16- and 18-Electron Ruthenium(II) Complexes of the Neutral, Potentially Tridentate Triamine Ligand 2,6-[Bis(dimethylamino)methyl]pyridine (NN′N)

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The potentially tridentate coordinating ligands **NN′N** (2,6-bis[[(dimethylamino)methyl]pyridine) and **PNP** (2,6-bis[(diphenylphosphino)methyl]pyridine) react with [RuCl$_2$(PPh$_3$)$_3$] to give [*mer,trans*-RuCl$_2$(**NN′N**)(PPh$_3$)] (**1**) and [*mer,trans*-RuCl$_2$(**PNP**)(PPh$_3$)] (**2**), respectively. Complex **1** functions as a starting material for a variety of Ru[**NN′N**] complexes. It reacts with either 1 or 2 equiv of AgOTf (OTf$^-$ = SO$_3$CF$_3$$^-$) to yield monocationic [RuCl(**NN′N**)(PPh$_3$)]OTf (**3**) and [RuOTf(**NN′N**)(PPh$_3$)]OTf (**4**), respectively. The molecular structure of **4** shows a pentacoordinated ruthenium(II) center with a square-pyramidal environment. The reaction of **1** with either 1 or 2 equiv of AgOTf in the presence of MeCN results in the formation of the six-coordinate mono- or dicationic complexes [*mer*-RuCl(MeCN)(**NN′N**)(PPh$_3$)]X (**6a**) (X = OTf$^-$) and [*mer,trans*-Ru(MeCN)$_2$(**NN′N**)(PPh$_3$)](OTf)$_2$ (**7**), respectively. At 55 °C in acetonitrile, **1** converts quantitatively into **6b** (X = Cl$^-$) which is isostructural with **6a**. Reaction of polymeric [RuCl$_2$(nbd)]$_n$ (nbd = 2,5-norbornadiene) with **NN′N** under a nitrogen atmosphere leads to the formation of neutral, dinitrogen-bridged dimeric [(μ-N$_2$)(*mer,trans*-RuCl$_2${**NN′N**})$_2$] (**8**). The dinitrogen ligand is readily replaced when **8** is treated with CO, giving the neutral complex [*mer,trans*-RuCl$_2$(CO)(**NN′N**)] (**9**). The 16-electron complex **3** reacts with CO giving [*mer,cis*-RuCl(CO)$_2$(**NN′N**)]OTf (**10**), involving the formation of [RuCl(CO)(**NN′N**)(PPh$_3$)]OTf (**11**), followed by substitution of PPh$_3$ by a second CO molecule. This stepwise mechanism was confirmed by the isolation of **11**. The 16-electron complex **4** reacts with CO under the formation of monocationic [*mer*-RuOTf(CO)(**NN′N**)(PPh$_3$)]OTf (**12**) and a number of unidentified complexes. In the presence of ethyl alcohol, **4** reacts with CO to give monocationic [*mer*-RuOTf(CO)(**NN′N**)(HOEt)]OTf (**13**). The X-ray crystal structures of **1**, **4**, **6a**, **8**, **11**, and **13** are reported in abbreviated form.

Introduction

Although a wide range of (chiral) bidentate ligands has been used in (asymmetric) catalysis,[1−3] application of terdentate, especially neutral C_2 symmetrical, ligands in homogeneous catalysis[3−4] has received much less attention. Recently, a number of such terdentate ligands, bearing three sp²-hybridized nitrogen donor atoms, have been reported, *e.g.* bis(oxazolinyl)-pyridines[5] and bis(pyrazolyl)pyridines ("pybox").[6] Moreover, a number of related C_2 symmetrical, neutral, mixed phosphorus−nitrogen tridentate ligands of type **PNP** have been reported, in which a central pyridine ring contains bis-ortho (a)chiral phosphine substituents.[7] We are currently investigating the use of *monoanionic*, terdentate ligand systems [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$^-$ ([**NCN**]$^-$) or [C$_6$H$_3$(CH$_2$PPh$_2$)$_2$-2,6]$^-$ ([**PCP**]$^-$) which differ from neutral tridentate ligands **NN′N** and **PNP** by the fact that **NCN** and **PCP** are bonded to the (transition) metal by a metal−carbon σ bond (see Figure 1).[8,9]

Ruthenium(II) complexes containing the [**NCN**]$^-$ and [**PCP**]$^-$ ligand systems have proven to be very active catalysts in base co-catalyzed hydrogen-transfer reactions of ketones and imines with 2-propanol.[10,11] In these reactions, turnover numbers up to 25 000 were observed.[12] Recently, we have also developed C_2 symmetric chiral analogs of the [**NCN**]$^-$ ligand by introducing chirality at the benzylic carbon atom positions.[13] In order to study the effect of the replacement of a metal−carbon σ bond in **NCN** and **PCP** metal complexes by a metal−nitrogen

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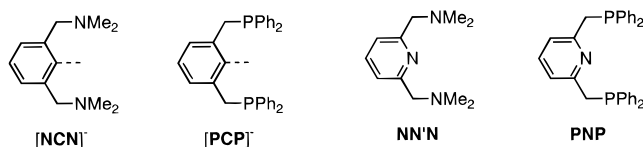(12) Karlen, T.; Grove, D. M.; van Koten, G. Manuscript in preparation.

Figure 1. Ligands used and their abbreviations.

coordinate bond, we applied the neutral pyridine analogue [C$_5$H$_3$N(CH$_2$NMe$_2$)$_2$-2,6] (**NN′N**) to ruthenium coordination chemistry.[14] Like the [**NCN**]⁻ ligand, neutral **NN′N** contains two flexible *ortho*-CH$_2$NMe$_2$ substituents, each carrying a tertiary amine donor atom. Furthermore, the **NN′N** ligand has some similarity with the well-known 2,2′,6:2″-terpyridine (terpy) but differs with respect to the nature of two of the N-donor atoms. Where terpyridine contains three sp²-hybridized nitrogen donor atoms, the **NN′N** ligand is based on a combination of one sp²- and two sp³-hybridized donor atoms. Moreover, the use of terpyridine is restricted to 18-electron complexes. In this paper, we report on the synthesis, characterization, and reactivity of 16- and 18-electron ruthenium(II) complexes of the **NN′N** ligand [C$_5$H$_3$N(CH$_2$NMe$_2$)$_2$-2,6].

Experimental Section

Syntheses were performed in a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Et$_2$O (predried on CaH$_2$) and pentane were carefully dried and distilled from sodium benzophenone ketyl prior to use. ¹H, ¹³C, and, ³¹P NMR spectra were recorded on 200 and 300 MHz spectrometers at 298 K. ¹H and ¹³C chemical shifts are referenced to Me$_4$Si, and ³¹P NMR data to 85% H$_3$PO$_4$, respectively. ¹⁹F shifts were referenced to CFCl$_3$. IR measurements were made on a FT-IR spectrophotometer set to a resolution of 2 cm⁻¹. Raman measurements were performed on a spectrophotometer equipped with a Nd:YAG laser using a laser power of 10 mW set to a resolution of 2 cm⁻¹ in combination with an InGaAs detector. FAS-MS spectra were recorded using Cs as a bombardment gas and NBA as a matrix. Elemental analyses were carried out by Dornis und Kölbe, Microanalytisches Laboratorium (Mülheim a.d. Ruhr, Germany). RuCl$_2$(PPh$_3$)$_3$,[15] RuCl$_2$(PMe$_3$)$_4$,[16] [RuCl$_2$(norbornadiene)]$_n$,[17] 2,6-bis[(dimethylamino)methyl]pyridine (**NN′N**),[14] and 2,6-bis[(diphenylphosphino)methyl]pyridine (**PNP**),[18] were prepared according to literature procedures. Full ¹H, ¹³C, and ³¹P NMR data of the ligands are added as Supporting Information.

Synthesis of [*mer,trans*-RuCl$_2$(NN′N)(PPh$_3$)] (1). To a solution of RuCl$_2$(PPh$_3$)$_3$ (0.67 g, 0.70 mmol) in CH$_2$Cl$_2$ (50 mL) was added a solution of **NN′N** (0.14 g, 0.70 mmol) in CH$_2$Cl$_2$ (5 mL) over 1 min. After the mixture was stirred for 30 min, the solvent was removed *in vacuo*. The remaining brown oil was extracted with Et$_2$O (10 mL, 2×) leaving a yellow brown solid as the pure product (0.42 g, 96%). No decomposition at *T* < 200 °C. ¹H NMR (CDCl$_3$, ppm): δ 8.15 (t, 6H, *o*-H PPh$_3$), 7.65 (t, 1H, *p*-H py), 7.34–7.25 (m, 11H, *m*-H py, ar-H), 4.00 (s, 4H, CH$_2$), 2.10 (s, 12H, NMe$_2$). ¹³C NMR (CDCl$_3$, ppm): δ 161.7 (*o*-C py), 138.9 (d, ¹J_{PC} = 31.7 Hz, *ipso*-C PPh), 135.0 (*p*-C py), 134.4 (d, ³J_{PC} = 9.2 Hz, *m*-C PPh$_3$), 128.3 (*p*-C PPh), 127.5 (d, ²J_{PC} = 8.3 Hz, *o*-C PPh$_3$), 119.3 (*m*-C py). ³¹P NMR (CDCl$_3$, ppm): δ 37.0 (PPh$_3$). UV/vis, λ_{max} (ϵ): 390 (4949). Anal. Calcd for C$_{29}$H$_{34}$Cl$_2$N$_3$PRu: C, 55.50; H, 5.46; N, 6.70. Found: C, 55.38; H, 5.37; N, 6.66.

