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Palladium(II)-*C*-Malonate Ester Complexes

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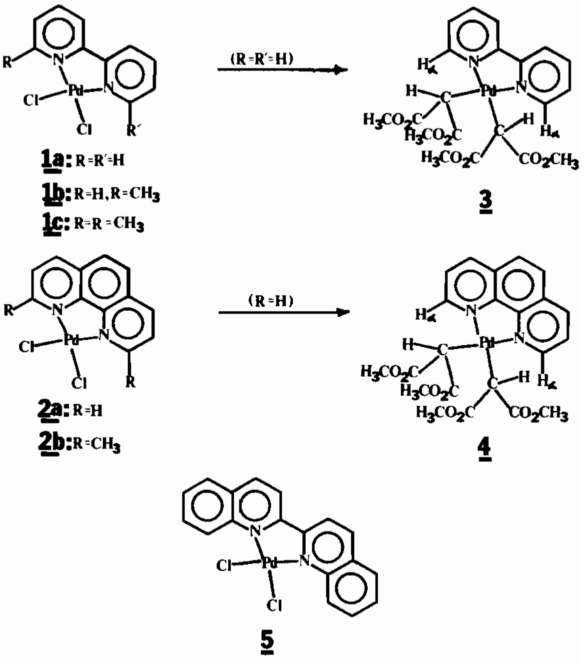
β-Dicarbonyl compounds, such as acetylacetone, alkyl acetoacetate, and dialkyl malonates, are very versatile ligands exhibiting either *C*- or *O*-bonding modes depending, in part, on the degree of enolization and the particular metal ions [1]. Although acetylacetonate [2, 3] and ethyl acetoacetate [4] ligands are best known for their *O*-bonded complexation, carbon–metal complexes are also documented but not as popular. Since dialkyl malonates do not enolize to any appreciable extent and due to limited examples of established *C*-bonded organometallics, we prepared a series of stable *cis*-[5] and *trans*-[6, 7] bis-(carbon-palladium) complexes *via* an intramolecular metallation sequence. We herein report an intermolecular exchange of chloro ligands with dialkyl potassiomalonate to generate unidentate *C*-malonate complexes and the dramatic effect of substituents within the environment of the exchangeable ligand.

Experimental

Dichloro 2,2′-dipyridinepalladium(II) (*1a*) or the corresponding phenanthroline analog *2a*, prepared from the heterocycle and $PdCl_2$ in acetonitrile, is treated directly with dimethyl malonate in DMF in the presence of K_2CO_3 to give *3*# [65%; m.p. 187 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.62 (s, OCH_3), 4.12 (s, C*H*), 7.56 (m, 5-py*H*), 8.00 (dd, 3-py*H*, J = 8.1, 1.2 Hz), 8.10 (dd, 4-py*H*, J = 8.1, 7.3 Hz), 9.74 (d, 6-pyH, J = 5.6 Hz); ^{13}C NMR δ 50.9 (CH_3), 52.4 (*C*H), 121.6 (C3), 126.4 (C5), 138.9 (C4), 153.1 (C6), 155.4 (C2), 174.8 (*C*O)] or *4*# [76%. m.p. 202 °C (dec); ^{1}H NMR δ 3.66 (s, OCH_3), 4.25 (s, C*H*), 7.86 (s, 5,6-ph*H*), 7.87 (dd, 3,8-ph*H*, J = 5.5, 7.9 Hz), 8.41 (dd, 4,7-ph*H*, J = 7.9, 1.2 Hz), 10.07 (dd, 2,9]ph*H*, J = 5.5, 1.2 Hz); ^{13}C NMR δ 50.9 (CH_3), 52.8 (*C*H), 125.2 (C3), 126.9 (C5), 129.3 (C4a), 137.8 (C4), 146.0 (C10a), 153.2 (C2), 174.9 (*C*O)], respectively. These characterized complexes are the first examples to the best of our knowledge of Pd(II)-bis-*C*-bonded unsubstituted malonate ligands coordinated through the central carbon atom; ethyl acetoacetate [4] and acetylacetonate [2] complexes have been prepared *via* an alternate procedure: rearrangement of the corresponding *O*-bonded complexes.



Results and Discussion

The spectral data firmly establish the Pd–C bond. The ^{1}H NMR data of the methine protons show singlets at δ 4.12 and 4.25, which fall within the δ 4.0–4.4 range for related *C*-bonded complexes and differ significantly from the *O*-bonded range (δ 4.7–5.4). The α-heteroaromatic protons exhibit signals at δ 9.74 and 10.07 indicating their close proximity to the ester groups. ^{13}C NMR further collaborate the assignments, in that the signal for the carbon directly bonded to palladium appears at δ 52.6 ± 0.2, which is 13 ppm downfield from free dimethyl malonate and *ca.* 50 ppm upfield of the related *O*-bonded complexes.

In order to evaluate the effect of substituents, under a variety of conditions, *1b*, *1c*, *2b*, and *5* were each treated with dimethyl potassiomalonate and in all cases either the initial complex or initial hetero-

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#Analytical data within acceptable limits for assigned structure.

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cyclic ligand was isolated. These failures and the enhanced downfield chemical shift exhibited by the α-hydrogens in *3* and *4* are supportive of the so-called 'obstacle effect' [8]. Such an interaction between the α-methyl substituent(s) and the carbomethoxy groups inhibits the approach of the carbanion to the palladium nucleus. Similar trends have been observed for formation of *trans*-palladium(II) complexes from hindered pyridine and pyrazine bases [7].

Interestingly, reaction of diethyl ethylmalonate with *1a* or *2a* in DMF and K_2CO_3 did *not* give any *C*-bonded complex due to a combination of steric interactions to either anion generation or, if formed, nucleophilic approach to the palladium core. Abstraction of the acidic hydrogen in either *3* or *4* with base and subsequent treatment reaction with 1,2-dichloroethane, 1,3-dibromopropane, or 1,5-bis-(carbomethoxy)pentane, all failed to generate a new carbon–carbon bond.

In an attempt to form a new carbon-carbon bond, *3*, when treated with bromine in chloroform, afforded dimethyl bromomalonate (oil) [9] and dibromo (2,2′-dipyridine)palladium(II) [10], whereas with chlorine in chloroform *3* afforded (>95%), along with dimethyl chloromalonate [11], the oxidized tetrachloro(2,2′-dipyridine)palladium(IV) [10]. Similar reactions were realized with *4* [12]. When *3* or *4* was treated with CO in THF, the corresponding heterocycle, palladium(0), and dimethyl malonate were obtained (40%) along with balance being unchanged starting complex. Subjecting *3* or *4* to methylvinylketone in CH_2Cl_2 under reflux for 6 hrs, resulted in a quantitative recovery of the initial complex.

Acknowledgements

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