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Synthesis and catalytic properties of cationic palladium(II) and rhodium(I) complexes bearing diphosphinidinecyclobutene ligands

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Abstract

Cationic palladium(II) and rhodium(I) complexes bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene ligands (DPCB–Y) were prepared and their structures and catalytic activity were examined (aryl = phenyl (DPCB), 4-methoxyphenyl (DPCB–OMe), 4-(trifluoromethyl)phenyl (DPCB–CF_3)). The palladium complexes $[Pd(MeCN)_2(DPCB–Y)]X_2$ (X = OTf, BF_4, BAr_4 (Ar = 3,5-bis(trifluoromethyl)phenyl)) were prepared by the reactions of DPCB–Y with $[Pd(MeCN)_4]X_2$, which were generated from $Pd(OAc)_2$ and HX in MeCN. On the other hand, the rhodium complexes $[Rh(MeCN)_2(DPCB–Y)]OTf$ were prepared by the treatment of $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ with DPCB–Y in CH_2Cl_2, followed by treatment with AgOTf in the presence of MeCN. The cationic complexes catalyzed conjugate addition of benzyl carbamate to α,β-unsaturated ketones.

Keywords: Cationic complex; Palladium; Rhodium; Low-coordinated phosphorus ligand; Conjugate addition to enones

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1. Introduction

There has been considerable recent interest in the coordination chemistry of low-coordinate phosphorus compounds due to their unique electronic properties, differing significantly from common tertiary phosphine ligands [1]. We recently found that the 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes (DPCB–Y) shown in Chart 1 serve as particularly useful ligands [2]. Thus, while the DPCB–Y ligands structurally resemble diimine ligands, they possess extremely low-lying π^* orbitals located around the phosphorus, and exhibit a strong π-acceptor property towards transition metals [3]. We have documented that this property is useful for catalysis, leading to hitherto unknown reactivity and selectivity in hydroamination of dienes [4], direct conversion of allylic alcohols into *N*- and *C*-allylation products [5], (*Z*)-selective hydrosilylation of alkynes [6], cross-coupling reactions [7], and so on.

In effort to further explore the coordination behavior of this unique class of ligand and the reactivity of the resulting compounds, we prepared in this study a series of dicationic palladium(II) and cationic rhodium(I) complexes bearing DPCB–Y ligands listed in Chart 1. Dicationic palladium(II) complexes have proven to be efficient catalysts for copolymerization of CO and alkenes [8] and for conjugate addition of *C*- and *N*-nucleophiles to α,β-unsaturated carbonyl compounds [9,10]. For the latter catalysis, the electron-deficient nature of the dicationic palladium center should be of particular importance. Therefore, we have been interested in the construction of dicationic palladium complexes bearing DPCB–Y ligands with strong π-accepting ability. As described below, DPCB–Y ligands have

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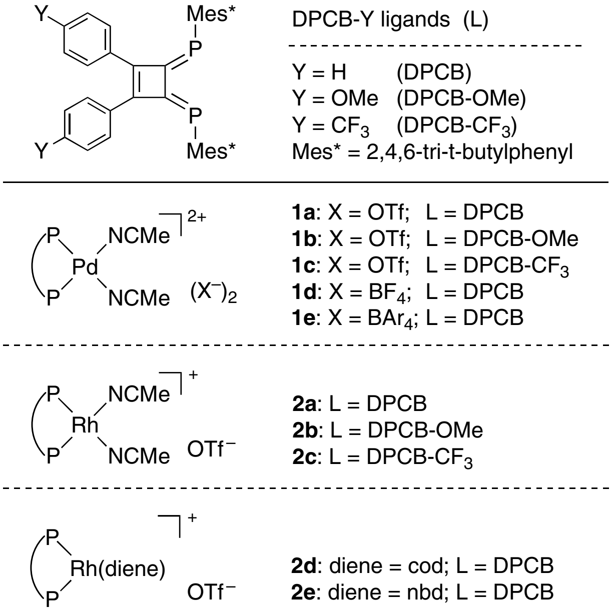

Chart 1. Listing of DPCB–Y ligands and cationic complexes.

been successfully coordinated with the $[Pd(MeCN)_2]^{2+}$ moiety, and the resulting complexes exhibit high catalytic performance towards conjugate addition of benzyl carbamate to enones [11].

2. Results and discussion

2.1. Preparation of $[Pd(MeCN)_2(DPCB–Y)](X)_2$ (1a–e)

Palladium complexes having OTf as counter anions (**1a**–**c**) were synthesized by ligand displacement of $[Pd(MeCN)_4](OTf)_2$ with DPCB–Y in MeCN/Et_2O at room temperature. The starting complex was prepared from $Pd(OAc)_2$ and 2 equiv of TfOH in MeCN [12], and then combined with DPCB–Y without isolation. Complexes **1a**–**c** were obtained as purple crystalline solids by recrystallization from MeCN/Et_2O. The DPCB complexes having BF_4 and BAr_4 (Ar = 3,5-$(CF_3)_2C_6H_3$) anions (**1d** and **1e**, respectively) were similarly prepared by using the corresponding boric acids instead of TfOH. Complexes **1a**–**e** were identified by IR and NMR spectroscopy and/or elemental analysis.

