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Note

Ruthenium vinylidene and carbyne complexes containing a multifunctional tridentate ligand with a PNN donor set

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Abstract

The neutral, octahedral ruthenium vinylidene complexes *mer*,*trans*-[(PNN)Cl_2Ru(CCHR)] (PNN = *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine; R = Ph, **1a**; R = ^{t}Bu, **1b**) are reported. An X-ray crystallographic study of **1a** confirms the tridentate, meridional coordination mode of the PNN ligand. Compounds **1a** and **1b** undergo regioselective electrophilic addition with $HBF_4 \cdot Et_2O$ at C_β of the vinylidene ligand at low temperatures, and are cleanly and quantitatively converted to the ruthenium carbynes *mer*,*trans*-[(PNN)Cl_2Ru(CCH_2R)][BF_4] (R = Ph, **2a**; R = ^{t}Bu, **2b**). Carbynes **2a** and **2b** are stable only at low temperatures (<−50 °C). Complex **1a** undergoes ligand substitution with L to yield *mer*,*trans*-[(PNN)Cl_2Ru(L)] (L = MeCN, **3a**; L = CO, **3b**).

Keywords: Ruthenium; Vinylidene; Carbyne; Electrophilic addition; Hemilabile

1. Introduction

Over the past decade, the explosive development of well-defined and highly efficient catalysts for olefin metathesis has been accompanied by a rapid expansion in applications of these catalysts in a variety of C–C bond forming reactions in organic and polymer synthesis [1]. Many of the greatest advances have involved the Grubbs' class of ruthenium carbene catalysts [2]. Despite the tremendous interest in refining and applying these catalysts, considerably less attention has been given to the development of well-defined catalysts capable of mediating alkyne metathesis [3]. Currently, alkyne metathesis is limited to catalysts based on early metals, primarily molybdenum and tungsten. Alternatively, late metal ruthenium carbyne complexes [4] may possess similar properties, and demonstrate novel reactivity patterns and substantial promise as alkyne metathesis catalysts, much like their ruthenium carbenoid counterparts.

In our continuing quest to develop alkyne metathesis-active ruthenium carbyne complexes [4b,4f], we wish to report some results which illustrate the capacity and extent of the potentially tridentate ligand *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine [5] (PNN, Scheme 1) to serve as a supporting ligand in ruthenium carbyne chemistry. Our decision to consider this ligand was motivated by the expectation that the diphenylphosphino and imino groups of the PNN ligand might form a substitutionally inert anchor to the metal, while the pyridyl group could be reversibly displaced by substrate (i.e., hemilabile behaviour) under catalytic conditions [4a,5a,5d]. In this way, the hemilabile PNN ligand could facilitate metal carbyne-mediated alkyne metathesis by furnishing a vacant site for alkyne substrate to coordinate to the carbyne catalyst, but also stabilize the catalyst in its resting state through re-attachment of the pyridyl group to the metal.