Synthesis of [*mer,trans*-RuCl$_2$(PNP)(PPh$_3$)] (2).[7d] To a solution of RuCl$_2$(PPh$_3$)$_3$ (3.76 g, 3.92 mmol) in CH$_2$Cl$_2$ (50 mL) was added a

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solution of **PNP** (1.86 g, 3.92 mmol) in CH$_2$Cl$_2$ (10 mL). After the mixture was stirred for 30 min, the solvent was removed *in vacuo* and the residue extracted with Et$_2$O (20 mL, 2×), leaving the pure product as a yellow solid (3.35 g, 94%). No decomposition at *T* < 200 °C. ¹H NMR (CDCl$_3$, ppm): δ 7.53 (t, 1H, *p*-H py), 7.45–7.20 (m, 22H, ar-H), 7.15–7.00 (m, 10H, ar-H), 6.90–6.85 (m, 5H, *m*-H py and ar-H), 4.55 (t, |²J_{HP} + ⁴J_{HP}| = 9.4 Hz, 4H, CH$_2$). ¹³C NMR (CDCl$_3$, ppm): δ 162.36 (*o*-C pyr), 137.75 (d, ¹J_{PC} = 39.9 Hz, *ipso*-C PPh$_2$), 136.55 (*p*-C py), 134.82 (d, ³J_{PC} = 9.3 Hz, *m*-C PPh$_3$), 133.78 (t, J_{PC} = 9.6 Hz, *m*-C PPh$_2$), 133.12 (t, J_{PC} = 38.0 Hz, *ipso*-C PPh$_3$), 129.03 (*p*-C PPh$_2$), 128.36 (*p*-C PPh$_3$), 127.54 (t, J_{PC} = 8.4 Hz, *o*-C PPh$_2$), 127.74 (d, J_{PC} = 8.9 Hz, *o*-C PPh$_3$), 120.47 (*m*-C py), 46.98 (t, J_{PC} = 4.1 Hz, CH$_2$). ³¹P NMR (CDCl$_3$, ppm): δ 41.83 (t, 1P, J_{PP} = 29 Hz, PPh$_3$), 35.41 (d, 2P, J_{PP} = 29 Hz, PPh$_2$). UV/vis, λ_{max} (ϵ): 327 (5136), 398 (2351). Anal. Calcd for C$_{49}$H$_{42}$Cl$_2$N$_3$P$_3$Ru: C, 64.69; H, 4.65; N, 1.54. Found: C, 64.55; H, 4.40; N, 1.47.

Synthesis of [RuCl(NN′N)(PPh$_3$)]OTf (3). To a solution of **1** (0.65 g, 1.04 mmol) in CH$_2$Cl$_2$ (50 mmol) was added solid AgOTf (0.27 g, 1.04 mmol). After it was stirred for 45 min, the reaction mixture had changed color from brown to purple, and a newly formed flaky white precipitate was filtered off. The volume of the remaining solution was reduced *in vacuo* to 3 mL. Pentane (20 mL) was added upon which the product precipitated. After filtration and subsequent drying *in vacuo*, the pure product was isolated as a purple solid (0.61 g, 92%). No decomposition at *T* < 200 °C. ¹H NMR (acetone-d_6, ppm): δ 7.90–7.80 (m, 6H, *m*-H PPh$_3$), 7.48–7.30 (m, 12H, ar-H and py-H), 4.05 (d, ²J_{HAHB} = 16.2 Hz, CH$_A$H$_B$), 3.51 (d, ²J_{HAHB} = 16.2 Hz, CH$_A$H$_B$), 2.68 (s, 6H, N(*Me*)(Me)), 2.32 (s, 6H, N(Me)(*Me*)). ¹³C NMR (acetone-d_6, ppm): δ 162.7 (*o*-C py), 137.3 (*p*-C py), 134.4 (d, ³J_{PC} = 9.9 Hz, *m*-C PPh$_3$), 134.3 (d, ¹J_{PC} = 51.9 Hz, *ipso*-C PPh$_3$), 131.2 (d, ⁴J_{PC} = 2.7 Hz, *p*-C PPh$_3$), 129.2 (d, ²J_{PC} = 10.5 Hz, *o*-C PPh$_3$), 122.6 (*m*-C py), 73.7 (CH$_2$), 52.8 (N(*Me*)(Me)), 47.6 (N(Me)(*Me*)). ³¹P NMR (acetone-d_6, ppm): δ 86.6 (PPh$_3$). UV/vis, λ_{max} (ϵ): 365 (11 144), 530 (3500). Anal. Calcd for C$_{30}$H$_{34}$ClF$_3$N$_3$O$_3$PRuS: C, 48.61; H, 4.62; N, 5.67. Found: C, 48.25; H, 4.44, N, 5.66.

Synthesis of [RuOTf(NN′N)(PPh$_3$)]OTf (4). To a solution of **1** (1 g, 1.6 mmol) in CH$_2$Cl$_2$ (50 mL) was added AgOTf (0.85 g, 3.2 mmol). After the suspension was stirred for 30 min, a newly formed flaky white precipitate was filtered off, and from the remaining purple solution the solvent was removed *in vacuo*, leaving a purple solid as the pure product (1.27 g, 93%). No decomposition at *T* < 200 °C. ¹H NMR (CDCl$_3$, ppm): δ 7.75 (t, 1H, *p*-H py), 7.49–7.40 (m, 9H, ar-H), 7.32–7.25 (m, 8H, ar-H), 3.95 (d, ²J_{HAHB} = 16 Hz, CH$_A$H$_B$), 3.21 (d, ²J_{HAHB} = 16 Hz, CH$_A$H$_B$), 2.71 (s, 6H, N(*Me*)(Me)), 2.31 (s, 6H, (NMe)(*Me*)). ¹³C NMR (CDCl$_3$, ppm): δ 162.6 (*o*-C py), 137.8 (*p*-C py), 133.4 (d, ³J_{PC} = 9.6 Hz, *m*-C PPh$_3$), 131.6 (d, ¹J_{PC} = 46.1 Hz, *ipso*-C PPh$_3$), 131.3 (*p*-C PPh$_3$), 128.9 (²J_{PC} = 10.6 Hz, *o*-C PPh$_3$), 122.6 (*m*-C py), 118.50 (q, ¹J_{CF} = 310 Hz, SO$_3$CF$_3$), 72.1 (CH$_2$), 52.6 (N(*Me*)(Me)), 45.7 (N(Me)(*Me*)). ³¹P NMR (CDCl$_3$, ppm): δ 74.5 (PPh$_3$). UV/vis, λ_{max} (ϵ): 342 (5532), 508 (1691). Anal. Calcd for C$_{31}$H$_{34}$F$_6$N$_3$O$_6$PRuS$_2$: C, 43.56; H, 4.01; N, 4.92. Found: C, 43.42; H, 4.08; N, 4.86.

Synthesis of [*mer*-RuCl(MeCN)(NN′N)(PPh$_3$)]OTf (6a). To a solution of **1** (0.16 g, 0.25 mmol) in CH$_2$Cl$_2$ (30 mL)/MeCN (5 mL) was added AgOTf (0.07 g, 0.27 mmol). After the reaction mixture was stirred for 30 min, a newly formed flaky white precipitate was filtered off. After the solvent was removed *in vacuo*, the crude product was extracted with Et$_2$O (10 mL, 2×), leaving the pure product as a light brown solid (0.18 g, 90%). No decomposition at *T* < 200 °C. ¹H NMR (CDCl$_3$, ppm): δ 8.13 (t, 6H, *o*-H PPh$_3$), 7.87 (t, 1H, *p*-H py), 7.47 (d, 2H, *m*-H py), 7.44–7.36 (m, 9H, ar-H), 4.30 (d, 2H, ²J_{HAHB} = 15 Hz, CH$_A$H$_B$), 3.89 (d, 2H, ²J_{HAHB} = 15 Hz, CH$_A$H$_B$), 2.37 (s, 6H, N(*Me*)(Me)), 2.11 (s, 6H, N(Me)(*Me*)), 1.91 (s, 3H, MeCN). ¹³C NMR (CDCl$_3$, ppm): δ 159.6 (*o*-C py), 137.8 (*p*-C py), 136.1 (d, ¹J_{PC} = 35.5 Hz, *ipso*-C PPh$_3$), 133.0 (d, ³J_{PC} = 9.8 Hz, *m*-C PPh$_3$), 129.4 (*p*-C PPh$_3$), 128.6 (d, ²J_{PC} = 8.8 Hz, *o*-C PPh$_3$), 127.3 (Me*CN*), 121.0 (*m*-C py), 73.6 (CH$_2$), 55.7 (N(*Me*)(Me)), 55.1 (N(Me)(*Me*)), 4.1 (*Me*CN). ³¹P NMR (CDCl$_3$, ppm): δ 32.8 (PPh$_3$). UV/vis, λ_{max} (ϵ): 350 (4663). Anal. Calcd for C$_{32}$H$_{37}$ClF$_3$N$_4$O$_3$PRuS: C, 49.13; H, 4.77; N, 7.16. Found: C, 48.96; H, 4.72; N, 7.06.

Synthesis of [*mer*-RuCl(MeCN)(NN′N)(PPh₃)]Cl (6b). A suspension of **1** (0.31 g, 0.49 mmol) in acetonitrile (30 mL) was gently heated to 55 °C for 5 min, upon which a clear brown solution was formed. After MeCN was evaporated, the crude product was dissolved in CHCl₃ (25 mL). After pentane (50 mL) was added, the pure product was collected by centrifugation as a cream-colored solid (0.30 g, 91%). ¹H NMR (CDCl₃, ppm): δ 8.13 (t, 6H, *o*-H py), 7.84 (t, 1H, *p*-H py), 7.53 (d, 2H, *m*-H py), 7.44−7.35 (m, 9H, ar-H py), 4.33 (d, 2H, $^2J_{HAHB}$ = 15.5 Hz, C*H*$_A$H$_B$), 4.12 (d, 2H, $^2J_{HAHB}$ = 15.5 Hz, CH$_A$*H*$_B$), 2.36 (s, 6H, N(*Me*)(Me)), 2.15 (s, 3H, MeCN), 2.12 (s, 6H, N(Me)(*Me*)). ¹³C NMR (CDCl₃, ppm): δ 159.7 (*o*-C py), 137.6 (*p*-C py), 136.1 (d, $^1J_{PC}$ = 35.1 Hz, *ipso*-C PPh₃), 133.0 (d, $^3J_{PC}$ = 9.3 Hz, *m*-C PPh₃), 129.3 (*p*-C PPh₃), 128.6 (d, $^2J_{PC}$ = 8.8 Hz, *o*-C PPh₃), 127.6 (Me*CN*), 121.0 (*m*-C py), 73.9 (CH₂), 55.8 (N(*Me*)(Me)), 55.3 (N(Me)(*Me*)), 5.6 (*Me*CN). ³¹P NMR (CDCl₃, ppm): δ 33.0 (PPh₃). UV/vis, λ$_{max}$ (ε): 350 (4609). Anal. Calcd for C₃₁H₃₇Cl₂N₄PRu·³/₂CH₂Cl₂: C, 49.04; H, 5.07; N, 7.04. Found: C, 49.36; H, 5.10; N, 7.27.

