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Mono- and dinuclear palladium(II) cyclometallates with 4-R-*N*′-(mesitylidene)benzohydrazides and mono- and diphosphines

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ABSTRACT

Reactions of $PdCl_2$, LiCl, 4-R-*N*′-(mesitylidene)benzohydrazides (H_2L^n; n = 1 and 2 for R = H and OMe, respectively) and $NaOAc\cdot 3H_2O$ in 1:2:1:1 mol ratio in methanol produce $[Pd(HL^n)Cl]$ (**1** (n = 1) and **2** (n = 2)) in ~77% yields. Reactions of $[Pd(HL^n)Cl]$ (**1** and **2**) with PPh_3 in 1:2 mol ratio in acetone provide $[Pd(L^n)(PPh_3)]$ (**3** (n = 1) and **4** (n = 2)) in ~76% yields. Whereas, treatment of 2 mol equivalents of $[Pd(HL^n)Cl]$ (**1** and **2**) with 1 mol equivalent of 1,4-bis(diphenylphosphino)butane (dppb) in acetone affords the dinuclear $[Pd_2(\mu\text{-dppb})(L^n)_2]$ (**5** (n = 1) and **6** (n = 2)) in ~74% yields. Analogous reaction between $[Pd(HL^2)Cl]$ (**2**) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) provides $[Pd_2(\mu\text{-dppf})(L^2)_2]$ (**7**) in 67% yield. Elemental (CHN) analysis, X-ray crystallographic and spectroscopic (IR, UV-Vis and NMR) measurements have been used to characterize all the complexes. In these complexes, the metal centers are in square-planar CNOCl or CNOP coordination geometry formed by the 6,5-membered fused chelate rings forming methylene-C, azomethine-N and amide- or amidate-O donor $(HL^n)^-$ or $(L^n)^{2-}$ and the ancillary ligand chloride or phosphine. The spectroscopic properties of the complexes are consistent with the corresponding molecular structures established by X-ray crystallography.

1. Introduction

Cyclometallation reactions and the cyclometallated complexes continue to be of immense interest primarily due to their applications in the design and synthesis of complex and intricate organic molecules [1–5]. The majority of cyclometallated complexes are formed due to activation of a proximal $C(sp^2)$–H bond of an aryl moiety pendant from a chelated ligand. In comparison, cyclometallated species *via* $C(sp^3)$–H activation in a similar way are relatively scarce. Generally this scarcity arises due to the chemical inertness and thermodynamic stability of the $C(sp^3)$–H bond. We have been working on cyclometallated complexes of platinum metal ions with aroylhydrazones and thiosemicarbazones of various mono- and polycyclic aromatic aldehydes for the past several years [6–9]. These Schiff bases in presence of base coordinate the metal center *via* the azomethine-N and the amidate-O or the thioamidate-S atoms and form a 5-membered chelate ring [6]. Chelation brings the aromatic ring of the arylidene fragment of the aroylhydrazonate or of the thiosemicarbazonate near to the metal center leading to $C(sp^2)$–H activation and eventual cyclometallation. In the cyclometallated complexes thus obtained, the ligands act as pincer-like CNO- or CNS-donor and form either 5,5-membered fused chelate rings in the case of *ortho*-metallation or 6,5-membered fused chelate rings in the case of *peri*-metallation. The process of bidentate chelation followed by cyclometallation reaction is the most effective and commonly used strategy for the synthesis of cyclometallated complexes [2,6,10,11]. In the present work, we have used 4-R-*N*′-(mesitylidene)benzohydrazides (H_2L^n; n = 1 and 2 for R = H and OMe, respectively) to examine whether similar NO-chelation followed by activation of the relatively more inert $C(sp^3)$–H bond in an *ortho*-methyl group of the mesityl fragment is possible or not. We have indeed been able to isolate a new series of cyclometallated palladium(II) complexes of formulas $[Pd(HL^n)Cl]$, $[Pd(L^n)(PPh_3)]$, $[Pd_2(\mu\text{-dppb})(L^n)_2]$ and $[Pd_2(\mu\text{-dppf})(L^2)_2]$ where $(HL^n)^-$ and $(L^n)^{2-}$ behave as 6,5-membered fused chelate rings forming CNO-donor ligands (Scheme 1). The syntheses, X-ray structures and spectroscopic properties of these complexes are described in the following sections.

