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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, $[Ag_3(PC^{NHC}P)_2Cl]Cl_2$ (**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 CH_2Cl_2 giving *cis,mer*-$Rh^{III}(PC^{NHC}P)(CH_2Cl)Cl_2$ (**3**) as the final product. Attempts to isolate **A** affords the oxidative degradation product of *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ 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.

Keywords: Rhodium complex; *N*-heterocyclic carbene; Phosphine; Hybrid ligand; Hydrosilylation; X-ray structural determination

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*-$[Ru_2(\mu\text{-}Cl)_3(PC^{NHC}P)_2]Cl$, 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, $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (**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*-$Rh^{III}(PC^{NHC}P)(CH_2Cl)Cl_2$ (**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 $Rh^{III}(CH_2Cl)Cl$ 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*-$Rh^{III}(PC^{NHC}P)Cl_3$ (**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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ 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 ^{13}C spectra were in ppm relative to residual proton of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.0) or DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.5). ^{31}P NMR chemical shifts were relative to 85% H_3PO_4 external standard (^{31}P: 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-$Rh(PC^{NHC}P)(CH_2Cl)Cl_2$ (3)

A 10 mL dichloromethane solution of $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (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 $C_{32}H_{32}N_2P_2Cl_3Rh$: 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 ($CDCl_3$): δ 2.69–2.77 (m, 2H, PC*H*H), 2.96–3.04 (m, 2H, PCH*H*), 3.61 (td, $^3J_{HP} = 8.1$ Hz, $^2J_{RhH} = 2.8$ Hz, 2H, CH_2Cl), 4.34 (pentet, $^2J_{HH} = {}^3J_{HH} = {}^3J_{HP} = 11.6$ Hz, 2H, NC*H*H), 4.78 (pentet, $^2J_{HH} = {}^3J_{HH} = {}^3J_{HP} = 11.6$ Hz, 2H, NCH*H*), 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*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.9 (t, $J_{CP} = 13.5$ Hz, P*C*H_2), 46.3 (s, N*C*H_2), 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–*C*H_2Cl and Rh–carbene were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.4 (d, $^1J_{RhP} = 103.3$ Hz).

2.3. Preparation of $Rh(PC^{NHC}P)Cl_3$ (4)

A 10 mL DMF solution of $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (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 Ag^0 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 $C_{31}H_{30}N_2P_2Cl_3Rh$: 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 ($CDCl_3$): δ 2.90 (br, 4H, PCH_2), 4.58 (br q, $^3J_{HH} = {}^3J_{HP} = 11.2$ Hz, 4H, NCH_2), 7.29–7.52 (m, 12H, Ph-*H*), 7.59 (s, 2H, imi-*H*), 7.95–8.09 (m, 8H, Ph-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 24.5 (t, $J_{CP} = 13.5$ Hz, P*C*H_2), 45.2 (N*C*H_2), 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. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 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 $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (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%).

Anal. Calc for $C_{32}H_{30}N_2P_2ClORh$: C, 58.33; H, 4.59; N, 4.25. Found: C, 58.11; H, 4.54; N, 4.21, m.p.: 208 °C. ^{1}H NMR ($CDCl_3$): δ 2.69–2.72 (br, 4H, PCH_2), 4.42–4.53 (br m, 4H, NCH_2), 7.33 (s, 2H, imi-*H*), 7.40–7.50 (m, 12H, Ph-*H*), 7.67–7.72 (m, 8H, Ph-*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 25.8 (t, $J_{CP} = 15.2$ Hz, P*C*H$_2$), 47.3 (N*C*H$_2$), 123.5 (imi-*C*), 129.6 (t, $J_{CP} = 5.1$ Hz, C_{ortho}), 131.5 (s, C_{para}), 133.3 (t, $J_{CP} = 6.7$ Hz, C_{meta}), 134.1 (t, $^1J_{CP} = 23.4$ Hz, P–*C*), signals for the Rh–*C* and *C*≡O were not observed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.7 (d, $^1J_{RhP} = 126.2$ Hz). IR (KBr): ν(C≡O) 1933 cm^{-1}.

2.5. General procedure for the hydrosilylation of alkynes

In a typical run, a mixture of alkyne (0.77 mmol), an appropriate amount of hydrosilane (1.1–3 equiv.), and 0.1 mol% of catalyst in 5 mL of chloroform was stirred at 60 °C for an appropriate duration under nitrogen. The solution was allowed to cool and filtered through a pad of Celite. The volatiles were removed under reduced pressure. The residue was then re-dissolved in $CDCl_3$ for ^{1}H NMR or GC/MS analyses. The assignments of (*Z*)-, (*E*)-, and α-alkenylsilanes were based upon spectroscopic comparison with literature [15].