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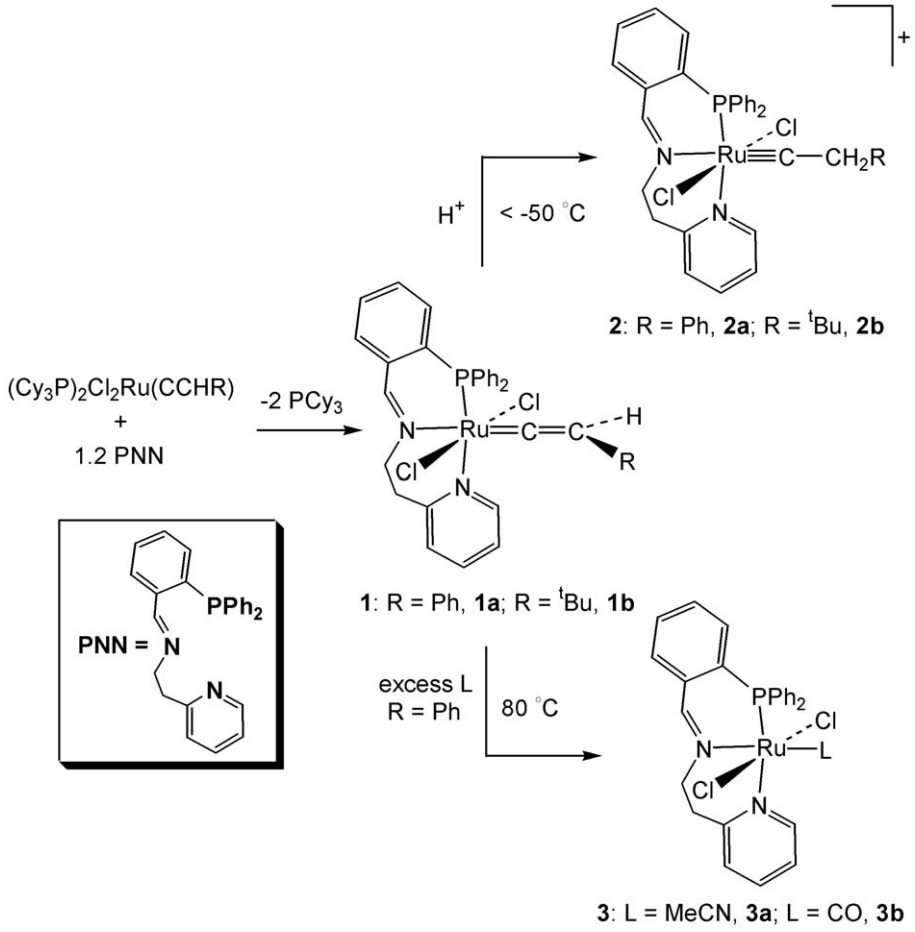

Scheme 1.

2. Experimental

All experiments and manipulations were conducted under an inert atmosphere of prepurified N_2 using standard Schlenk techniques. Bulk solvents used in large-scale preparations were rigorously dried, and either distilled under nitrogen immediately prior to use, or stored over activated 4A molecular sieves in bulbs with Teflon taps and purged with nitrogen prior to use: CH_2Cl_2 (CaH_2); benzene, toluene, diethyl ether and hexanes (sodium metal/benzophenone); acetonitrile (4A molecular sieves). NMR solvents used in solution structure elucidations were dried with appropriate drying agents, vacuum distilled, freeze–pump–thaw degassed three times, and stored in bulbs with Teflon taps: $CDCl_3$ (anhydrous $CaCl_2$); CD_2Cl_2 (CaH_2). NMR spectra (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) were obtained using a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to solvent peaks (^1H and ^{13}C) or external 85% H_3PO_4(^{31}P). Elemental analyses were performed on a CEC 240XA analyzer by the Lakehead University Instrumentation Laboratory. The ruthenium vinylidene precursors [$(Cy_3P)_2Cl_2Ru(CCHR)$] (R = Ph or ^{t}Bu) [6] and the ligand *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine (PNN) [5a] were prepared as described in the literature.

2.1. Synthesis of *mer,trans*-[(PNN)Cl_2Ru(CCHR)] (**1**: R = Ph, **1a**; R = ^{t}Bu, **1b**)

A typical procedure involved the following. The complex [$(Cy_3P)_2Cl_2Ru(CCHR)$] (0.599 mmol) and a slight excess of the ligand PNN (0.719 mmol) were combined and dissolved in benzene (20 mL). The mixture was stirred under nitrogen for 24 h (for R = Ph, the mixture requires an additional 60 min at reflux to ensure completion). The solvent was then removed under reduced pressure. The remaining residue was stirred in hexanes (60 mL) for ca. 10 min and then filtered. The solid was dried under reduced pressure. Analytically pure samples were obtained by recrystallizing the products from CH_2Cl_2/diethyl ether via slow diffusion. Data for complex **1a**: Yield: 75%. Anal. Calc. for $C_{34}H_{29}Cl_2N_2PRu$: C, 61.07; H, 4.38; N, 4.19. Found: C, 61.10; H, 4.77; N, 3.97%. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 9.97 (m, 1H, *o*-H of py), 8.65 (s, 1H, imino H), 7.74–6.97 (23H, benzylidene, Ph and py), 4.69 (d, 1H, CC*H*Ph, $^4J_{PH} = 5$ Hz), 4.94 (br m, 2H, NCH_2CH_2py), 3.60 (br m, 2H, NCH_2CH_2py). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 367.4 (d, Ru*C*, $^2J_{PC} = 22.1$ Hz), 165.6 (d, imino C), 162.1 (s, py), 155.5 (s, py), 137.6 (d, benzylidene), 137.4 (s, py), 137.0 (d, benzylidene), 135.5 (s, benzylidene), 134.5 (d, Ph), 132.7 (d,