Synthesis of [*mer,trans*-Ru(MeCN)₂(NN′N)(PPh₃)]OTf₂ (7). To a solution of **1** (0.75 g, 1.2 mmol) in CH₂Cl₂ (30 mL)/MeCN (5 mL) was added AgOTf (0.61 g, 2.4 mmol). After the suspension was stirred for 30 min, the newly formed flaky white precipitate was filtered off. After the solvent was removed *in vacuo* and the residue had been extracted with Et₂O (10 mL, 2×), the pure product was obtained as a yellow solid (0.97 g, 86%). No decomposition at *T* < 200 °C. ¹H NMR (DMSO-d_6, ppm): δ 8.11 (t, 1H, *p*-H py), 7.77−7.71 (m, 8H, ar-H), 7.55−7.46 (m, 9H, ar-H), 4.14 (s, 4H, CH₂), 2.41 (s, 6H, MeCN), 2.20 (s, 12H, NMe₂). ¹³C NMR (DMSO-d_6, ppm): δ 161.4 (*o*-C py), 141.8 (*p*-C py), 136.5 (d, $^1J_{PC}$ = 37.9 Hz, *ipso*-C PPh₃), 135.0 (d, $^3J_{PC}$ = 9.8 Hz, *m*-C PPh₃), 132.5 (*p*-C PPh₃), 132.3 (Me*CN*), 123.2 (q, $^1J_{CF}$ = 322 Hz, SO₃CF₃), 75.1 (CH₂), 57.2 (NMe₂), 6.73 (*Me*CN). ³¹P NMR (DMSO-d_6, ppm): δ 37.4 (PPh₃). UV/vis, λ$_{max}$ (ε): 282 (5933). Anal. Calcd for C₃₅H₄₀F₆N₅O₆PRuS₂: C, 44.87; H, 4.30; N, 7.47. Found: C, 44.72; H, 4.31; N, 7.38.

Synthesis of [(μ-N₂)(*mer,trans*-RuCl₂(NN′N))₂] (8). To a suspension of [RuCl₂(nbd)]$_n$ (1.28 g, 4.85 mmol) in C₆H₆ (100 mL) was added **NN′N** (1.02 g, 5.28 mmol) at room temperature, after which the reaction mixture was refluxed for 24 h. Subsequently the solvent was removed *in vacuo*. The resulting residue was extracted with CH₂Cl₂ (20 mL), separated from insoluble starting material, and extracted with pentane (20 mL, 2×). After the solvent was removed *in vacuo*, almost pure crude product was obtained in about 60% yield. Slow diffusion of Et₂O into a CH₂Cl₂ solution of this crude product resulted in the formation of yellow-brown, block-shaped crystals (1.0 g, 30%). ¹H NMR (CDCl₃, ppm): δ 7.60 (t, 1H, *p*-H py), 7.27 (d, 2H, *m*-H py), 4.15 (s, 4H, CH₂), 2.80 (s, 12H, NMe₂). ¹³C NMR (CDCl₃, ppm): δ 162.5 (*o*-C py), 134.6 (*p*-C py), 119.5 (*m*-C py), 71.7 (CH₂), 55.0 (NMe₂). FAB-MS 760.0 (M⁺). Raman (cm⁻¹): 2099 (N≡N). UV/vis, λ$_{max}$ (ε): 426 (14 632). Anal. Calcd for C₂₂H₃₈Cl₄N₈Ru₂: C, 34.84; H, 5.05; N, 14.77. Found: C, 33.54; H, 4.80; N, 13.27 (incorrect, but C/H, C/N, and H/N ratios consistent with **8**·*x*RuCl$_y$).

Synthesis of [*mer,trans*-RuCl₂(CO)(NN′N)] (9). Through a solution of **8** (100 mg, 0.132 mmol) in CH₂Cl₂ (20 mL) was bubbled CO for 90 min at room temperature, during which the color of the solution changed from green-yellow to light brown. After this, the solvent was removed *in vacuo* and the residue was extracted with pentane (10 mL), upon which the pure product remained as a green-brown solid (100 mg, 96%, based on **8**). ¹H NMR (CD₂Cl₂, ppm): δ 7.93 (t, 1H, *p*-H py), 7.48 (d, 2H, *m*-H py), 4.22 (s, 4H, CH₂), 2.68 (s, 12H, NMe₂). ¹³C NMR (CD₂Cl₂, ppm): δ 185.4 (CO), 160.1 (*o*-C py), 139.0 (*m*-C py), 121.0 (*m*-C py), 72.5 (CH₂), 56.4 (NMe₂). IR (KBr): ν$_{CO}$ 1948 cm⁻¹. Anal. Calcd for C₁₂H₁₉Cl₂N₃ORu: C, 36.65; H, 4.87; N, 10.68. Found: C, 36.52; H, 4.85; N, 10.54.

Synthesis of [*mer,cis*-RuCl(CO)₂(NN′N)]OTf (10). Through a solution of **3** (1.64 g, 1.92 mmol) in CH₂Cl₂ (10 mL) was bubbled CO for 4 min, upon which a distinct color change from deep purple to clear yellow was observed. After the reaction mixture was stirred for 30 min under a CO atmosphere, pentane (40 mL) was added, upon which a yellow solid precipitated. ¹H NMR analysis confirmed that this crude product consisted of about 80% of **10** along with 20% of **11**. Further treatment of the crude product with CO in a CH₂Cl₂ solution (10 mL) did not lead to significant improvement of product

distribution. Fractional crystallization by slow diffusion of pentane in a CH₂Cl₂ solution of the crude product afforded almost pure product as a light-yellow microcrystalline solid (0.2 g, 20%). No decomposition at *T* < 200 °C. ¹H NMR (CD₃CN, ppm): δ 7.96 (t, 1H, *p*-H py), 7.54 (d, 2H, *m*-H py), 4.36 (d, $^2J_{HAHB}$ = 16.2 Hz, C*H*$_A$H$_B$), 4.13 (d, $^2J_{HAHB}$ = 16.2 Hz, CH$_A$*H*$_B$), 2.84 (s, 6H, N(*Me*)(Me)), 2.66 (s, 6H, N(Me)(*Me*)). ¹³C NMR (CD₃CN, ppm): δ 206.42, 200.98 (CO), 160.92 (*o*-C py), 139.61 (*p*-C py), 122.52 (*m*-C py), 74.24 (CH₂), 58.36 (N(*Me*)(Me)), 54.27 (N(Me)(*Me*)). IR (KBr): ν$_{CO}$ 1967, 1936 cm⁻¹. Anal. Calcd for C₁₄H₁₉ClF₃N₃O₅RuS: C, 31.43; H, 3.58; N, 7.86. Found: C, 26.40; H, 3.85; N, 6.63.

Synthesis of [*mer*-RuCl(CO)(NN′N)(PPh₃)]OTf (11). Through a solution of **3** (0.8 g, 1.15 mmol) in CH₂CH₂ (10 mL) was bubbled CO until the purple color of the solution had disappeared and the reaction mixture had turned light brown (2−3 min). Slow diffusion of pentane into the reaction mixture gave the pure product as large pale yellow-brown crystals which proved to contain 1 equiv of dichloromethane (0.82 g, 83%). ¹H NMR (CD₂Cl₂, ppm): δ 8.22−8.10 (m, 6H, *o*-H PPh₃), 8.03 (t, 1H, *p*-H py), 7.65 (d, 2H, *m*-H py), 7.51−7.48 (m, 9H, ar-H), 4.63 (d, 2H, $^2J_{HAHB}$ = 15.7 Hz, C*H*$_A$H$_B$), 3.97 (d, 2H, $^2J_{HAHB}$ = 15.7 Hz, CH$_A$*H*$_B$), 2.50 (s, 6H, N(*Me*)(Me)), 2.48 (s, 6H, N(Me)(*Me*)). ¹³C NMR (CD₂Cl₂, ppm): δ 200.52 (d, $^2J_{PC}$ = 13.6 Hz, CO), 159.78 (*o*-C py), 142.13 (*p*-C py), 136.01 (d, $^1J_{PC}$ = 41.4 Hz, *ipso*-C PPh₃), 134.73 (d, $^3J_{PC}$ = 8.9 Hz, *m*-C PPh₃), 132.58 (d, $^4J_{PC}$ = 1.9 Hz, *p*-C PPh₃), 131.04 (d, $^2J_{PC}$ = 9.4 Hz, *o*-C PPh₃), 123.92 (*m*-C py), 76.66 (CH₂), 60.46 (N(*Me*)(Me)), 57.11 (N(Me)(*Me*)). ³¹P NMR (CD₂Cl₂, ppm): δ 17.31 (PPh₃). IR (KBr): ν$_{CO}$ 1964 cm⁻¹. UV/vis, λ$_{max}$ (ε): 238 (39 950). Anal. Calcd for C₃₁H₃₄ClF₃N₃O₄PRuS·CH₂Cl₂: C, 45.00; H, 4.25; N, 4.92. Found: C, 44.64; H, 4.18; N, 4.87.

[*mer,cis*-RuOTf(CO)(NN′N)(PPh₃)]OTf (12). ¹H NMR (CDCl₃, ppm): δ 7.95 (t, 1H, *p*-H py), 7.50 (d, 2H, *m*-H py), 7.45−7.05 (m, 15H, ar-H), 4.58 (d, 2H, $^2J_{HAHB}$ = 16.5 Hz, C*H*$_A$H$_B$), 4.11 (d, 2H, $^2J_{HAHB}$ = 16.5 Hz, CH$_A$*H*$_B$), 2.97 (s, 6H, N(*Me*)(Me)), 2.76 (s, 6H, N(Me)(*Me*)). ³¹P NMR (CDCl₃, ppm): δ 7.94 (PPh₃). IR (KBr): ν$_{CO}$ 1964 cm⁻¹.

Synthesis of [*mer*-RuOTf(CO)(NN′N)(HOEt)]OTf (13). To a solution of **4** (1.0 g, 1.17 mmol) in a mixture of CH₂Cl₂ (8 mL) and EtOH (2 mL) was bubbled CO for 2 min, during which the color of the solution changed from purple to clear light yellow. Slow diffusion of pentane into the reaction mixture afforded the pure product as large yellow to orange block-shaped crystals (0.3 g, 38%). No NMR data could be obtained due to instability and/or insolubility in different deuterated solvents. IR (KBr): ν$_{CO}$ 1968 cm⁻¹. UV/vis, λ$_{max}$ (ε): 230 (7700), 264 (5287). Anal. Calcd for C₁₆H₂₅F₆N₃O₈RuS₂: C, 28.83; H, 3.78; N, 6.30. Found: C, 28.76; H, 3.86; N, 6.25.