2.6. X-ray data collection

Crystals of **3** and **4** were obtained by vapor diffusion of diethyl ether into their corresponding dichloromethane solution. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighting paper. A suitable crystal of **4** was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. Crystal of **3** was similarly mounted and collected on a Bruker SMART 1000 CCD with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K at the Instruments Center, National Chung Hsing University, Taiwan. Crystallographic data of **3** and **4** are listed in Table 1.

2.7. Solution and structure refinements

All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97 [16]. Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from a standard source [17]. Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. There are two orientations (0.5 occupancy each) for each of the three disordered dichloromethane solvent molecules in **3**.

Table 1
Crystallographic data of **3**–**4**

	Complex **3**	Complex **4**
Empirical formula	$C_{32}H_{32}Cl_3N_2P_2Rh \cdot 2CH_2Cl_2$	$C_{31}H_{30}Cl_3N_2P_2Rh$
Formula weight	885.65	701.77
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	22.379(4)	11.9793(6)
b (Å)	24.663(4)	15.6200(8)
c (Å)	14.263(3)	15.6674(8)
α (°)	90	90
β (°)	102.899(8)	90
γ (°)	90	90
V (Å^3)	7674(2)	2931.6(3)
T (K)	298(2)	150(2)
Z	8	4
No. of unique data	15066	7772
No. of parameters refined	857	352
R_1[a] [$I > 2\sigma I$]	0.0721	0.0583
wR_2[b] (all data)	0.2301	0.1378
Refined flack parameter	–	−0.01(4)

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$.
[b] $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

3. Results and discussion

3.1. Preparation of cis,mer-Rh^{III}(PC^{NHC}P)(CH$_2$Cl)Cl$_2$ (3)

The trinuclear silver complex, [Ag$_3$(PC^{NHC}P)$_2$Cl]Cl$_2$ (**2**), has been utilized successfully as the PC^{NHC}P transfer reagent in the preparation of palladium [10a] and ruthenium complexes of PC^{NHC}P [10f]. Here, we continue to employ **2** as a general PC^{NHC}P transfer reagent for the preparation of its new rhodium complexes (Scheme 1). Initially, we stirred a mixture of **2** and [Rh(COD)Cl]$_2$ in dichloromethane with an anticipated formation of a 16-electron Rh^{I}(PC^{NHC}P)Cl complex (**A**) and AgCl as by-product. In fact, grey solid of AgCl was slowly formed and after a simple workup procedure, a greenish-yellow solid was obtained. Markedly, the subsequent NMR and structural studies reveal that the compound produced is *cis*,*mer*-Rh^{III}(PC^{NHC}P)-(CH$_2$Cl)Cl$_2$ (**3**), formed by the oxidative addition of a dichloromethane solvent molecule to **A**. Complex **3** is air-stable with a good solubility in halogenated solvent. It was characterized by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy and elemental analysis. The presence of a single doublet at δ 6.4 ($^1J_{RhP} = 103.3$ Hz) in its ^{31}P{^{1}H} NMR spectrum shows that the two coordinating phosphorus atoms are chemically equivalent and, therefore, the PC^{NHC}P ligand is chelated in the meridional fashion. In its ^{1}H NMR spectrum, the two multiplets in the upfield region can be assigned to the diastereotopic PCH$_2$ protons, whereas the two apparent pentets at δ 4.34 and 4.78 are due to the diastereotopic NCH$_2$ protons. The presence of the CH$_2$Cl moiety is evidenced

by the presence of a triplet of doublets at δ 3.61 with $^3J_{HP}$ and $^2J_{RhH}$ coupling constants of 8.1 and 2.8 Hz. The CH_2Cl moiety most likely occupies an axial position such that the two chlorides are *cis* to other, as evidenced by the disasterotopic nature of the CH_2 protons. However, the $^{13}C\{^1H\}$ NMR signals due to the CH_2Cl and carbene moieties are not observed.