benzylidene), 131.8 (d, benzylidene), 131.5 (s, py), 130.2 (s, Ph), 128.7 (m, Ph), 127.9 (d, Ph), 127.8 (d, Ph), 126.1 (s, Ph), 124.9 (s, benzylidene), 123.2 (s, py), 113.3 (s, RuC*C*), 62.4 (s, N*C*H_2CH_2py), 36.9 (s, NCH_2*C*H_2py). $^{31}P\{^1H\}$ (202.3 MHz, $CDCl_3$, 22 °C): 50.2 (s, *P*Ph_2). Data for complex **1b**: Yield: 75%. Anal. Calc. for $C_{32}H_{33}Cl_2N_2PRu$: C, 59.26; H, 5.13; N, 4.32. Found: C, 59.35; H, 5.26; N, 4.22%. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 10.39 (m, 1H, *o*-H of py), 8.64 (s, 1H, imino H), 7.71–7.03 (18H, benzylidene, Ph and py), 4.47 (br m, 2H, NCH_2CH_2py), 3.64 (d, 1H, CC*H* ^{t}Bu, $^4J_{PH} = 5$ Hz), 3.60 (br m, 2H, NCH_2CH_2py), 0.95 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): 364.3 (d, Ru*C*, $^2J_{PC} = 21.6$ Hz), 165.8 (d, imino C), 162.6 (s, py), 154.8 (s, py), 137.5 (d, benzylidene), 137.3 (s, py), 137.2 (d, benzylidene), 135.4 (s, benzylidene), 134.5 (d, Ph), 132.6 (d, benzylidene), 132.5 (d, benzylidene), 131.3 (d, py), 130.0 (d, Ph), 128.8 (d, Ph), 127.9 (d, Ph), 125.9 (d, benzylidene), 122.4 (s, py), 119.5 (s, RuC*C*), 62.4 (s, N*C*H_2CH_2py), 37.0 (s, NCH_2*C*H_2py), 32.6 (s, *C*Me_3), 32.2 (s, C*Me*). $^{31}P\{^1H\}$ (202.3 MHz, $CDCl_3$, 22 °C): 51.3 (s, *P*Ph_2).

