

Rhodium complexes of PC^{NHC}P: Oxidative addition of dichloromethane and catalytic hydrosilylation of alkynes affording (*E*)-alkenylsilanes

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Abstract

New rhodium complexes of PC^{NHC}P have been synthesized by using the silver transfer reagent, [Ag₃(PC^{NHC}P)₂Cl]₂ (**2**). In the reaction between **2** and [Rh(COD)Cl]₂ in dichloromethane, the presumably formed nucleophilic Rh^I(PC^{NHC}P)Cl intermediate (**A**), undergoes a C–Cl bond activation of CH₂Cl₂ giving *cis,mer*-Rh^{III}(PC^{NHC}P)(CH₂Cl)Cl₂ (**3**) as the final product. Attempts to isolate **A** affords the oxidative degradation product of *mer*-Rh^{III}(PC^{NHC}P)Cl₃ complex (**4**). In contrast, the rhodium(I) center in Rh(PC^{NHC}P)(CO)Cl (**5**) is stabilized by the π-back bonding of C≡O ligand; a robust complex is, therefore, obtained. The solid-state structures of **2** and **3** were determined by X-ray diffraction. Complexes **3–5** are catalyst precursors for efficient, chemoselective hydrosilylation of alkynes. For the reaction between phenylacetylene and dimethylphenylsilane, a rapid hydrosilylation occurs, producing isomers of alkenylsilanes; then a slow isomerization pathway converts (*Z*)-alkenylsilane to its (*E*)-isomer. For **3**, under catalytic condition, a facile reductive elimination of dichloromethane giving **A** is anticipated. The similarity in reactivity and selectivity between **3**, **4** and **5** suggests the involvement of **A** as the active species in a common catalytic cycle.

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1. Introduction

N-heterocyclic carbenes (NHCs) have attracted much attention because their transition metal complexes display rich coordination chemistry and have wide applicability in catalysis [1]. While monodentate NHC ligands have been shown to be highly active in various catalytic reactions [1c,1d,1e,1f], research efforts have also been devoted to the synthesis of hybrid ligands containing NHC and classical donors, such as nitrogen and phosphorus. Some of these show interesting coordination chemistry [2–5], efficient catalytic applications [6–8], and biological activities [9]. Currently, our laboratory

is also interested in preparing and exploring the potential utilities of new hybrid ligands of NHC [10]. For example, we have synthesized the phosphine-functionalized NHC ligand, PC^{NHC}P (**1**) [10a]. We found that, while palladium complexes of PC^{NHC}P is efficient Heck catalysts [10a], the binuclear ruthenium complex, *fac*-[Ru₂(μ-Cl)₃(PC^{NHC}P)₂]Cl, is active in catalytic transfer hydrogenation [10f]. The reactivity study also shows that the PC^{NHC}P ligand is capable of accommodating extra steric requirement by switching readily from facial to meridional chelating mode [10f].

In this paper, continuing on our interest in PC^{NHC}P, we report on its new rhodium complexes. We followed our previous established procedure of using the trinuclear silver NHC complex, [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂ (**2**), as the PC^{NHC}P transfer reagent [10f]. We found that a reaction between **2** and

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[Rh(COD)Cl]₂ in dichloromethane produced cleanly the intriguing rhodium(III) complex, *cis,mer*-Rh^{III}-(PC^{NHC}P)(CH₂Cl)Cl₂ (**3**), formed by a dichloromethane molecule oxidatively added to the reactive rhodium(I) intermediate, Rh^I(PC^{NHC}P)Cl (**A**). Oxidative addition of small molecules to reactive metal complexes is an important step for the activation of substrates in homogeneous catalysis. Because of the relatively inert C–Cl bond, the activation of dichloromethane requires electron-rich rhodium centers. Rhodium complexes of phosphine [11] and nitrogen ligands [12] and hybrid ligands containing both P- and N-donors [13] are able to mediate the oxidative addition of dichloromethane and in several cases the crystal structures of Rh^{III}(CH₂Cl)Cl were obtained [11b,12b,12c,12d,13b]. Although rhodium complexes of NHC are numerous [1e,1g], **3** represents the first reported case of an oxidative addition of dichloromethane to a rhodium(I) complex containing a NHC moiety. We have also prepared the rhodium(III) trichloride complex, *mer*-Rh^{III}(PC^{NHC}P)Cl₃ (**4**) and the rhodium(I) complex, *mer*-Rh^I(PC^{NHC}P)(CO)Cl (**5**). All the new metal complexes **3–5** are efficient catalyst precursors in hydrosilylation of alkynes affording (*E*)-vinylsilanes as the major product.

2. Experimental section

2.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using a Schlenk line and standard Schlenk technique. All solvents used were purified according to standard procedures [14]. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded at 300.13, 75.48, and 121.49 Hz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ¹H and ¹³C spectra were in ppm relative to residual proton of CDCl₃ (¹H: δ 7.24; ¹³C: δ 77.0) or DMSO-*d*₆ (¹H: δ 2.50; ¹³C: δ 39.5). ³¹P NMR chemical shifts were relative to 85% H₃PO₄ external standard (³¹P: δ 0.0). Infrared spectra were recorded with a Digilab Scimitar FTS 2000 spectrometer. GC/MS analyses were performed on a HP 6890 Series GC system with a HP 5973 mass selective detector, equipped with a HP-5MS capillary column (length: 30 mm, ID: 0.25 mm, film thickness: 0.25 μm). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, National Chung Hsing University, Taiwan. [Rh(COD)Cl]₂ and [Rh(CO)₂Cl]₂ are purchased from commercial source.