Substitutional Reactivity of [*mer,trans*-RuCl₂(NN′N)(PPh₃)] (1) toward PMe₃. To a solution of **1** (0.45 g, 0.72 mmol) in CH₂Cl₂ (50 mL) was added a solution of PMe₃ (133 mg, 1.75 mmol) in MeOH (2.5 mL), which led to a slight color change from brown to reddish brown. ³¹P{¹H} and ¹H NMR of the resulting solution indicated that RuCl₂(PMe₃)₄ (by comparison with an authentic sample[16]) had been formed. ¹H NMR (CDCl₃, ppm): δ 1.50 (s, PMe₃). ¹³C NMR (CDCl₃, ppm): δ 17.42 (m, PMe₃). ³¹P NMR (CDCl₃, ppm): δ −5.95.

Crystal Structure Determinations

All crystals were sampled and mounted with the oil technique and cut to size when needed. X-ray data were collected at 150 K on an Enraf-Nonius CAD4T on a rotating anode using graphite-monochromated Mo Kα radiation. Unit cell parameters were derived from the SET4[19] setting angles of 25 reflections. Unit cells were checked for higher symmetry with the programs LEPAGE[20] and PLATON/MISSYM.[21] All geometrical calculations and the ORTEP illustrations were done with PLATON[22] (Table 1).

[*mer,trans*-RuCl₂(NN′N)(PPh₃)] (1). A total of 23 464 reflections (θ$_{max}$ = 25°) were scanned and averaged into a unique set of 5795

(19) (a) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410. (b) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264−269.
(20) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578−579.
(21) Spek, A. L. *Am. Cryst. Assoc.* **1997** (Abstract).
(22) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table 1. Experimental Data for the X-ray Diffraction Studies of **1**, **4**, **6a**, **8**, **11**, and **13**

	1	**4**	**6a**	**8**	**11**	**13**
empirical formula	$C_{29}H_{34}Cl_2N_3PRu \cdot$ $^3/_2CH_2Cl_2$	$C_{30}H_{34}F_3N_3O_3PRuS \cdot$ $CF_3SO_3 \cdot CH_2Cl_2$	$C_{31}H_{37}ClN_4PRu \cdot$ $CF_3SO_3 \cdot 2.75CHCl_3$	$C_{22}H_{38}Cl_4N_8Ru_2 \cdot$ $^1/_2C_4H_{10}O$	$C_{30}H_{34}ClN_3OPRu \cdot$ $CF_3SO_3 \cdot ^5/_4CH_2Cl_2$	$C_{15}H_{25}F_3N_3O_5RuS \cdot$ CF_3SO_3
fw	754.96	939.73	1110.51	795.61	875.35	666.58
color	orange	red	yellow	red	yellowish	yellowish
space group	$Fdd2$ (No. 43)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
a (Å)	23.472(9)	9.3763(10)	12.4610(8)	14.8201(12)	12.335(1)	10.169(1)
b (Å)	59.277(13)	13.484(5)	17.460(2)	14.0198(12)	21.523(2)	10.313(1)
c (Å)	9.4320(10)	15.946(3)	22.737(2)	15.1417(11)	27.393(2)	12.214(1)
α (deg)	–	84.23(2)	111.485(9)	–	–	–
β (deg	–	75.469(11)	91.413(6)	93.243(5)	–	101.19(1)
γ (deg)	–	78.13(2)	97.951(7)	–	–	–
V (Å^3)	13123(6)	1907.3(9)	4543.6(8)	3141.0(4)	7272(1)	1256.6(2)
λ (Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
Z	16	2	4	4	8	2
d_{calc} (g·cm^{-3})	1.528	1.636	1.623	1.682	1.599	1.762
μ (Mo Kα) (cm^{-1})	9.6	7.7	10.11	13.09	8.36	8.8
R$_1$ [$I > 2\sigma(I)$]^a	0.0738	0.0720	0.0529	0.0297	0.0589	0.0231
wR$_2$	0.1799	0.1893	0.1436	0.0771	0.1263	0.0593

^{a} R$_1 = \Sigma(F_o - |F_c|)/\Sigma F_o$; wR$_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

reflections (5083 with $I > \sigma(I)$). The structure was solved by automated Patterson methods (DIRDIF[23]) and refined on F^2 with SHELXL93.[24] Hydrogen atoms were taken into account at calculated positions.

[RuOTf(NN′N)(PPh₃)]OTf (4). A total of 7294 reflections (θ_{max} = 25.4°) were scanned and averaged into a unique set of 6851 reflections (4903 with $I > 2\sigma(I)$). The structure was solved by automated Patterson methods (DIRDIF[23]) and refined on F^2 with SHELXL93.[24] No satisfactory disorder model for the CH₂Cl₂ solvent molecules of crystallization at 0.5, 0.5, 0.5 could be refined. Therefore, its contribution in the structure factor calculations was taken into account using the PLATON/SQUEEZE[25,26] method. Hydrogen atoms were taken into account at calculated positions.

[mer-RuCl(MeCN)(NN′N)(PPh₃)]OTf (6a). A total of 16 898 reflections (θ_{max} = 25.4°) were scanned and averaged into a unique set of 16 116 reflections (11 985 with $I > 2\sigma(I)$). The structure was solved by direct methods (SHELXS86[27]) and refined on F^2 with SHELXL93.[24] Disordered solvents (CHCl₃) were taken into account using PLATON/SQUEEZE.[25,26] Hydrogen atoms were taken into account at calculated positions.

[(μ-N₂)(mer,trans-RuCl₂(NN′N))₂] (8). A total of 19 600 reflections (θ_{max} = 27.5°) were scanned and averaged into a unique set of 7205 reflections (6402 with $I > 2\sigma(I)$). The structure was solved by direct methods (SHELXS86[27]) and refined on F^2 with SHELXL96.[28] Disordered diethyl ether was handled with the PLATON/SQUEEZE[25,26] technique. Hydrogen atoms were taken into account at calculated positions.

[mer-RuCl(CO)(NN′N)(PPh₃)]OTf (11). A total of 9670 reflections (θ_{max} = 27.5°) were scanned and averaged into a unique set of 9571 reflections (6554 with $I > 2\sigma(I)$). The structure was solved by Patterson methods (DIRDIF[23]) and refined on F^2 with SHELXL96.[28] One of the SO₃CF₃ ions is heavily disordered and was taken into account along with the disordered solvent with the PLATON/SQUEEZE[25,26] technique. Hydrogen atoms were taken into account at calculated positions. The racemic twin parameter refined to 0.41(6).

[mer-RuOTf(CO)(NN′N)(HOEt)]OTf (13). A total of 4100 reflections (θ_{max} = 27.5°) were scanned and averaged into a unique set of 3036 reflections (2982 with $I > 2\sigma(I)$). The structure was solved by

(23) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykala, C. *The DIRDIF96 Program System*; Technical Report of the Crystallographic Laboratory, Universiteit of Nijmegen: Nijmegen, The Netherlands, 1996.
(24) Sheldrick, G. M. *SHELXL93. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.
(25) Spek, A. L. *Am. Cryst. Assoc. Abstr.* **1994**, *22*, 66.
(26) Spek, A. L. *Acta Crystallogr.* **1987**, *C43*, 1233−1235.
(27) Sheldrick, G. M. *SHELXS86. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.
(28) Sheldrick, G. M. *SHELXS96. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1996.

direct methods with SIR[29] and refined on F^2 with SHELXL96.[28] Hydrogen atoms were taken into account at calculated positions. The racemic twin parameter for this model refined to 0.05(3).

Results and Discussion

The synthesis and reaction routes of the new **EN′E**−ruthenium(II) (**E = N, P**) complexes are presented in Scheme 1. Relevant spectroscopic data for the complexes are given in Tables 2 and 3.

Synthesis of [*mer,trans*-RuCl₂(NN′N)(PPh₃)] (1) and [*mer,trans*-RuCl₂(PNP)(PPh₃)] (2). The dichloride complex [RuCl₂-(NN′N)(PPh₃)] (**1**) is conveniently prepared by a ligand exchange reaction of [RuCl₂(PPh₃)₃] with a stoichiometric amount of **NN′N** in CH₂Cl₂. The complex is a yellow-brown solid, stable in both the solid state and in oxygen-free solutions. The retention of one PPh₃ ligand in **1** is clearly shown by elemental analysis and NMR spectroscopy. In principle, the octahedral complex **1** has four stereoisomers. In addition to one *trans*-dichloro isomer, the *cis*-dichloro isomer may exist in three diastereomeric forms with mer or fac arrangement of the **NN′N** donor atoms, made possible by the flexibility of the o-CH₂NMe₂ substituents (Chart 1).

The ¹H and ³¹P NMR spectra of **1** show a single resonance pattern at all temperatures for all nuclei, indicating the presence of a single stereoisomer in solution. Singlet resonances are observed for the benzylic protons as well as for the NMe₂ groups, which point to homotopic benzylic protons and NMe₂ groups, respectively. Moreover, the ³¹P{¹H} NMR shows one high-field singlet resonance for PPh₃ at 37.0 ppm. This is a characteristic chemical shift for coordinated PPh₃ trans to a neutral donor ligand. These observations rule out the cis stereoisomers **III** and **IV** (of Chart 1) having a fac arrangement but are in agreement with a *mer,trans*-**I** structure, analogous to that established for [RuCl₂(terpy)(PPh₃)] (terpy = 2,2,6:2″-terpyridine).[30] Of the latter complex, both the mer,trans and the mer,cis isomers can be synthesized.[30] The quantitative formation of [*mer,cis*-RuCl₂(terpy)(PPh₃)] by a direct ligand exchange reaction of RuCl₂(PPh₃)₃ with terpy in benzene at reflux for 1 h has been reported.[30] However, the analogous reaction with **NN′N** results in an almost quantitative formation

(29) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.
(30) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404−1407.