To probe the structure of **3** and distinguish its *cis*/*trans* configuration, we performed a single-crystal X-ray structural determination. Suitable crystals of **3** were obtained by vapor diffusion of diethyl ether into its corresponding solution. Indeed, the X-ray analysis reveals **3** to be *cis*,*mer*-$Rh^{III}(PC^{NHC}P)(CH_2Cl)Cl_2$ (Fig. 1). Its selected bond distances and angles are tabulated in Table 2. The structure is solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains two independent molecules of **3** and four dichloromethane solvent molecules, three of which are disordered. Because of the almost identical geometrical parameters of the two independent molecules, only one of them will be used for structural discussion. The Rh(1) is in an octahedral coordination environment with the $PC^{NHC}P$ chelated in a meridional fashion and the chloromethyl ligand *trans* to a chloride. The Rh–CH_2Cl distance of 2.086(9) Å is comparable to that found in $[RhCl(CH_2Cl)(edpp)_2]Cl$ (2.078(7) Å) [13b]; shorter than that in $[RhCl(CH_2Cl)(dmpe)_2]Cl$ (2.161(2) Å) [11b]; but longer than those found in $[Rh(py)_3(CH_2Cl)Cl_2]$ (2.045(10) Å) [12c], $[RhCl(CH_2Cl)(edmp)_2]Cl$ (2.050(7) Å) [13b], $[RhCl(CH_2Cl)(dmbpy)(DMSO)]$ (2.046(2) Å) [12d], and $[RhCl_2(CH_2Cl)(2,6\text{-}(C(H)=N\text{–}R)_2C_5H_3N)]$ (R: *i*-Pr, 2.052(5) Å; Cy, 2.052(3) Å and 2.059(3) Å) [12b]. The Rh–carbene bond distance (2.008(9) Å) is slightly shorter than the Rh–CH_2Cl distance; the Rh–Cl bond *trans* to the carbene (2.423(2) Å) is slightly shorter than that *trans* to the chloromethyl ligand (2.501(2) Å). Similar to those reported for $Pd(PC^{NHC}P)$ and $Ru(PC^{NHC}P)$ complexes, the central imdazole ring in **3** is twisted aside forming an overall chiral environment of the complex in the solid state. The twist angle between the best planes defined by the imidazole ring and the equatorial coordination plane is 24.8°, which is the smallest among those found in the ruthenium (27–28°) [10f] and palladium (27–49°) complexes [10a].

3.2. Preparation of *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ (**4**)

Complex **3** contains the chloromethyl ligand which was formed by the oxidative addition of a dichloromethane solvent molecule to the presumably very nucleophilic intermediate **A**. Therefore, we decided to carry out the reaction between **2** and $[Rh(COD)Cl]_2$ in nonhalogenated solvent in the hope of isolating $Rh^I(PC^{NHC}P)$-Cl. Hence, stirring a solution of **2** and the rhodium dimer in DMF at 60 °C slowly produced a turbid solution under an inert atmosphere. After filtration of the solid AgCl, removal of the solvent gave an air-stable yellow solid, which is slightly soluble in halogenated solvent, but dissolves more readily in high polar solvents, such as DMSO and DMF. The compound is characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as elemental analysis. Its $^{31}P\{^1H\}$ NMR spectrum displays a doublet at δ 1.7, which is slightly upfield to that of **3**. The observation of only one phosphorus signal suggests the complex is symmetry-related. In the ^1H NMR spectrum, the NCH_2 and PCH_2 protons are observed as broad signals at δ 2.90 and 4.58, respectively. The

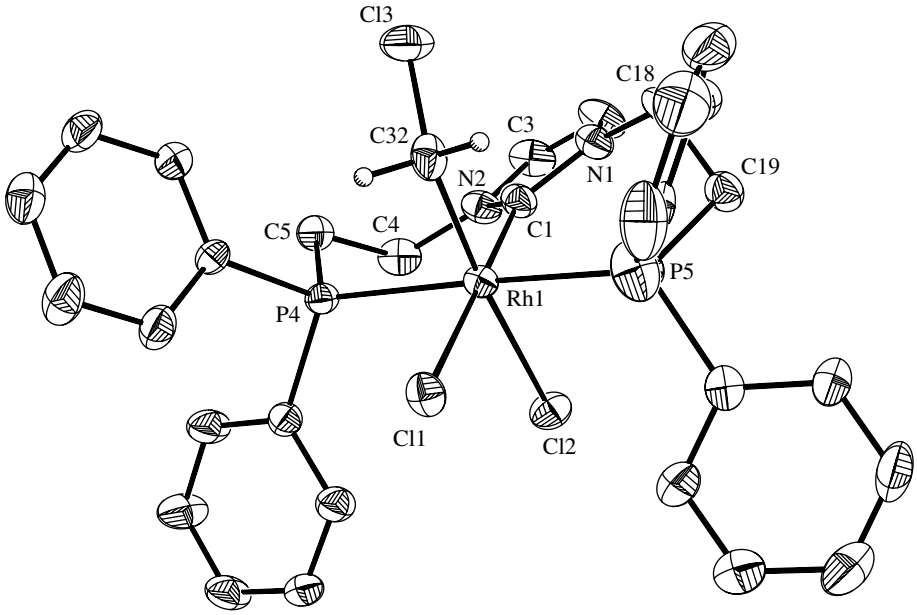


Fig. 1. Thermal ellipsoid plot of **3** at the 30% probability level. Hydrogen atoms (except those on C32) are omitted for clarity.

broadening of these signals suggest a fast interconversion between the left- and right-twist forms, similar to that observed in related palladium complexes [10a]. However, separate signals cannot be obtained even if the DMF-d_6 solution was cooled down to −52 °C, indicating the rapidity of the fluxional process.