2.2. Low temperature observation of mer,trans-[(PNN)Cl_2Ru(CCH_2R)][BF_4] (2: R = Ph, **2a**; R = ^{t}Bu, **2b**)

A typical procedure involved the following. Complex **1** (0.0484 mmol) was added to a 5 mm NMR tube which was then fitted with a rubber septum and finally evacuated/purged with N_2. CD_2Cl_2 (0.6 mL) was added via syringe and the solution was cooled to −78 °C. Once cool, the deep red solution was treated with a slight excess of $HBF_4 \cdot Et_2O$ (0.0532 mmol, 8.7 μL of a 54% solution in Et_2O). An instant colour change from deep red to orange was observed. The sample was then transferred quickly to a precooled (−50 °C) NMR probe and data acquisition was performed immediately. The quantitative formation of **2** was confirmed by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. Data for complex **2a**: ^1H NMR (499.9 MHz, CD_2Cl_2, −50 °C): 8.83 (m, 1H, *o*-H of py), 8.63 (s, 1H, imino H), 7.98–6.83 (23H, benzylidene, Ph and py), 4.13 (br m, 2H, NCH_2CH_2py), 3.86 (s, 2H, RuCCH_2Ph), 3.35 (br m, 2H, NCH_2CH_2py). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, −50 °C): 334.5 (d, Ru*C*, $^2J_{PC} = 17.7$ Hz), 168.5 (d, imino C), 161.7 (d, py), 157.5 (s, py), 140.3 (s, py), 138.3 (d, benzylidene), 135.2 (d, benzylidene), 134.8 (m, benzylidene), 134.7 (d, Ph), 134.0 (s, py), 133.3 (s, Ph), 131.4–129.9 (m, Ph), 129.5 (d, Ph), 129.0 (d, benzylidene), 126.0 (d, Ph), 125.0 (s, py), 122.9 (s, Ph), 122.1 (d, benzylidene), 70.4 (s, RuCCH_2Ph), 59.7 (s, N*C*H_2CH_2py), 36.0 (s, NCH_2*C*H_2py). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −50 °C): 32.2 (s, *P*Ph_2). Data for complex **2b**: ^1H NMR (499.9 MHz, CD_2Cl_2, −20 °C): 9.15 (m, 1H, *o*-H of py), 8.69 (s, 1H, imino C), 8.00–7.05 (18H, benzylidene, Ph and py), 4.12 (br m, 2H, NCH_2CH_2py), 3.53 (br m, 2H, NCH_2CH_2py), 2.51 (s, 2H, RuCCH_2^{t}Bu), 1.07 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, −20 °C): 346.9 (d, Ru*C*, $^2J_{PC} = 18.2$ Hz), 169.5 (d, imino C), 162.3 (d, py), 157.9 (d, py), 140.6 (s, py), 138.5 (d, benzylidene), 135.6 (d, benzylidene), 135.3 (d, benzylidene), 134.7 (d, Ph), 134.5 (d, benzylidene), 134.0 (d, py), 133.2 (d, Ph), 129.5 (d, Ph), 128.8 (d, benzylidene), 125.6 (d, Ph), 124.6 (s, py), 122.7 (d, benzylidene), 69.8 (s, RuCCH_2^{t}Bu), 59.5 (s, N*C*H_2CH_2py), 39.3 (s, NCH_2*C*H_2py), 35.9 (s, *C*Me_3), 31.4 (s, C*Me*$_3$).$^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −20 °C): 30.9 (s, *P*Ph_2).

2.3. Synthesis of mer,trans-[(PNN)Cl_2Ru(MeCN)] (**3a**)

Complex **1a** (0.210 g, 0.315 mmol) was dissolved in benzene (10 mL). Excess acetonitrile (1 mL) was added via syringe and the mixture was refluxed for 48 h. During this time, a red solid had deposited. Once the mixture had cooled, the solid was filtered off and washed with diethyl ether (2 × 10 mL) before drying under reduced pressure. Complex **3a** was found to be insoluble in benzene and toluene, and only sparingly soluble in $CHCl_3$ and CH_2Cl_2. Yield: 87%. Anal. Calc. for $C_{28}H_{26}Cl_2N_3PRu$: C, 55.58; H, 4.33; N, 6.95. Found: C, 56.07; H, 4.58; N, 6.82%. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 9.45 (br m, 1H, *o*-H of py), 8.77 (br s, 1H, imino H), 7.70–7.09 (18H, benzylidene, Ph and py), 4.42 (br m, 2H, NCH_2CH_2py), 3.51 (br m, 2H, NCH_2CH_2py), 1.92 (s, *Me*CN). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): 60.7 (s, *P*Ph_2).

2.4. Synthesis of mer,trans-[(PNN)Cl_2Ru(CO)] (**3b**)

Complex **1a** (0.189 g, 0.283 mmol) was dissolved in toluene (20 mL). A gentle stream of CO was passed through the solution while it was maintained at 80 °C for 72 h. During this time, a yellow solid had deposited. The mixture was allowed to cool to room temperature and the volatiles were removed under reduced pressure. The yellow solid that remained was washed with diethyl ether (3 × 20 mL) and dried under reduced pressure. Yield: 77%. An analytically pure sample was obtained by recrystallizing the product from CH_2Cl_2/diethyl ether via slow diffusion. Anal. Calc. for $C_{27}H_{23}Cl_2N_2OPRu$: C, 54.64; H, 3.91; N, 4.72. Found: C, 54.21; H, 4.18; N, 4.50%. IR (Nujol): ν(CO) = 1945 (s) cm^{-1}. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): 9.43 (m, 1H, *o*-H of py), 8.74 (s, 1H, imino H), 7.75–7.05 (18H, benzylidene, Ph and py), 4.44 (br m, 2H, NCH_2CH_2py), 3.55 (br m, 2H, NCH_2CH_2py). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): 53.3 (s, *P*Ph_2).