Scheme 1. Reaction Routes to Ru[II][ENE] Complexes
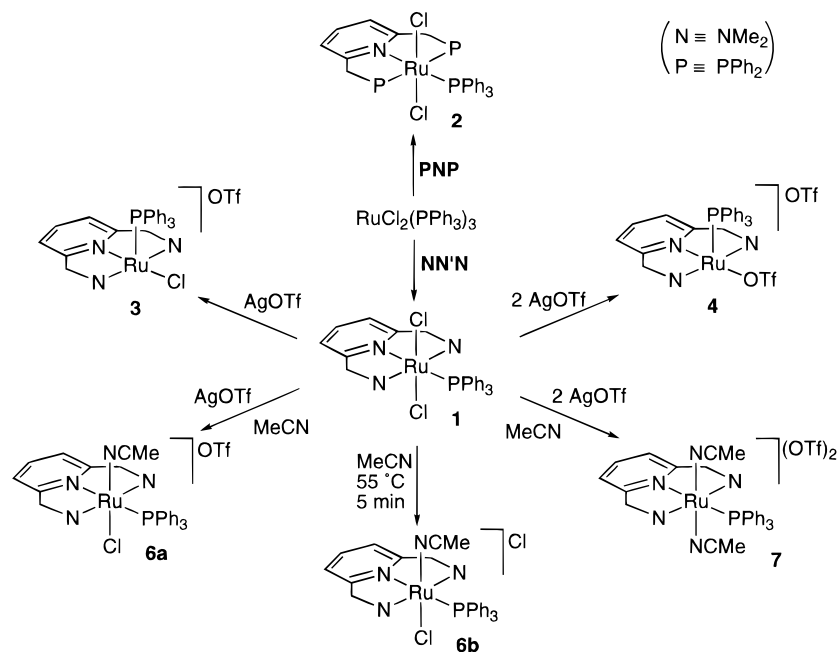
Table 2. Relevant ^{1}H, ^{31}P, and UV/Vis Data for **NN′N**−Ru[II] Complexes[a]

| complex | ^{1}H NMR[a,b] | | | ^{31}P NMR[a,c] | UV/vis[d] |
	NMe$_2$	CH$_2$[e]	p-HNN′N[f]	PPh$_3$	λ_{max} (ϵ)
NN′N	2.20	3.50	7.54		
1	2.10	4.00	7.65	37.0	390 (4949)
3[g]	2.68, 2.32	4.05, 3.51 (16)	h	86.6	365 (11 144), 530 (3500)
4	2.71, 2.31	3.95, 3.21 (16)	7.75	74.5	342 (5532), 508 (1691)
6a	2.37, 2.11	4.30, 3.89 (15)	7.87	32.8	350 (4663)
7[i]	2.20	4.14	8.10	37.4	282 (5933)

[a] In CDCl$_3$ at 298 K (unless stated otherwise). [b] 300 MHz. Chemical shift values (δ, ppm) indirectly referenced to SiMe$_4$ using solvent signals. [c] 81 MHz. Chemical shift values (δ, ppm) are relative to 85% H$_3$PO$_4$ with positive values being downfield from the standard. [d] In CH$_2$Cl$_2$, λ_{max} in nm; ϵ in L mol^{-1} cm^{-1}. [e] $^2J_{HAHB}$ (Hz) given in parentheses. [f] Triplet. [g] Acetone-d_6. [h] Not isolated. [i] DMSO-d_6.

Table 3. Relevant ^{13}C NMR Data for **NN′N**−Ru[II] Complexes[a]

| complex | **NN′N** | | | PPh$_3$ | | | | | |
	CH$_2$	NMe$_2$	C$_{ortho}$	C$_{meta}$	C$_{para}$	C$_{ipso}$[b]	C$_{ortho}$[c]	C$_{meta}$[d]	C$_{para}$
NN′N	65.8	45.6	158.5	121.2	136.6				
1	73.7	55.6	161.7	119.3	135.0	138.9 (31.7)	127.5 (8.3)	134.4 (9.2)	128.3
3[e]	73.7	52.8, 47.6	162.7	122.6	137.3	134.3 (51.9)	129.2 (10.5)	134.4 (9.9)	131.2
4	72.1	52.6, 45.7	162.6	122.6	137.8	131.6 (46.1)	128.9 (10.6)	133.4 (9.6)	131.3
6a	73.6	55.1, 55.7	159.6	121.0	137.8	136.1 (35.5)	128.6 (8.8)	133.0 (9.6)	129.4
7[f]	75.1	57.2	161.4	123.9	141.8	136.5 (37.9)	131.6 (9.4)	135.0 (9.8)	132.5

[a] 75.469 MHz, CDCl$_3$ at 298 K (unless stated otherwise). Chemical shift values (δ, ppm) indirectly referenced to SiMe$_4$ using solvent signals. [b] $^1J_{PC}$ given in parentheses. [c] ^2J(P,C) given in parentheses. [d] $^3J_{PC}$ given in parentheses. [e] Acetone-d_6. [f] DMSO-d_6.

of [*mer,trans*-RuCl$_2$(**NN′N**)(PPh$_3$)] (**1**) only. No mer,cis product is formed according to the ^{31}P{^{1}H} NMR spectrum. The crystal structure of **1** (Figure 2) also reveals this mer,trans configuration. Some selected crystallographic data for **1** are summarized in Table 4.

In contrast to RuCl$_2$(PPh$_3$)$_3$, RuCl$_2$(PMe$_3$)$_4$ does not react with the **NN′N** ligand at room temperature in CH$_2$Cl$_2$. Obviously, the PMe$_3$ ligands are too strongly bound to ruthenium(II) for a ligand exchange reaction to take place. Accordingly, PMe$_3$ was found to react with complex **1** with dissociation of both **NN′N** and less basic[31] PPh$_3$ to RuCl$_2$(PMe$_3$)$_4$.

Using the same type of ligand exchange reaction of RuCl$_2$-(PPh$_3$)$_3$ with **PNP**, the structurally closely related complex

(31) Basicity of phosphines:[32] PPh$_3$, pK_a = 2.73; PMe$_3$ = 8.65.
(32) Henderson, W. A., Jr.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791−5794.

[RuCl$_2$(**PNP**)(PPh$_3$)] (**2**) was obtained.[7d] Also, the ^{1}H NMR spectrum of **2** shows a singlet resonance for the benzylic protons indicating again a meridional coordination mode of the **PNP** ligand with trans-positioned chloride ligands. Moreover, the ^{31}P{^{1}H} NMR spectrum of **2** shows a set of a doublet and a triplet resonance with a coupling constant of 29 Hz which is characteristic for a MX$_2$Y ligand system and is independent proof for the cis arrangement of PPh$_3$ and the phosphine substituents of the **PNP** ligand.

Reaction of 1 with Silver Triflate, Preparation of [RuCl-(NN′N)(PPh$_3$)]OTf (3) and [RuOTf(NN′N)(PPh$_3$)]OTf (4). When a solution of complex **1** in CH$_2$Cl$_2$ is reacted with either 1 or 2 equiv of AgOTf, purple complexes RuCl(OTf)(**NN′N**)-(PPh$_3$) (**3**) and Ru(OTf)$_2$(**NN′N**)(PPh$_3$) (**4**), respectively, are obtained. The ^{19}F{^{1}H} NMR spectrum of **4** in CDCl$_3$ at 300 K, shows two distinct singlet resonances at −77.82 and −78.17
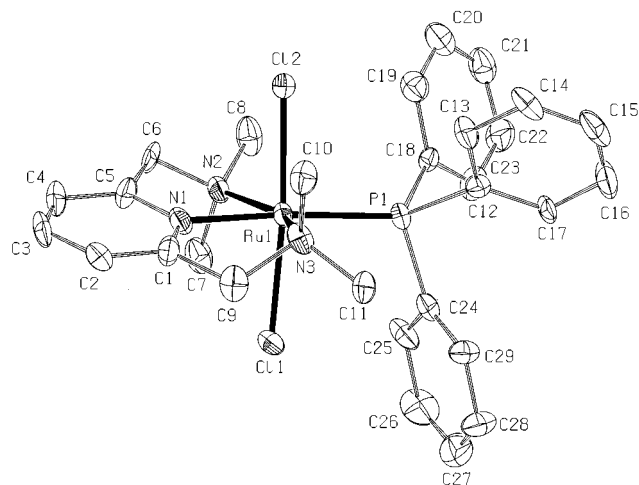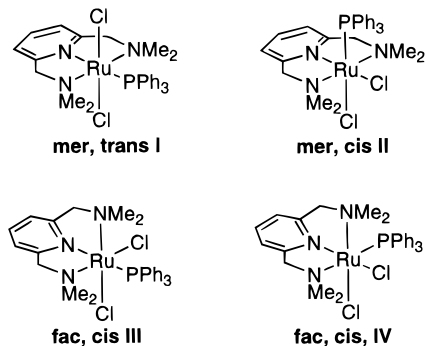
Figure 2. Thermal motion ellipsoid plot (50% probability level) of **1**. H atoms are omitted for clarity.

Chart 1. Potential Coordination Modes of **NN′N** in Ru^{II}[**NN′N**] Complexes

ppm. The signal at −78.17 ppm has been assigned to a free triflate anion;[33] this is supported by the observation that the ^{19}F NMR signal of [Bu$_4$N]OTf in CDCl$_3$ under the same conditions occurs at −78.27 ppm. The ^{19}F NMR spectrum of RuCl(OTf)-(**NN′N**)(PPh$_3$) in acetone-d_6 shows only one signal for free triflate anion at −77.76 ppm ([Bu$_4$N]OTf: −77.73 ppm). These observations lead to the conclusion that these complexes can be best described as cationic 16-electron species [RuCl(**NN′N**)-(PPh$_3$)]OTf (**3**) and [RuOTf(**NN′N**)(PPh$_3$)]OTf (**4**) respectively. The ^{1}H NMR spectra of both **3** and **4** consist of a characteristic *AX* pattern for the benzylic protons and two distinct resonances for the NMe$_2$ groups, indicating C_{2v} symmetry in the complexes. Moreover, the ^{31}P{^{1}H} NMR spectra of both **3** and **4** show a sharp singlet resonance at relatively low field (δ = 85.6 and 74.7 ppm, respectively), which is characteristic for a deshielded PPh$_3$ donor. Such low-field resonances of PPh$_3$ have also been observed for the related five-coordinate, neutral 16-electron ruthenium(II) complexes [RuCl(**NCN**)(PPh$_3$)] and [RuI(**NCN**)-(PPh$_3$)] (**5**) (δ = 91.1 and 89.0 ppm, respectively[10]) containing the terdentate, monoanionic [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$^-$ ([**NCN**]$^-$) ligand. The structural description of these complexes in solution is similar to their structure in the solid state.

