**3h'**) which is derived from the reaction of the bis(tetrazolato) **3h** with propionitrile, with concomitant formation of 5-ethyl-1*H*-tetrazole, via a suggested unusual oxidative addition of the nitrile to Pd^{II}. The [2 + 3] cycloadditions of [Pd(N₃)₂(PTA)₂] (**4**) (PTA = 1,3,5-triaza-7-phosphaadamantane) with RCN (**2**), under heating for 12 h, give the bis(tetrazolato) complexes *trans*-[Pd(N₄CR)₂(PTA)₂] (**5**) [R = Ph (**5a**), 2-NC₅H₄ (**5b**), 3-NC₅H₄ (**5c**), 4-NC₅H₄ (**5d**)]. All these reactions are greatly accelerated by microwave irradiation (1 h, 125 °C, 300 W). Taking advantage of the hydro-solubility of PTA, a simple liberation of 5-phenyl-1*H*-tetrazole from the coordination sphere of *trans*-[Pd(N₄CPh)₂(PTA)₂] (**5a**) was achieved. The complexes were characterized by IR, ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies, ESI⁺-MS, elemental analyses and, for **3b**, also by X-ray structure analysis. Weak agostic interactions between the CH groups of the triphenylphosphines and the palladium(II) centre were found.

Słowa kluczowe

atom, Ion, 5-Triaza-7-phosphaadamantane (PTA), Azides, Nitriles, [2 + 3] Cycloadditions, Tetrazoles, Microwaves

Adres publiczny

<https://doi.org/10.1016/j.jorganchem.2011.07.047>

Artykuł

<http://www.elsevier.com>

Plik został wygenerowany dnia 2026-10-08 09:39:30

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/nJlbtdr>.