2.5. X-ray crystallographic study

Suitable crystals of complex **1a** were grown from a CH_2Cl_2/diethyl ether solution at room temperature under nitrogen over a period of several weeks. A crystal was mounted on a glass fibre and the diffraction data were collected on a Siemens SMART/CCD diffractometer equipped with an LT-II low-temperature device. The data

were collected at −50 °C using Mo Kα radiation; Lorentz and polarization corrections were applied. Diffraction data were corrected for absorption using SADABS. Direct methods and Fourier techniques were used to solve the structure; refinement was conducted using full-matrix least-squares calculations and SHELXTL PC V 5.03. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as riding models and updated after each refinement. Two molecules of recrystallization solvent were located in the lattice, each at approximately 0.5 occupancy and each positioned on an inversion centre. Diethyl ether was disordered; CH_2Cl_2 was not. Crystal data, conditions for the intensity collection and features of the structural refinement: $C_{36.5}H_{35}Cl_3N_2O_{0.5}PRu$, $M_W = 748.05$, $\lambda = 0.71073$ Å, monoclinic, space group $C2/c$, $a = 17.3346(11)$ Å, $b = 12.0982(7)$ Å, $c = 33.166(2)$ Å, $\alpha = 90°$, $\beta = 101.4890(10)°$, $\gamma = 90°$, $V = 6816.1(7)$ Å^3, $Z = 8$, d (calcd.) $= 1.458$ Mg/m^3, $F(000) = 3056$, $T = 223(2)$ K, $\mu = 0.772$ mm^{-1}, crystal size $= 0.4 \times 0.48 \times 0.5$ mm, data collection range $1.25 \leqslant \theta \leqslant 25.00°$, $-20 \leqslant h \leqslant 20$, $-14 \leqslant k \leqslant 14$, $-38 \leqslant l \leqslant 39$, $R_1 = 0.0391$, wR_2 (all data) $= 0.0766$.

3. Results and discussion

One essential goal of this work was to establish first a convenient route towards the synthesis of neutral ruthenium vinylidene complexes containing the PNN ligand. We reasoned that such complexes presumably would serve as suitable precursors to ruthenium carbyne complexes [4b,4f]. Within this context, we found that the ruthenium vinylidene complexes $[(Cy_3P)_2Cl_2Ru(CCHR)]$ (R = Ph or ^{t}Bu) [6] undergo a clean ligand exchange reaction with a slight excess of the ligand PNN to yield the complexes *mer*,*trans*-$[(PNN)Cl_2Ru(CCHR)]$ (**1**: R = Ph, **1a**; R = ^{t}Bu, **1b**) in good isolated yields (typically ca. 70–80%) as air-stable light red (**1a**) or orange-brown (**1b**) solids (Scheme 1).

Preservation of the vinylidene ligand, and the tridentate coordination mode of the PNN ligand in each of **1a** and **1b** were established using multinuclear NMR spectroscopy. For example, the C_α atom of the vinylidene ligand in each complex gives rise to a doublet (**1a**, $\delta = 367.4$; **1b**, $\delta = 364.3$) in the $^{13}C\{^1H\}$ NMR spectrum, with $^2J_{PC}$ coupling constants (22.1 Hz and 21.6 Hz for **1a** and **1b**, respectively) in the range typically observed for neutral, octahedral ruthenium vinylidene complexes [7]. The C_β vinylidene hydrogen atom in each of complexes **1a** and **1b** also appears as a doublet in the ^1H NMR spectrum (**1a**, $\delta = 4.69$, $^4J_{PH} = 5$ Hz; **1b**, $\delta = 3.64$, $^4J_{PH} = 5$ Hz). Confirmation that the pyridyl group of the PNN ligand is coordinated to the metal in **1a** and **1b** is obtained from the considerable downfield shift observed in the ^1H NMR spectrum for the *o*-H atom on the pyridine ring [8] ($\delta = 9.97$ for **1a**, $\delta = 10.39$ for **1b**) compared to that observed for the free ligand ($\delta = 8.49$) [5a]. Two ^1H NMR signals corresponding to the two sets of methylene hydrogens of the ruthenium–iminoethylpyridyl ring are observed as broadened multiplets of equal intensity at room temperature. Considering the conformational flexibility of the six-membered ring, this broadening most likely can be attributed to a wagging motion of the ethylene bridge [9]. This motion could not be frozen out on the NMR time scale, even at −50 °C. While this complicated efforts to establish unambiguously the overall symmetry of the complex using NMR spectroscopy, the number of signals observed for the ethylene bridge is consistent with C_s symmetry, and suggests a meridionally coordinated PNN ligand and *trans* chlorides.