Suitable crystals of **4** were grown from a CH$_2$Cl$_2$ solution layered with pentane. The solid state structure of **4** (Figure 3) clearly shows the separation of cation and anion. Some selected crystal data are summarized in Table 4. The η^1-bonding mode of the triflate anion is rather unusual in ruthenium coordination

chemistry, and only a limited number of ruthenium complexes with such anions have been reported.[34] The molecular structure of the [RuOTf(**NN′N**)(PPh$_3$)] cation shows a five-coordinate square-pyramidal ruthenium(II) center with one η^1-O bonded triflate anion. The five-coordinate square-pyramidal structure of the cation of **4** is distorted to a trigonal bipyramidal one by a 77% movement along the Berry pseudorotation axis toward the latter.[35] The cationic nature, as well as the square-pyramidal geometry of the [**4**]$^+$ cation of **4** found in the solid state, is also consistent with the solution NMR data. In [**4**]$^+$ the **NN′N** ligand functions as a terdentate ligand system that occupies three positions in the basal plane of the square pyramid; the N(2)−Ru−N(3) angle is 150.7(2)°. The η^1-bonded triflate occupies the other basal position (∠N(1)−Ru−O(1) = 168.50(20)°), while the PPh$_3$ is coordinating apically (∠N(1)−Ru−P = 95.50-(18)°). Interestingly, the monocation [**4**]$^+$ is isostructural with the neutral 16-electron Ru−NCN complex [RuI(**NCN**)(PPh$_3$)] (**5**).[10] However, the ruthenium−phosphine distance in the solid state structure of **5** (2.1757(7) Å) is lengthened significantly to 2.212(2) Å in the monocation of **4**, pointing to a weaker Ru−P interaction in [**4**]$^+$. On first sight, this is surprising as one would expect the cationic ruthenium center in [**4**]$^+$ to have a higher Lewis acidity than the Ru in **5** due to the presence of the *monoanionic* (**NCN**) ligand in the latter. Although it is difficult to evaluate the possible influence of the difference in anionic character of iodine and triflate, these results seem to indicate that the [**NCN**]$^-$ ligand (in **5**) is a weaker σ-donating ligand as compared with **NN′N** (in **4**). However, when compared to the Ru−P bond lengths of 2.337(3) and 2.3451(12) Å in the six-coordinate complexes **1** and **6a**, respectively, the Ru−P distance in **4** is considerably shortened (2.212(2) Å). Obviously, the ruthenium center in the five-coordinate **4** has a higher Lewis acidic character as compared to both six-coordinate complexes **1** and **6a**. Moreover, the Lewis acidic character of the six-coordinate complexes **1** and **6a** is comparable, despite the cationic character of the latter.

Preparation and Characterization of [*mer*-RuCl(MeCN)-(NN′N)(PPh$_3$)]OTf (6) and [*mer,trans*-Ru(MeCN)$_2$(NN′N)-(PPh$_3$)]OTf$_2$ (7). The chloride ligands in complex **1** can be readily substituted for acetonitrile molecules when a solution of **1** in dichloromethane is treated with 1 or 2 equiv of AgOTf in the presence of MeCN. In this way, the complexes with the stoichiometry [RuCl(OTf)(**NN′N**)(MeCN)(PPh$_3$)] (**6a**) and [Ru-(OTf)$_2$(**NN′N**)(MeCN)$_2$(PPh$_3$)] (**7**) were obtained as light yellow solids. The ^{19}F{^{1}H} NMR spectrum of **6** in CDCl$_3$ shows one singlet resonance at −78.26 ppm, corresponding to free triflate anion (*vide infra*). Moreover, the ^{19}F NMR spectrum of **7** also shows one singlet resonance for free triflate ion at −77.15 ppm ([Bu$_4$N]OTf: −77.17 ppm). These observations point to the formation of mono- and dicationic complexes of type [RuCl-(MeCN)(**NN′N**)(PPh$_3$)]OTf (**6a**) and [Ru(MeCN)$_2$(**NN′N**)(PPh$_3$)]-OTf$_2$ (**7**), respectively. The proton NMR spectrum of **6a** (in CDCl$_3$) shows an *AX* resonance pattern for the benzylic protons and two distinct singlet resonances for NMe$_2$ units, indicating that the benzylic carbons and the nitrogen atoms of the NMe$_2$ units lie in a molecular plane of symmetry. In the ^{31}P{^{1}H} NMR spectrum, a singlet resonance appears at 32.8 ppm which is illustrative for triphenylphosphine coordinating trans to the pyridine nitrogen.

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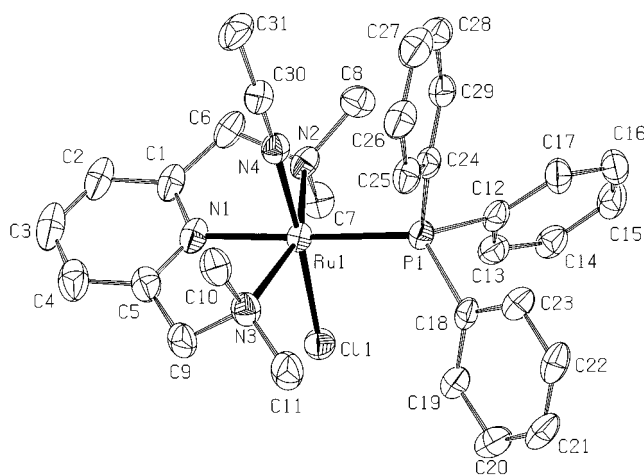(35) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119 and references cited therein.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **4**, **6a**, **11**, and **13**

	1	**4**	**6a**	**11**	**13**
			Bond Distances		
Ru1−N1	2.023(8)	1.953(7)	2.024(4)	2.058(7)	1.973(2)
Ru1−N2	2.229(10)	2.143(6)	2.226(4)	2.230(7)	2.188(3)
Ru1−N3	2.211(8)	2.151(6)	2.222(4)	2.201(6)	2.177(3)
Ru1−P1	2.337(3)	2.212(2)	2.3451(12)	2.2384(2)	−
Ru1−Cl1	2.421(3)	−	2.4060(14)	2.445(2)	−
Ru1−Cl2	2.429(3)	−	−	−	−
Ru1−**OSO₂**	−	2.141(6)	−	−	2.143(2)
Ru1−**HOEt**	−	−	−	−	2.159(2)
Ru1−N4	−	−	1.996(4)	−	−
Ru1−**CO**	−	−	−	1.851(8)	1.815(3)
			Bond Angles		
N2−Ru1−N3	155.8(3)	150.7(2)	156.16(14)	157.1(3)	160.65(9)
N1−Ru1−N2	77.9(3)	81.3(2)	78.00(16)	78.3(3)	80.19(13)
N1−Ru1−N3	78.0(3)	79.7(3)	78.18(16)	78.7(3)	80.55(13)
Cl1−Ru1−C12	174.48(8)	−	−	−	−
Cl1−Ru1−N1	84.7(3)	−	89.53(11)	87.70(19)	−
Cl1−Ru1−N2	92.8(3)	−	93.13(10)	93.0(2)	−
Cl1−Ru1−N3	86.8(3)	−	87.70(10)	86.32(16)	−
Cl1−Ru1−N4	−	−	175.89(11)	−	−
N1−Ru1−P1	175.9(3)	95.50(18)	177.67(11)	178.97(19)	−
N2−Ru1−P1	102.0(2)	103.97(16)	101.91(10)	101.9(2)	−
N3−Ru1−P1	102.1(2)	99.92(18)	101.84(10)	101.1(2)	−
P1−Ru1−**OSO₂**	−	94.27(16)	−	−	−
N1−Ru1−**OSO₂**	−	168.5(2)	−	−	170.07(11)
Cl1−Ru1−**CO**	−	−	−	177.3(3)	−
Et**OH**−Ru1−**CO**	−	−	−	−	176.78(12)
N1−Ru1−**CO**	−	−	−	89.6(3)	94.31(13)
N2−Ru1−**CO**	−	−	−	86.7(3)	93.68(13)
N3−Ru1−**CO**	−	−	−	92.9(3)	89.48(13)
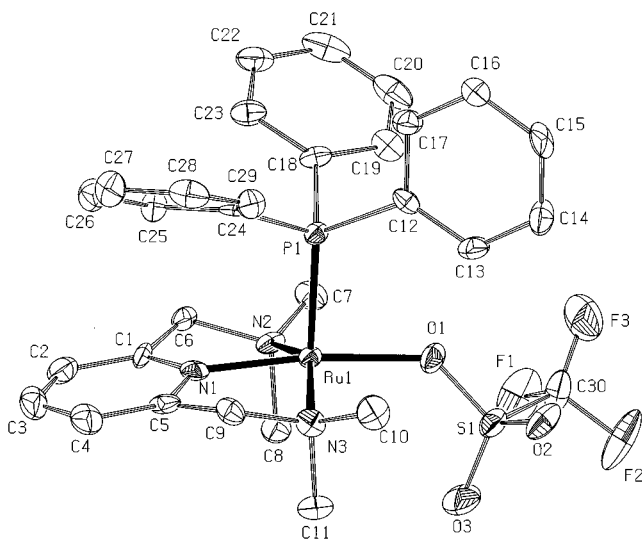
Figure 3. Thermal motion ellipsoid plot (50% probability level) of **4**. H atoms are omitted for clarity.

Figure 4. Thermal motion ellipsoid plot (50% probability level) of **6a**. H atoms are omitted for clarity.

The solid state molecular structure of **6a** (Figure 4) shows *meridional* coordination of **NN′N** with the chloride and MeCN ligand in *apical* positions and a PPh₃ trans-positioned relative to the pyridine nitrogen. Some selected bond distances and angles are given in Table 4.

The NMR data for complex **7** indicate a high degree of symmetry within a complex cation; in its ¹H NMR spectrum (DMSO-d_6) the **NN′N** ligand shows singlet resonances for the four methylene protons and for the methyl groups of the NMe₂ units. It also reveals the presence of two coordinating MeCN ligands. The ³¹P{¹H} NMR spectrum of complex **7** shows, like those of **1** and **6a**, a high-field singlet resonance (37.4 ppm). These data suggest a simple *trans,mer*-**I** (see Chart 1) octahedral geometry at the dicationic metal, with **NN′N** coordinating meridionally.