2. Experimental

2.1. Materials

All chemicals used in this work were of analytical grade

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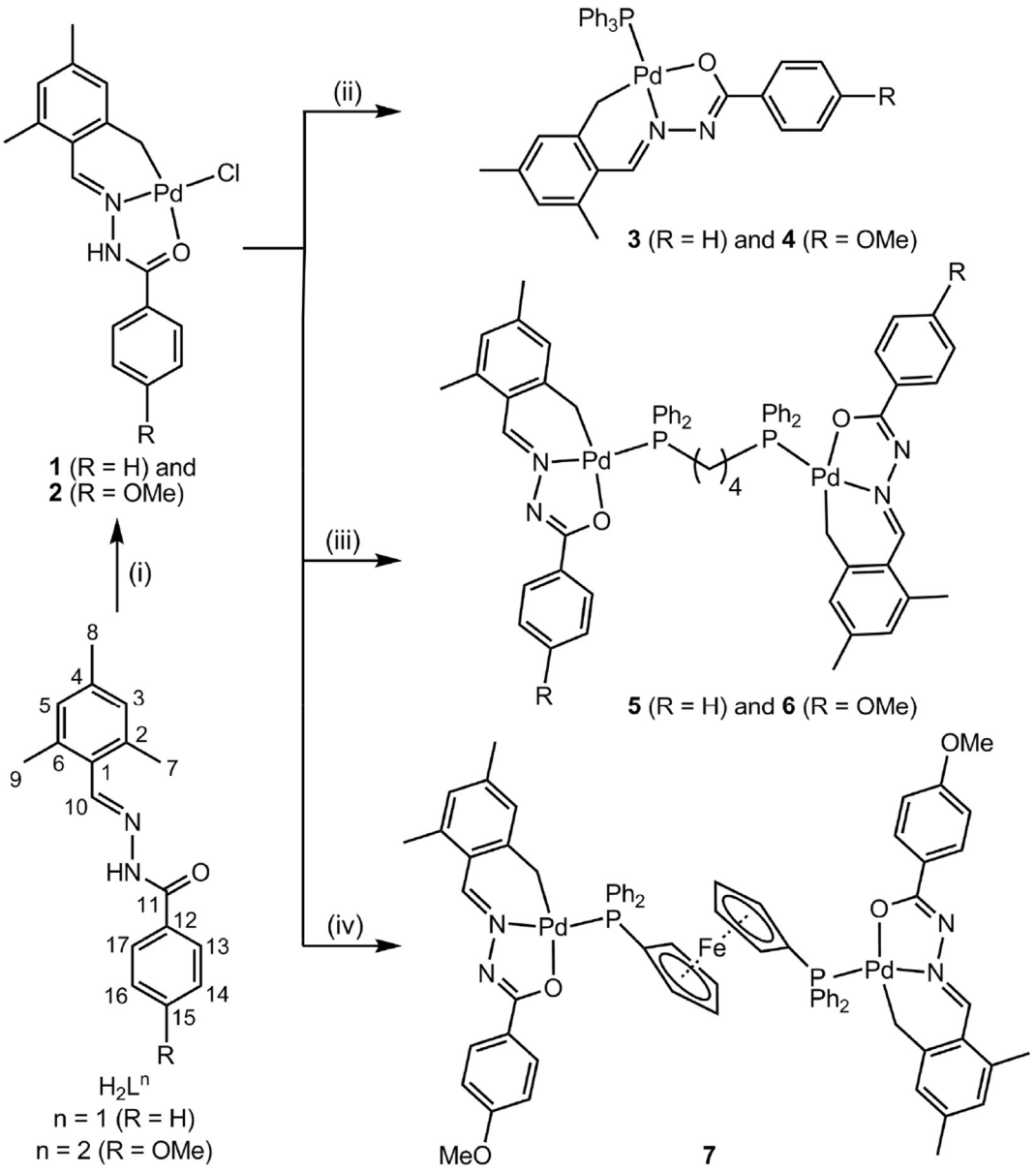

Scheme 1. (i) $PdCl_2$, LiCl and $NaOAc \cdot 3H_2O$ (1:2:1 mol ratio) in methanol under reflux. (ii) PPh_3 (2 mol equivalents) in acetone at room temperature. (iii) $Ph_2P(CH_2)_4PPh_2$ (0.5 mol equivalent) in acetone at room temperature. (iv) $[Fe(C_5H_4PPh_2)_2]$ (0.5 mol equivalent) in acetone at room temperature.

available commercially and were used as received without further purification. The solvents used were purified by standard methods [12].

2.2. Physical measurements

A Thermo Finnigan Flash EA-1112 elemental analyzer was used for elemental (CHN) analysis. Purities of H_2L^1 and H_2L^2 were verified with a Shimadzu LCMS 2010 liquid chromatograph mass spectrometer. Room temperature (298 K) magnetic susceptibility measurements were performed with a Sherwood scientific balance. Infrared spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. A Digisun DI-909 conductivity meter was used for electrical conductivity measurements in solution. Electronic spectra were recorded with the help of a Shimadzu UV3600 UV-Vis-NIR spectrophotometer. The ^1H (400 MHz) and ^{31}P (160 MHz) NMR spectra were recorded with the help of a Bruker NMR spectrometer.

2.3. Synthesis of H_2L^1

Benzohydrazide (1.36 g, 10 mmol) and mesitaldehyde (1.48 g, 10 mmol) were dissolved in methanol (70 ml). To this solution a few drops of acetic acid were added and the mixture was refluxed for 7 h. Upon cooling to room temperature, the white solid separated was collected by filtration, washed with 20 ml of methanol in three portions and finally dried in air. The compound thus obtained was recrystallized from 30 ml of chloroform. Yield: 2.18 g (81%). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.67; H, 6.81; N, 10.52. Found: C, 76.51; H, 6.74; N, 10.38. LCMS in CH_2Cl_2: m/z $(M-H)^-$ = 265.2. UV-Vis in Me_2NCHO: λ_{max} (nm) (ε (10^3 M^{-1} cm^{-1})) = 300 (12.8). Selected IR bands: ν (cm^{-1}) = 3199 (N–H), 1657 (C=O), 1606 (C=N). ^1H NMR in $(CD_3)_2SO$: δ (ppm) (J_{H-H} (Hz)) = 11.72 (s, 1H, NH), 8.75 (s, 1H, H^{10}), 7.91 (8) (d, 2H, H^{13}, H^{17}), 7.60–7.49 (m, 3H, H^{14-16}), 6.90 (s, 2H,