Confirmation of the coordination mode of the PNN ligand was obtained through a single-crystal X-ray crystallographic study on complex **1a**. Single crystals were grown by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of **1a** at room temperature. A labelled view of **1a** is provided in Fig. 1, and selected bond distances and angles are provided in the caption.

A number of notable features of the structure of **1a** warrant additional comments. Although several structures of **1a** could be envisioned, the solid state structure confirms that the PNN ligand does adopt a meridional coordination mode, with *trans* chloride ligands and the vinylidene ligand *trans* to the imino nitrogen. The chelate rings are not strained i.e., ∠P(1)–Ru(1)–N(1) = 88.84(7)° and ∠N(1)–Ru(1)–N(2) = 90.81(9)°, as one might expect for six-membered rings. The Ru–C(1) (C_α of the vinylidene ligand) distance of 1.809(3) A compares well with other neutral, octahedral ruthenium vinylidene complexes [7], but is larger compared to five-coordinate ruthenium vinylidene complexes in which the site *trans* to the vinylidene is vacant

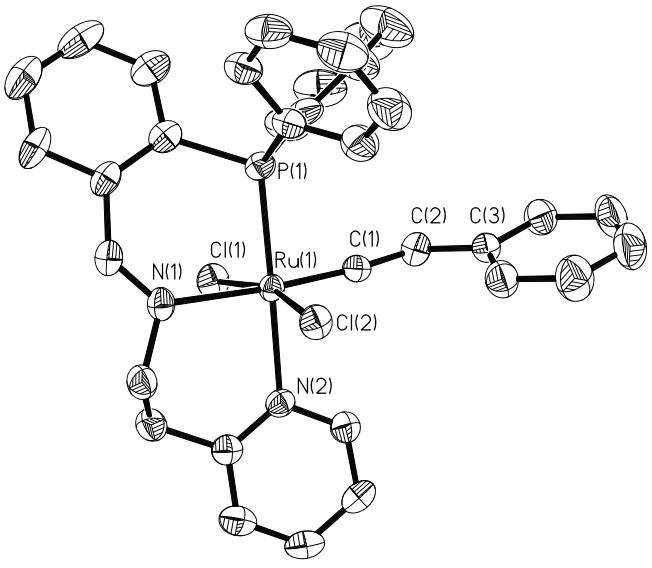

Fig. 1. Molecular structure of **1a** (the hydrogen atoms have been omitted for clarity). Selected bond lengths (A) and angles (°): Ru(1)–C(1) 1.809(3), Ru(1)–P(1) 2.2798(8), Ru(1)–Cl(1) 2.3833(7), Ru(1)–Cl(2) 2.3980(7), Ru(1)–N(1) 2.208(2), Ru(1)–N(2) 2.208(2), C(1)–C(2) 1.318(4), P(1)–Ru(1)–N(1) 88.84(7), N(1)–Ru(1)–N(2) 90.81(9), Cl(1)–Ru(1)–Cl(2) 165.36(3), P(1)–Ru(1)–N(2) 178.60(6), Ru(1)–C(1)–C(2) 175.5(2).

(d(Ru–C_α) ≈ 1.75 A) [6]. The relatively large *trans* influence exerted by the vinylidene ligand on the imino moiety can be seen in the Ru–N(1) distance of 2.208(2) A, which is slightly longer than that observed in other ruthenium–iminophosphine chelate complexes (d(Ru–N_{imine}) ≈ 2.10 Å) [10].