A subsequent X-ray structural analysis shows that the product is actually *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ (**4**). Crystals suitable for the structural analysis were grown following a similar procedure of that for **3**. Fig. 2 shows a perspective drawing of the structure. Its selected bond length and bond distances are also listed in Table 2. The structure is solved in the orthorhombic noncentrosymmetric space group $P2_12_12_1$. The asymmetric unit contains a single molecule of $Rh^{III}(PC^{NHC}P)Cl_3$. The Rh(1) atom is in a slightly distorted octahedral coordination environment. The Rh(1)–Cl(2) distance of 2.4395(16) Å is ~0.07 Å longer than the two mutually trans Ru–Cl bond distances, clearly reflecting the bigger *trans* influence of the carbene. The central imidazole ring is also twisted (twist angle = 27.2°) resulting in a chiral conformation with a noncyrstallographic pseudo-C_2 rotation axis passing through the Cl–Ru–C axis. Unlike related structures of $Pd(PC^{NHC}P)$ [10a] and $Ru(PC^{NHC}P)$ complexes [10f] and **3** described above, **4** crystallizes in one of the enantiomeric forms in the crystal lattice. In solution, however, a rapid interconversion between the enantiomers occurs, as evidenced by the broadening of the ethylene protons.

Notably, the formation of *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ from **2** and $[Rh(COD)Cl]_2$ is peculiar. Conceivably, the intermediate complex **A** is highly reactive, which was demonstrated by its capability to activate inert C–Cl bond to afford **3**. Therefore, in the absence of carbon halide, presumably, the reactive $Rh^{I}(PC^{NHC}P)Cl$ is highly unstable, which undergoes oxidative degradation in the presence of Ag^+ and chloride anions affording the Rh(III) product. Arnold et al. [18] has shown that a Ru(III) carbene complex can be obtained from a reaction between the Ru(II) precursor, $RuCl_2(PPh_3)_3$, and the corresponding silver alkoxy carbene transfer reagent. Electrochemical study showed that the silver carbene complex itself is a poor oxidant [18].

3.3. *mer*-$Rh(PC^{NHC}P)(CO)Cl$ (**5**)

Because the electron rich intermediate **A** is not isolable, it can be anticipated that this nucleophilic species can be stabilized by the presence of a carbonyl ligand. Hence, in order to obtain a stable Rh(I) complex of $PC^{NHC}P$, we carry out a reaction between **2** and the Rh(I) precursor, $[Rh(CO)_2Cl]_2$. Following a similar procedure for **3**, an air-stable dark yellow solid was obtained. This compound is also characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR signal for the two equivalent phosphorus atoms is observed at δ 21.7 as a doublet, indicating the meridional coordination of $PC^{NHC}P$. In the ^1H NMR spectrum, the two broad multiplets in the aliphatic region can be assigned to the PCH_2 and NCH_2 protons, respectively. The broadening of these signals suggests a fluxional process similar to that in **4**. Even though in its $^{13}C\{^1H\}$ NMR spectra, the signal due to the carbonyl resonance is not observable, the IR spectrum clearly exhibits an intense absorption band for the carbonyl ligands at 1933 cm^{-1}. The carbonyl absorption of **5** is in accord with rhodium chlorocarbonyl complexes of tridentate ligands reported in the literature. For example, the corresponding absorption band for [RhCl(CO)(PNCHP-κ^3P,N,P)], (PNCHP =