The IR spectrum of **1a** exhibited two $\nu_{C\equiv N}$ bands at 2332 and 2303 cm^{-1}; the absorption pattern was consistent with cis arrangement of the two MeCN ligands. In the ^1H NMR spectrum recorded in $CDCl_3$, the methyl proton signal of MeCN appeared as a sharp singlet (δ 2.46) at −40 °C, but was significantly broadened and shifted upfield (ca. δ 2.1) at room temperature. Because complex **1d** having BF_4^- anions showed a singlet in a coordination region (δ 2.39) even at room temperature, it is considered that **1a** undergoes rapid ligand exchange between MeCN and OTf^- on an NMR time scale. The loss of MeCN from the complex was observed in the solid state as well. The ^{31}P NMR signals appeared at δ 135.7 (**1a**), 127.3 (**1b**), and 143.1 (**1c**), respectively. The chemical shifts are 34–38, 28–31, and 8–12 ppm higher than that of free DPCB–Y [3], $PdMe_2$(DPCB–Y) [3], and [Pd(η^3-allyl)-(DPCB–Y)]OTf [5b], respectively.

2.2. Preparation of $[Rh(MeCN)_2(DPCB–Y)]OTf$ (2a–c) and related complexes (2d,e)

Rhodium DPCB–Y complexes **2a**–**e** were prepared from $[Rh(\mu\text{-}Cl)(olefin)_2]_2$ complexes [$(olefin)_2 = (cyclooctene)_2$, 1,5-cyclooctadiene (cod), norbornadiene (nbd)] [13]. The cyclooctene ligands of $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ were readily replaced by DPCB–Y in CH_2Cl_2 at room temperature to afford $[Rh(\mu\text{-}Cl)(DPCB–Y)]_2$ in quantitative yields, which were treated subsequently with AgOTf (1 equiv/Rh) in CH_2Cl_2 in the presence of MeCN to give the MeCN complexes **2a**–**c**. On the other hand, since $[Rh(\mu\text{-}Cl)(cod)]_2$ and $[Rh(\mu\text{-}Cl)(nbd)]_2$ bearing diene ligands were unreactive towards direct ligand displacement, they were treated with DPCB–Y in the presence of AgOTf to provide [Rh(cod)(DPCB–Y)]OTf (**2d**,**e**) and [Rh(nbd)(DPCB)]OTf (**2e**). Complexes **2a**–**e** were isolated as purple crystalline solids by recrystallization from CH_2Cl_2/Et_2O.

Unlike the palladium complex **1a**, the rhodium analog **2a** showed an MeCN proton signal in a coordination region without broadening (δ 2.35 at 20 °C), suggesting lower reactivity of **2a** than **1a** towards ligand exchange. The IR spectrum displayed two $\nu_{C\equiv N}$ bands at 2316 and 2279 cm^{-1}. The ^{31}P NMR signal appeared at δ 162.4 in CD_3CN; the chemical shift is lower than that of **1a** (135.7), **2d** (152.4), and **2e** (153.1). It was further noted that the $^1J_{RhP}$ values are strongly dependent on trans influence: **2a** (228 Hz), **2d** (176 Hz), **2e** (189 Hz).

2.3. X-ray structures

ORTEP drawings of **1a**, **2a**, and **2d** are given in Fig. 1. Selected bond distances and angles are listed in Table 1. Complex **1a** adopts a twisted square planar arrangement around palladium; the dihedral angle between the PdP_2 (A) and PdN_2 (G) planes is 6.78(3)°. The C≡N bonds of the MeCN ligands (2.059(3) Å) are somewhat shorter than those reported for $[Pd(MeCN)_2(diphosphine)]^{2+}$ complexes (2.07–2.12 Å) [14]. Furthermore, the Pd–P distance (2.264(1) Å) is considerably shorter than that of [Pd(η^3-allyl)(DPCB–Y)]OTf (2.322(1), 3.326(1) Å) [4].

It has been documented that the phenyl groups at the 1,2-positions of DPCB ligands (E and F in Fig. 1) tend to adopt a parallel orientation with respect to the diphosphinidenecyclobutene skeleton (B) upon coordination [3]. This is due to the occurrence of strong π-back donation from metal to DPCB ligand. Thus, DPCB complexes are stabilized by the formation of a widely spread π-conjugation system including the metal, diphosphinidenecyclobutene skeleton, and phenyl groups. Accordingly, dihedral angles between the DPCB skeleton (B) and the two benzene