The lability of chloride in complex **1** is clearly demonstrated by its reaction with acetonitrile in the absence of silver triflate. When a suspension of **1** in acetonitrile is gently heated at 55 °C for a few minutes, a clear brown solution is formed, which, after evaporation of MeCN, yields a yellow-brown solid with molecular formula [RuCl₂(MeCN)(**NN′N**)(PPh₃)] (**6b**) in almost quantitative yield. The ¹³C and ³¹P NMR spectra of this new complex closely resemble those of the monocationic complex **6a**; however, the ¹H NMR spectrum in CDCl₃ differs. Although the resonances arising from the pyridine and PPh₃ units are quite similar, the singlet resonance of coordinated MeCN is shifted to higher field (from 1.91 ppm in **6a** to 2.15 ppm in **6b**). Along with this, the chemical shifts of the doublet resonances of the *AX* pattern of the benzylic protons are significantly shifted (from 4.30 and 3.88 ppm for **6a** to 4.33 and 4.12 ppm). Upon exchange of one chloride anion for one triflate anion by reaction of **6b** with 1 equiv of AgOTf, the ¹H NMR spectrum of the

product becomes identical with that of **6a**. The UV/visible spectrum of **6b** in dichloromethane closely matches the spectrum of **6a**. Both complexes show an absorption maximum at the same wavelength (350 nm) along with an extinction coefficient of about 4600, proving that both complexes must be isostructural and that **6b** can be described as [RuCl(MeCN)(**NN′N**)(PPh₃)]-Cl. We believe that the differences observed in the ¹H NMR spectra arise from differences in the anion−cation pair associations in CDCl₃ solution.[7d]

During the reaction of **1** with acetonitrile at 55 °C, no formation of dicationic [Ru(MeCN)₂(**NN′N**)(PPh₃)]²⁺, analogous to **7**, is observed. At reflux conditions, besides the formation of **6b**, partial dissociation of triphenylphosphine from **1** is observed along with the formation of unidentified side products. From ¹H NMR spectra, crystalline samples of **6b** proved to contain non-coordinating CH₂Cl₂. Attempts to obtain a CH₂Cl₂-free sample of **6b** by heating powdered crystals of **6b**·xCH₂Cl₂ *in vacuo* at 80 °C overnight failed because of partial dissociation of MeCN and re-formation of **1**.

Unexpected Formation of (μ-Dinitrogen)({*mer*,*trans*-RuCl₂(NN′N)}₂) (8).** When a slurry of polymeric [RuCl₂(nbd)]ₙ (nbd = 2,5-norbornadiene) is reacted with the **NN′N** ligand in refluxing benzene under a dinitrogen atmosphere, a yellow-brown reaction mixture is obtained from which, after workup, light reddish-brown crystals of a new ruthenium complex are obtained which readily turn green upon exposure to air. ¹H as well as ¹³C NMR analyses of this crystalline product showed only singlet resonances for the benzylic protons and NMe₂ units, pointing to a meridionally coordinating **NN′N** ligand. Assuming the presence of a RuCl₂ fragment, it was anticipated that the chloride ligands are trans-positioned as observed in the complexes **1** and **2**. According to elemental analysis, C/H and C/N ratios were consistent with a product with molecular formula [N₂Ru₂Cl₄(**NN′N**)₂], *i.e.* of two RuCl₂(**NN′N**) moieties and one molecule of N₂. However, the analyzed values of both carbon, hydrogen, and nitrogen were consistently lower than the ones calculated. Transition metal complexes containing dinitrogen as a ligand have been extensively studied[36] in view of their relevance to nitrogen fixation.[37] In fact, the dinitrogen metal complex [(N₂)Ru(NH₃)₅]²⁺, Allen and Senoff's ion,[38] was the first stable transition metal−dinitrogen complex synthesized, and it shows a characteristic $\nu_{N\equiv N}$ vibration. However, in the IR spectrum of the new complex, no stretching vibration $\nu_{N\equiv N}$ is observed, which suggests that this complex has a symmetric dimeric structure with a μ²-bridging dinitrogen molecule. Indeed, in the Raman spectrum a strong signal for a N−N stretching vibration at 2099 cm⁻¹ is found, proving the presence of a bridging dinitrogen ligand. Support for this assignment is provided by the vibrational data of the tetracationic complexes [(NH₃)₅Ru(N₂)Ru(NH₃)₅][(BF₄)₄] (2100 cm⁻¹) and [(NH₃)₅Ru-(N₂)Ru(H₂O)₅][(BF₄)₄] (2080 cm⁻¹).[39c,40]

To obtain conclusive evidence about the nature of the crystalline product, a single crystal X-ray determination was

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 8

Bond Distances			
Ru1−N11	1.9695(19)	Ru2−N21	1.969(2)
Ru1−N12	2.166(2)	Ru2−N22	2.172(2)
Ru1−N13	2.169(2)	Ru2−N23	2.177(2)
Ru1−Cl11	2.4121(7)	Ru1−Cl21	2.4223(7)
Ru1−Cl12	2.4202(6)	Ru2−Cl22	2.4233(7)
Ru1−N14	1.9562918)	Ru2−N24	1.953(2)
N14−N24	1.110(3)		

Bond Angles			
N11−Ru1−N12	80.48(9)	N21−Ru2−N22	80.37(9)
N11−Ru1−N14	177.07(8)	N21−Ru2−N24	177.83(8)
N12−Ru1−N13	161.61(9)	N22−Ru2−N23	160.07(9)
Cl11−Ru1−Cl12	178.71(2)	Cl21−Ru3−Cl22	177.07(3)
Ru1−N14−N24	172.75(18)	Ru2−N24−N14	174.10(18)

performed. Some selected bond distances and angles are collected in Table 5. The solid state structure of the product (Figure 5) shows two RuCl₂(**NN′N**) moieties, which are symmetrically bridged by molecular nitrogen. Both **NN′N** ligands are coordinating meridonally, with a resulting trans-positioning of the chloride ligands.

On basis of this data, the complex can be formulated as [(μ-N₂){*mer*,*trans*-RuCl₂(**NN′N**)}₂] (**8**, Scheme 2). The **NN′N** ligands are twisted in such a way that the planes defined by N(11)N(14)Cl(11)Cl(12) and N(21)N(24)Cl(21)Cl(22) are orientated almost perpendicularly, the actual angle being 89.38-(5)°. Moreover, the Ru(1)−N(14)−N(24)−Ru(2) bonding unit is slightly bent, as indicated by the dihedral angle of Ru(1)N-(14)N(24)Ru(2) of 6(3)°. The N(14)−N(24) distance is 1.110-(3) Å (*cf.* N−N = 1.0977 Å for free N₂[41]); consistent with back-donation of electron density from Ruᴵᴵ to N₂.[39c] A comparable lengthening of the N≡N distance to 1.124 Å was also observed for the closely related tetracationic dimer [(NH₃)₅Ru(N₂)Ru-(NH₃)₅][(BF₄)₄].[39c] The almost perpendicular twisting of the two **NN′N** ligand systems in complex **8** can be accounted for by a simple orbital argument. As Ru²⁺ is a 6-electron metal ion in an octahedral coordination sphere, the t₂g set of orbitals is filled. Therefore, π back-donation of electron density from ruthenium t₂g orbitals will occur into two orthogonal sets of empty π* antibonding orbitals of the nitrogen. By perpendicular twisting of the RuCl₂(**NN′N**) moieties, this back-donation will be optimally effective.

Reactions of 3 and 4 with CO. In view of the expected reactivity of our 16-electron, coordinatively unsaturated complexes **3** and **4** toward potential substrates, we have carried out some reactions with CO.

When CO is bubbled through a purple solution of the chloride complex [RuCl(**NN′N**)(PPh₃)]OTf (**3**) in CH₂Cl₂, the color changes from purple to light brown. Upon *addition* of pentane, a yellow precipitate, consisting mostly of [RuCl(CO)₂(**NN′N**)]-OTf (**10**), is obtained. The presence of two coordinating CO ligands in this complex was clearly established by both ¹³C NMR and IR spectroscopy. The ¹³C NMR spectrum of **10** shows two CO resonances, and in the ν_{CO} region of the IR spectrum two absorptions are observed, pointing to a complex of type *cis*-L₄M(CO)₂.[42] The ¹H NMR spectrum of **10** shows a characteristic AB pattern for the benzylic protons as well as two distinct resonances for the NMe₂ units of the **NN′N** ligand, characteristic for meridionally coordinating **NN′N** together with a cis-orientation of the two CO ligands.

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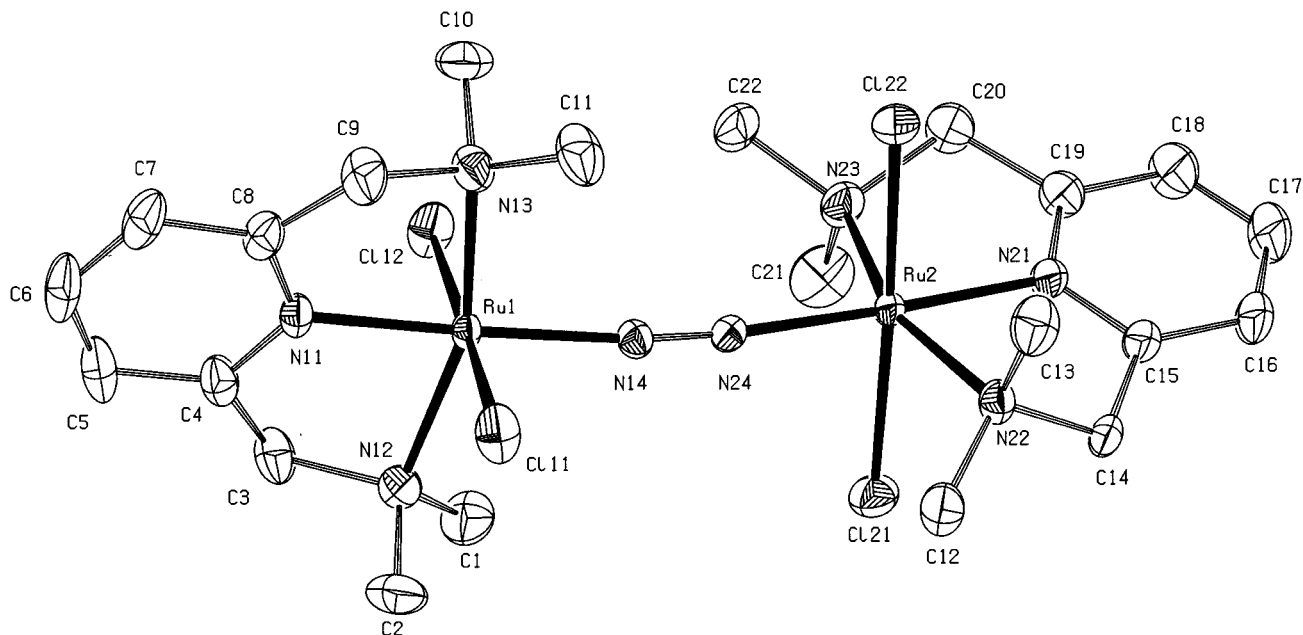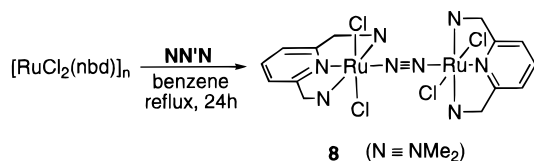
Figure 5. Thermal motion ellipsoid plot (50% probability level) of **8**. H atoms are omitted for clarity.