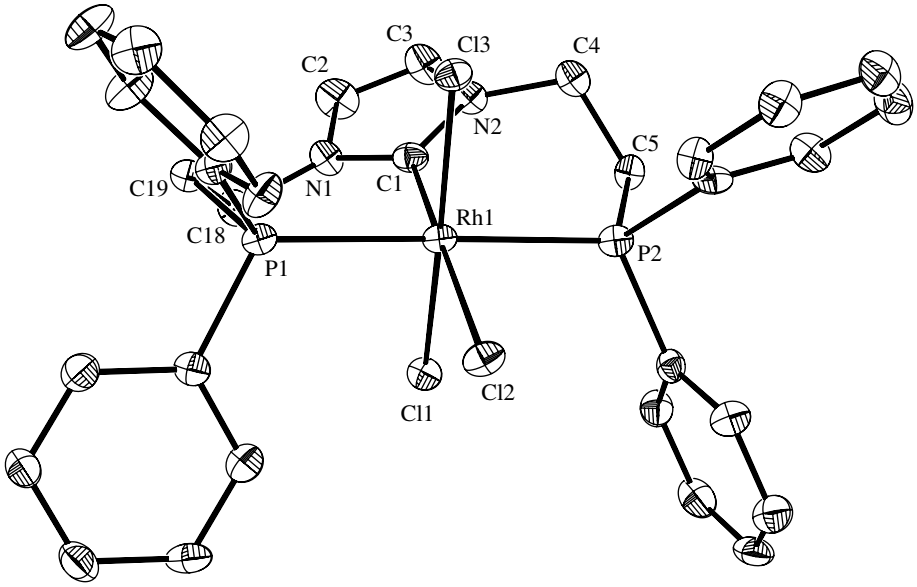


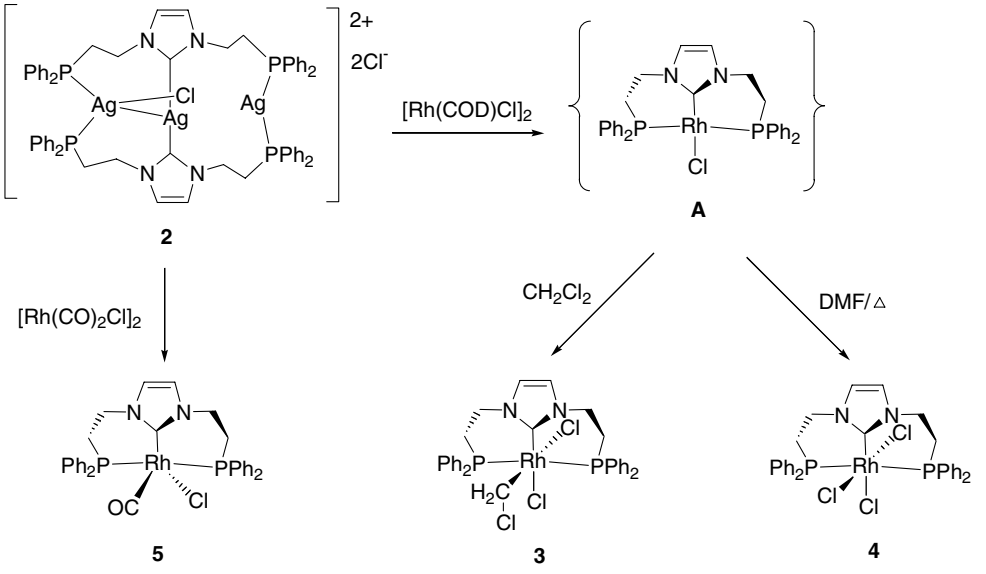
Fig. 2. Thermal ellipsoid plot of **4** at the 30% probability level. Hydrogen atoms are omitted for clarity.

2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCHP)) [19a] and RhCl(CO)(triphos) (triphos = $MeC(CH_2PPh_2)_3$) are at 1959 and 1920 cm^{-1} [19b], respectively. Unfortunately, crystals suitable for structural analysis were failed to obtain so that the stereochemistry of **4** is not fully established; but based on the meridional coordination of $PC^{NHC}P$ and the numerous five-coordinate rhodium(I) complexes reported, a trigonal bipyramidal coordination geometry of the rhodium(I) center can be safely assumed.

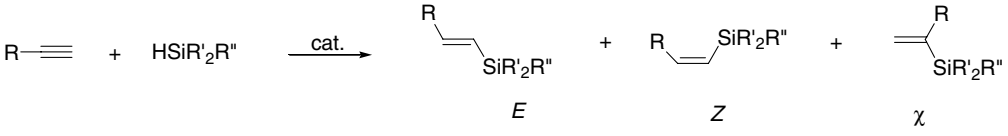
3.4. Catalytic hydrosilylation of alkynes with hydrosilanes

Alkenylsilanes are important building blocks in organic synthesis. They are commonly prepared by the transition metal-catalyzed hydrosilylation of alkynes [20]. Late transition metal complexes of platinum, rhodium, and, ruthenium are most frequently employed. However, the methods are usually encountered with regio- and stereo-selectivity problem (Scheme 2). Therefore, there is a continuous interest in searching metal catalysts with improved selectivity. Rhodium catalysts, in particular, are attracting attention because high regio- and stereoselectivity for the alkenylsilanes can be achieved [20a,21]. Recently, rhodium complexes of NHC have also been employed as catalysts in the hydrosilylation [22]. Along this direction, we are interested to explore if the two new Rh(III) complexes **3** and **4** and the Rh(I) complex **5** with the hybrid ligand $PC^{NHC}P$ are also effective catalysts.