The original intention of this work was to investigate the ability of the PNN ligand to support ruthenium carbyne complexes. We next turned our attention towards exploring regioselective electrophilic addition to the vinylidene ligand of **1** (Scheme 1) [4b,4f]. When cold (−78 °C) CD_2Cl_2 solutions of either **1a** or **1b** were treated with a slight excess of $HBF_4 \cdot Et_2O$, an immediate colour change from red to orange was observed, and the carbyne complexes *mer*, *trans*-[(PNN)Cl_2Ru(CCH_2R)][BF_4] (**2**: R = Ph, **2a**; R = ^{t}Bu, **2b**) formed immediately and quantitatively, as determined by low temperature ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopy. At low temperatures, new doublet resonances attributed to C_α of the carbyne ligands of **2** are observed in the ^{13}C{^{1}H} NMR spectrum (δ = 334.5, **2a**; δ = 346.9, **2b**). These signals are shifted upfield, and display smaller (by ca. 4 Hz) $^2J_{PC}$ coupling constants compared to the parent vinylidenes **1**, suggesting oxidation of the ruthenium centre upon protonation [4b,4f]. The pyridyl moiety remains bound to the ruthenium centres in **2**, as evidenced by the downfield shifts of the *o*-H atoms on the pyridine ring (δ = 8.83 for **2a** and δ = 9.15 for **2b**). Two broad signals are observed for the methylene hydrogens of the ethylene bridge of the ruthenium–iminoethylpyridyl ring at δ = 4.13 and 3.35 for **2a**, and δ = 4.12 and 3.53 for **2b**, consistent with a meridional PNN ligand and *trans* chlorides (vide supra). Disappointingly, the carbynes **2** proved to be stable only at low temperatures (<−50 °C for **2a**, <−20 °C for **2b**), and decomposed within minutes to yield unappealing mixtures of products (NMR) at higher temperatures. It is possible the observed instability is linked to the moderate donating abilities of the imino, pyridyl and PPh_2 moieties [5a,11], which may mitigate the ability of the PNN ligand to stabilize sufficiently the formally Ru(IV) centre of the carbynes [4f].

The thermal instability of carbynes **2a** and **2b** precluded efforts to investigate further the substitutional lability of the pyridyl moiety of the PNN ligand in these complexes. The labile behaviour of the pyridyl moiety of the PNN ligand has been observed [5a] or speculated [5d] in several ligand displacement reactions involving small molecules. Alternatively, we attempted to investigate the hemilability of the PNN ligand in the vinylidene complexes **1**. What we observed was substitution of the vinylidene ligand in the final products, rather than the pyridyl group (Scheme 1). For example, when complex **1a** is heated with either excess MeCN or CO in benzene or toluene over 48–72 h, the substitution products *mer*,*trans*-[(PNN)Cl_2Ru(L)] (**3**: L = MeCN, **3a**; L = CO, **3b**) deposit as either bright red (**3a**) or yellow (**3b**) solids. The ^{1}H NMR spectra of **3a** and **3b** are very similar, and suggest structures analogous to those observed for other complexes reported as part of this work (see Section 2 for details). A dissociative mechanism is likely operating here, however it may not necessarily involve the pyridyl group. There are several reports describing the displacement of vinylidene ligands on ruthenium by nucleophiles [12]. In the case of complex **1**, this presumably requires isomerization of the vinylidene ligand to the (unobserved) η^2-HCCR ligand prior to dissociation. This might be assisted by the *cis* chloride co-ligands and/or the π-accepting properties of the imino and pyridyl moieties of the PNN ligand which reduce both the σ- and π-bonding properties of the ruthenium fragment and weaken the Ru–vinylidene bond [12c].

4. Summary

The ruthenium vinylidene complexes **1** serve as convenient precursors to the ruthenium carbyne complexes **2**. The poor thermal stability observed for complexes **2** would seem to suggest the PNN ligand may be insufficiently Lewis basic to stabilize the oxidized ruthenium and π-acidic carbyne ligand. In addition, the vinylidene ligand of **1**, rather than the pyridyl moiety of the PNN ligand, can be displaced by small molecules under forcing conditions.

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Appendix A. Supplementary data

Crystallographic data for compound **1a** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 607401. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int. code +44 1223 336 033; email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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