2.2. Preparation of *cis*-Rh(PC^{NHC}P)(CH₂Cl)Cl₂ (**3**)

A 10 mL dichloromethane solution of [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂ (0.11 g, 0.078 mmol) and [Rh(COD)Cl]₂

(0.043 g, 0.087 mmol) was stirred at room temperature for 1 h. A grey solid of AgCl was slowly formed, which was filtered off through a plug of Celite. The solvent of the filtrate was removed completely under vacuum. Upon addition of diethyl ether, a greenish-yellow solid was formed which was filtered on a frit and dried under vacuum. Yield: 0.10 g (89%). Anal. Calc. for C₃₂H₃₂N₂P₂Cl₃Rh: C, 53.69; H, 4.51; N, 3.91. Found: C, 53.60; H, 4.49; N, 3.85, m.p.: 245–249 °C. ¹H NMR (CDCl₃): δ 2.69–2.77 (m, 2H, PCHH), 2.96–3.04 (m, 2H, PCHH), 3.61 (td, ³J_{HP} = 8.1 Hz, ²J_{RhH} = 2.8 Hz, 2H, CH₂Cl), 4.34 (pentet, ²J_{HH} = ³J_{HP} = 11.6 Hz, 2H, NCHH), 4.78 (pentet, ²J_{HH} = ³J_{HP} = 11.6 Hz, 2H, NCHH), 6.85 (s, 2H, imi-*H*), 7.31–7.60 (m, 14H, Ph-*H* and imi-*H*), 7.86–7.90 (m, 3H, Ph-*H*), 8.33–8.36 (m, 3H, Ph-*H*). ¹³C{¹H} NMR (CDCl₃): δ 23.9 (t, J_{CP} = 13.5 Hz, PCH₂), 46.3 (s, NCH₂), 121.3 (imi-*C*), 127.9 (dt, ²J_{RhC} = 24.1, J_{CP} = 5.2 Hz, P-*C*), 130.0 (d, ²J_{CP} = 15.0 Hz, C_{ortho}), 132.7 (t, J_{CP} = 4.1 Hz, C_{para}), 135.7 (t, J_{CP} = 5.4 Hz, C_{meta}), signals for the Rh–CH₂Cl and Rh–carbene were not observed. ³¹P{¹H} NMR (CDCl₃): δ 6.4 (d, ¹J_{RhP} = 103.3 Hz).

2.3. Preparation of Rh(PC^{NHC}P)Cl₃ (**4**)

A 10 mL DMF solution of [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂ (0.13 g, 0.091 mmol) and [Rh(COD)Cl]₂ (0.050 g, 0.10 mmol) was heated at 60 °C overnight. A dark brown solid of AgCl and Ag⁰ was slowly formed, which was filtered off through a plug of Celite. The solvent of the filtrate was removed completely under vacuum. Upon addition of diethyl ether, a yellow solid was formed which was filtered on a frit and dried under vacuum. Yield: 90 mg (70%). Anal. Calc for C₃₁H₃₀N₂P₂Cl₃Rh: C, 53.05; H, 4.31; N, 3.99. Found: C, 53.15; H, 4.21; N, 3.95, m.p.: >290 °C. ¹H NMR (CDCl₃): δ 2.90 (br, 4H, PCH₂), 4.58 (br q, ³J_{HH} = ³J_{HP} = 11.2 Hz, 4H, NCH₂), 7.29–7.52 (m, 12H, Ph-*H*), 7.59 (s, 2H, imi-*H*), 7.95–8.09 (m, 8H, Ph-*H*). ¹³C{¹H} NMR (DMSO-*d*₆): δ 24.5 (t, J_{CP} = 13.5 Hz, PCH₂), 45.2 (NCH₂), 123.7 (imi-*C*), 127.6 (t, J_{CP} = 4.8 Hz, C_{ortho}), 130.1 (s, C_{para}), 131.8 (t, J_{CP} = 25.1 Hz, P-*C*), 134.8 (t, ³J_{CP} = 4.6 Hz, C_{meta}), signal for the Rh–C was not observed. ³¹P{¹H} NMR (CDCl₃): δ 1.7 (d, ¹J_{RhP} = 89.1 Hz).

2.4. Preparation of Rh(PC^{NHC}P)(CO)Cl (**5**)

A 10 mL DMF solution of [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂ (0.15 g, 0.10 mmol) and [Rh(CO)₂Cl]₂ (0.040 g, 0.10 mmol) was stirred at room temperature for 2 h. A grey solid of AgCl was formed slowly, which was filtered off through a plug of Celite. The solvent of the filtrate was removed under vacuum. Upon addition of diethyl ether, a dark yellow solid was formed which was filtered on a frit and dried under vacuum. Yield: 0.11 g (77%).

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