The catalytic property of **3**–**5** in hydrosilylation of terminal alkynes with hydrosilanes was summarized in Tables 3–6. It has been shown that the selectivity in most transition-metal catalyzed hydrosilylation is highly dependent on factors such as substrates used, temperature, and solvent [23]; therefore, we employ the hydrosilylation of phenylacetylene (**6**) with dimethylphenylsilane (**7**) as the standard for the initial tuning of reaction conditions. In general, the reaction catalyzed by **3** affords the (*E*)-isomer as the major product (Table 3). The hydrosilylation is, in fact, very rapid as complete consumption of phenylacetylene was achieved in just 15 min with a catalyst loading of 0.1 mol% and 1:3 molar ratio of **6**/**7** (entry 5). The $E/Z/\alpha$ distribution is 60:23:17. Intriguingly, the E/Z selectivity is improved significantly with a prolonged reaction time (entries 5–11). In the initial first 6 h, the $E/Z/\alpha$ distribution remains approximately constant. But subsequently after 12 h, a stereoselective production of (*E*)-isomer was achieved (entry 9). Eventually, an optimum 88% yield of (*E*)-isomer was achieved at 24 h (entry 11). The amount of the α-isomer remains approximately constant with time. The catalytic data suggests the occurrence of a rapid hydrosilylation reaction producing isomers of alkenylsilanes. After the complete consumption of phenylacetylene, a relatively slow isomerization pathway, which converts the (*Z*)-alkenylsilane to its *E*-isomer is



Scheme 1.



Scheme 2.

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**–**4**

Complex ***3***			
Rh(1)–C(1)	2.008(9)	Rh(1)–Cl(1)	2.423(2)
Rh(1)–P(1)	2.332(3)	Rh(1)–Cl(2)	2.501(2)
Rh(1)–P(2)	2.366(3)	Rh(1)–C(32)	2.076(9)
C(1)–Rh(1)–Cl(1)	177.5(3)	Cl(1)–Rh(1)–P(2)	88.82(8)
Cl(2)–Rh(1)–C(32)	174.9(3)	Cl(1)–Rh(1)–Cl(2)	97.00(8)
P(1)–Rh(1)–P(1)	175.00(9)	Cl(1)–Rh(1)–C(32)	87.1(3)
C(1)–Rh(1)–P(1)	91.9(3)	C32–Rh(1)–P(1)	87.9(3)
C(1)–Rh(1)–P(2)	93.1(3)	C32–Rh(1)–P(2)	91.0(3)
C(1)–Rh(1)–Cl(2)	81.5(3)	Cl(2)–Rh(1)–P(1)	95.39(9)
C(1)–Rh(1)–C(32)	94.5(4)	Cl(2)–Rh(1)–P(2)	86.09(9)
Cl(1)–Rh(1)–P(1)	86.26(8)	Rh(1)–C32–Cl(3)	119.0(5)
Complex ***4***			
Rh(1)–C(1)	2.003(7)	Rh(1)–Cl(1)	2.3615(17)
Rh(1)–P(1)	2.3714(18)	Rh(1)–Cl(2)	2.4395(16)
Rh(1)–P(2)	2.3589(19)	Rh(1)–Cl(3)	2.3609(16)
C(1)–Rh(1)–Cl(2)	176.1(2)	Cl(2)–Rh(1)–P(2)	86.28(6)
Cl(1)–Rh(1)–Cl(3)	171.41(6)	Cl(2)–Rh(1)–P(1)	89.59(6)
P(1)–Rh(1)–P(2)	175.41(7)	Cl(1)–Rh(1)–Cl(2)	92.25(6)
C(1)–Rh(1)–Cl(1)	84.2(2)	Cl(3)–Rh(1)–P(1)	86.02(6)
C(1)–Rh(1)–Cl(3)	87.2(2)	Cl(3)–Rh(1)–P(2)	92.44(6)
C(1)–Rh(1)–P(2)	91.9(2)	Cl(1)–Rh(1)–P(1)	95.14(6)
C(1)–Rh(1)–P(1)	92.3(2)	Cl(1)–Rh(1)–P(2)	87.03(6)
Cl(2)–Rh(1)–Cl(3)	96.27(6)		

Table 3
Hydrosilylation of PhC≡CH (**6**) with $HSiMe_2Ph$ (**7**) catalyzed by **3**[a]

Entry	Cat. loading, mole%	**6**/**7**	Time	Yield, %[b]	*E*	*Z*	α
1	0.1	1/1.1	15 h	100	56	28	16
2	0.1	1/1.1	24 h	100	74	10	16
3	0.1	1/1.1	30 h	100	67	15	18
4	0.1	1/2	24 h	100	78	0	22
5	0.1	1/3	15 min	100	60	23	17
6	0.1	1/3	30 min	100	56	24	20
7	0.1	1/3	1 h	100	53	26	21
8	0.1	1/3	6 h	100	54	21	25
9	0.1	1/3	12 h	100	83	0	17
10	0.1	1/3	18 h	100	81	0	19
11	0.1	1/3	24 h	100	88	0	12
12	0.01	1/3	1 hr	100	38	30	32
13	0.001	1/3	30 min	100	42	19	39
14	0.001	1/3	24 h	100	75	8	17
15	0.001[c]	1/3	12 h	81	48	35	17
16	0.001[c]	1/3	24 h	100	43	34	23
17[d]	0.1	1/3	24 h	100	93	4	3
18[e]	0.1	1/3	24 h	100	93	3	4

[a] 60 °C, 0.5 mL of $CHCl_3$.
[b] NMR yield.
[c] At R.T.
[d] 0.1 mol% of NaI added.
[e] 0.2 mol% of NaI added.

in operation. The isomerization profile of **3** is consistent with the findings of Mori et al. [24] which showed that $RhI(PPh_3)_3$, in the presence of a hydrosilane, can catalyze the isomerization of (*Z*)-alkenylsilanes to (*E*)-isomers. Peris et al. [22a] reported a similar (*Z*)–(*E*) isomerization in the hydrosilyation of alkynes catalyzed

Table 4
Effect of the solvent on the hydrosilylation of PhC≡CH with $HSiMe_2Ph$ catalyzed by **3**[a]

Entry	Solvent	Yield, %[b]	*E*	*Z*	α
1	$CHCl_3$	100	83	0	17
2	THF	100	78	11	11
3	Acetone	100	61	10	29
4	DMF	100	79	0	21
5	Acetonitrile	100	89	5	6

[a] 0.1 mol% of **3**, 60 °C, 12 h, 0.5 mL of solvent, alkyne/hydrosilane = 1:3.
[b] NMR yield.

Table 5
Hydrosilylation of various alkynes and hydrosilanes catalyzed by **3**[a]

Entry	Alkyne	Hydrosilane	Yield, %[b]	*E*	*Z*	α
1	PhC≡CH	$HSiMe_2Ph$	100	88	0	12
2	PhC≡CH	$HSiEt_3$	100	71	3	26
3	PhC≡CH	$HSiMe_2(t\text{-Bu})$	100	54	26	20
4	3,3-Dimethyl-1-butyne	$HSiMe_2Ph$	100	83	0	17
5	3,3-Dimethyl-1-butyne	$HSiEt_3$	95	32	13	55
6	3,3-Dimethyl-1-butyne	$HSiMe_2(t\text{-Bu})$	0	0	0	0

[a] 0.1 mol% of **3**, 60 °C, 24 h, 0.5 mL of $CHCl_3$, alkyne/hydrosilane = 1:3.
[b] NMR yield.

Table 6
Hydrosilylation of PhC≡CH with $HSiR'_3$ catalyzed by **3**–**5**[a]

Entry	Catalyst	$HSiR'_3$	Yield, %[b]	*E*	*Z*	α
1	**3**	$HSiMe_2Ph$	100	88	0	12
2	**4**	$HSiMe_2Ph$	100	80	0	20
3	**5**	$HSiMe_2Ph$	100	85	0	15
4	**3**	$HSiEt_3$	100	71	3	26
5	**4**	$HSiEt_3$	100	81	2	17
6	**5**	$HSiEt_3$	100	82	0	18
7	**3**	$HSiMe_2(t\text{-Bu})$	100	54	26	20
8	**4**	$HSiMe_2(t\text{-Bu})$	100	55	23	22
9	**5**	$HSiMe_2(t\text{-Bu})$	100	54	21	25

[a] 0.1 mol% of cat., 60 °C, 24 h, 0.5 mL of $CHCl_3$, alkyne/hydrosilane = 1:3.
[b] NMR yield.

by the rhodium complexes with chelating and pincer NHC. A comparison of entries 2, 4, and 11 indicates the importance of excess hydrosilane in the isomerization. The hydrosilylation can be catalyzed by trace amount of catalyst as shown by entries 12–15. A catalyst loading of 0.001 mol% can afford quantitative production of alkenylsilanes in 30 min (entry 13) at 60 °C; however, when the reaction is conducted at room temperature, a prolonged reaction time of 12–24 h is required (entries 15–16). A comparison of entries 14 and 16 clearly shows the temperature dependence of the isomerization pathway. It has been shown that cationic rhodium complexes exhibit a general (*E*)-selectivity [21b,25], whereas neutral rhodium complex provides

(*Z*)-alkenylsilanes predominately [21a,26]. The addition of NaI to the catalytic reaction should suppress the dissociation of Rh–Cl bond and hence the (*Z*)-selectivity should be enhanced [21d]. In contrast, entries 17 and 18 show that, in the presence of NaI, the (*E*)-isomer still predominates with 93% of yield, whereas the amount of α-isomer formed is significantly suppressed. The observed (*E*)-selectivity can be attributed again to the presence of the isomerization pathway.

Initially, we employed chloroform as solvent. In Table 4, we looked in different solvents and found that both DMF and acetonitrile can replace chloroform to achieve same level of selectivity. A partially optimized reaction conditions: 0.1 mol% of catalyst at 60 °C with a 1:3 molar ratio of alkyne/hydrosilane in chloroform, is then applied for the hydrosilanes and catalyst screening (Tables 5 and 6). Table 5 shows that the selectivity depends markedly on the hydrosilanes used. A comparison of entries 1 and 3 indicates that the bulky *t*-Bu group on the hydrosilane lowers the stereoselectivity. The presence of steric bulkiness in both alkyne and hydrosilane stops the catalytic activity (entry 6). Entries 1–3 of Table 6 clearly shows that the trivalent *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ and monovalent *mer*-$Rh(PC^{NHC}P)(CO)Cl$ are as effective as *cis*,*mer*-$Rh^{III}(PC^{NHC}P)(CH_2Cl)Cl_2$ in the stereospecific production of *E*-isomer. However, consistent with the data in Table 5, use of hydrosilanes other than $HSiMe_2Ph$, reduces the selectivity (entries 4–9). The similarity of reactivity and selectivity between **3**, **4** and **5** suggests a common active species involved.

It should be noted that there are possible competing pathways for the consumption of alkynes; the dimerization, cyclotrimerization, and polymerization of phenylacetylene and the dehydrogenative silylation have been observed for various catalysts [15a,15b,21c,21d] which resulted in lower yields of the desirable alkenylsilanes. Complexes **3**–**5**, however, provide a high chemoselectivity for the hydrosilylation. A control experiment with a solution of **3** and phenylacetylene without the addition of dimethylphenylsilane shows that the alkyne is not consumed; the GC/MS analysis of a typical catalytic solution also confirms the absence of trimeric, dimeric and oligomeric products of alkyne and dehydrosilylation product. In this regard, even though the catalytic system, $[Rh(COD)_2]BF_4/2PPh_3$, is superior to **3** in stereo- and regio-selectivity, the hydrosilylation of phenylacetylene was accompanied by polymerization [22a,21b], whereas **3** is chemoselective.

4. Conclusions

We have successfully prepared new rhodium complexes of $PC^{NHC}P$ by silver carbene transfer reaction using $[Ag_3(PC^{NHC}P)_2Cl]Cl_2$ (**2**). In the reaction between **2** and $[Rh(COD)Cl]_2$ in dichloromethane, the final product of *cis*,*mer*-$Rh^{III}(PC^{NHC}P)(CH_2Cl)Cl_2$ is undoubtedly formed via the oxidative addition of dichloromethane to a $Rh^{I}(PC^{NHC}P)Cl$ complex. Even though attempts to isolate this intermediate **A** met without success, it is conceivable from its activation of inert C–Cl bond that the complex contains an electron rich rhodium(I) center supported by $PC^{NHC}P$. In the absence of carbon halide, this reactive $Rh^{I}(PC^{NHC}P)Cl$ undergoes oxidative degradation affording the *mer*-$Rh^{III}(PC^{NHC}P)Cl_3$ complex. In contrast, the rhodium(I) center in *mer*-$Rh(PC^{NHC}P)(CO)Cl$ is stabilized by the π-back bonding of C≡O ligand; consequently, a stable complex can be obtained.

Complexes **3**–**5** are highly efficient in the hydrosilylation of alkynes with hydrosilanes producing alkenylsilanes in chemoselective fashion. For the reaction between phenylacetylene and dimethylphenylsilane, a rapid hydrosilylation occurs producing isomers of alkenylsilanes and then a slow isomerization pathway converts (*Z*)-alkenylsilane to its (*E*)-isomer. A generally accepted catalytic cycles for the hydrosilylation involves a rhodium(I) catalytic species which allows the initial oxidative addition of hydrosilane substrate [21a]. Undoubtedly, complex **3**, via the reductive elimination of dichloromethane, produces $Rh^{I}(P^{NHC}P)Cl$, which is presumably the initial active species in the catalytic cycle. The similarity in reactivity and selectivity between **3**, **4** and **5**, in fact, suggests the involvement of $Rh^{I}(P^{NHC}P)Cl$ as the active species in a common catalytic cycle. In fact, the quantitative production of alkenylsilanes achieved by **3** in 15 min appears to be the most efficient reported in the literature (see Table 3, entry 5). However, the overall stereoselectivity (after the isomerization step) is inferior to that catalyzed by $[Rh(COD)_2]BF_4/2PPh_3$ [21b]. Nevertheless, complex **3** represents the most efficient catalyst among other rhodium NHC complexes reported [22a,22b].

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for **3** and **4** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 270936 and 270937. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated

with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.025.

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