Scheme 2

8   (N ≡ NMe₂)

Interestingly, when pentane is allowed to *slowly diffuse* into the reaction mixture, a compound with molecular formula [RuCl(CO)(**NN′N**)(PPh₃)]OTf (**11**) crystallizes in high yield. The ¹H NMR spectrum of this complex showed diastereotopic resonances of benzylic protons and NMe₂ units, indicating a molecular geometry involving meridional terdentate **NN′N** coordination. The presence of one coordinating CO was established by ¹³C NMR and IR spectroscopy. The ¹³C NMR spectrum showed only one carbonyl signal, with a small $^2J_{PC}$ coupling constant of 13.6 Hz, pointing to a mutual cis-position of CO and PPh₃. In the ν_{CO} region of the IR spectrum also only one signal was observed. In order to establish the stereochemistry of **11** and to obtain information about relevant bond angles and distances in the solid state, a single crystal X-ray determination was performed (Figure 6 and Table 4).

The mechanism of formation of **10** most probably involves the addition of one molecule of CO to the coordinatively unsaturated 16-electron complex **3**, followed by rearrangement of the intermediate through Berry-pseudorotation intermediates to **11**. Subsequent substitution of the PPh₃ ligand by CO then affords **10** (Scheme 3). This type of reactivity has also been observed in structurally closely related neutral ruthenium(II) complexes containing the monoanionic ligands [C₆H₃(CH₂-NMe₂)₂-2,6]⁻ ([**NCN**]⁻ and [C₆H₃(CH₂PPh₂)₂-2,6]⁻ ([**PCP**]⁻).[10,11] For example, reaction of [RuCl(**ECE**)(PPh₃)] with CO yields neutral complexes of type [RuCl(CO)₂(**ECE**)] with cis-positioned CO ligands, as in **10**. The formation of these complexes also proceeds *via* a neutral monocarbonyl [RuCl-(CO)(**ECE**)(PPh₃)] intermediate analogous to **10**.[43]

The reaction of the triflate complex [RuOTf(**NN′N**)(PPh₃)]-OTf (**4**) with CO was of interest because it could give insight

(43) Karlen, T.; Veldman, N.; Spek, A. L.; van Koten, G. Manuscript in preparation.
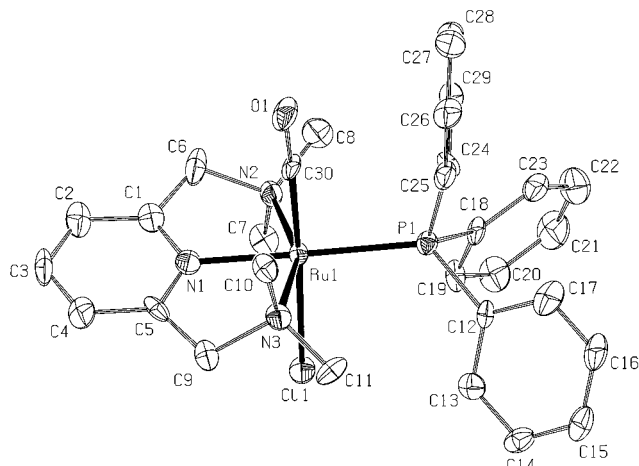
Figure 6. Thermal motion ellipsoid plot (50% probability level) of **11**. H atoms are omitted for clarity.

Scheme 3

3   **11**   **10**
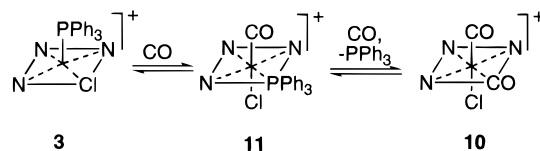
into the nature of the Ru−OTf bond. When CO is bubbled through a purple solution of **4** in CH₂Cl₂, a color change from purple to yellow is observed. Independent of the mode of addition of pentane to the reaction mixture, a precipitate is formed existing of at least four unidentified products. The yellow color of these products points to the formation of coordinatively saturated 18-electron complexes. From NMR analyses of this impure yellow solid, it could be concluded that no dissociation of the **NN′N** ligand has taken place. The presence of *AX* resonance patterns in the ¹H NMR spectrum points to meridionally coordinating **NN′N** in all of the newly formed complexes. One of the products formed (in 10−30% yield) is the monocarbonyl complex [*mer*-RuOTf(CO)(**NN′N**)-(PPh₃)]OTf (**12**). However, all attempts to isolate a pure product *via* crystallization failed. Obviously, upon changing from X
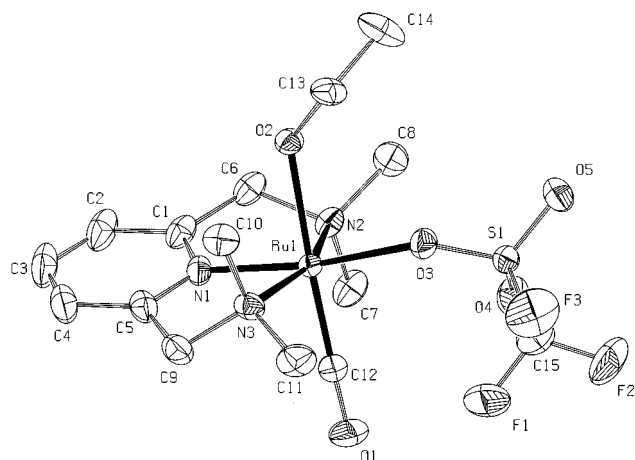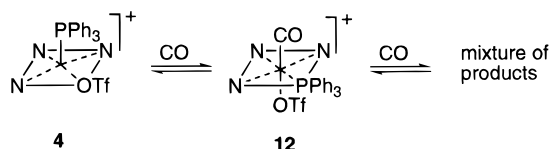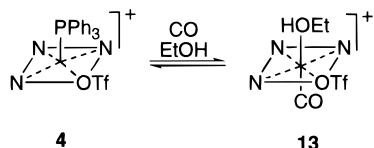
Figure 7. Thermal motion ellipsoid plot (50% probability level) of **13**. H atoms are omitted for clarity.

Scheme 4

Scheme 5

= chloride in **3** to X = triflate in **4**, no change of stereoselectivity in the initial reaction with CO is observed. In both cases, the intermediate monocarbonyl product is formed. However, as stated above, only in the case where X = Cl a pure dicarbonyl product could be isolated. It is noteworthy that the structurally related neutral complex [RuOTf(**PCP**)(PPh$_3$)] has been reported to be converted into [*trans*-Ru(**PCP**)(CO)$_2$(PPh$_3$)] upon reaction with CO.[43]

Remarkably, when the same reaction of [RuOTf(**NN'N**)-(PPh$_3$)]OTf (**4**) with CO is performed in the presence of ethyl alcohol (Scheme 4), upon slow diffusion of pentane in the reaction mixture, large orange to yellow crystals are obtained of which the IR spectrum shows only one resonance in the area of the ν_{CO} absorption frequency, pointing to the presence of only one CO ligand. ^{1}H NMR spectroscopy in acetone-d_6 or DMSO-d_6 revealed the presence of one molecule of ethanol in the product. However, due to partial or complete dissociation of the complex in the potentially coordinating solvents used, no NMR data could be obtained. According to elemental analysis, the product can be formulated as [RuOTf(CO)(**NN'N**)-(HOEt)]OTf (**13**). The solid state structure of **13** (Figure 7) shows an octahedrally coordinated ruthenium(II) center with meridionally coordinating **NN'N**. The axial positions are occupied by the ethyl alcohol and the CO ligand. The anionic triflate ligand is trans-positioned toward the central pyridine atom. Some structural data of complex **13** (Scheme 5) are collected in Table 4.

Coordination Behavior of NN'N. In the octahedral 18-electron complexes **1**, [**6**]X, **7**, **8**, and **13**, the **NN'N** ligand system is meridionally bonded with the ruthenium center lying in the plane defined by the pyridine ring. The ring strain in

the five-membered chelate rings Ru−N(1)−C−C−N(2) and Ru−N(1)−C−C−N(3) is partially released by ring puckering, which is of C_2 symmetry, placing one amino methyl group axially on each side of the plane defined by the pyridine ring. The flexibility of the nitrogen donor substituents of the **NN'N** ligand is clearly demonstrated in the 16-electron complex **4**. In this complex, the five-membered chelate rings are puckered with mirror plane symmetry (see plane through C(4)NRuO(1) and P(1)). Consequently in this structure, one of the methyl groups of each NMe$_2$ unit is axially positioned, and these reside at the same side of the pyridine plane. As a result the remaining NMe groups are in equatorial position. This structural motif has also been observed in the solid state structure of the related *pentacoordinated* complex [RuOTf(**NCN**)(PPh$_3$)].[10] However, in contrast to complexes containing the [**NCN**]$^-$ ligand,[10] no facial coordination of the **NN'N** ligand is found. Although bidentate coordination of terpyridine has been reported,[44] bidentate coordination of **NN'N** has so far not been observed either.

Conclusions

Although the **NN'N** ligand system bears some resemblance to the more rigid terpyridine, complexes containing the **NN'N** ligand are not restricted to six-coordination. The **NN'N** ligand forms well-defined, five- and six-coordinate Ru(II) complexes (16- and 18-electron species, respectively) in combination with a variety of unidentate ligands. In all complexes obtained so far, **NN'N** uses all three nitrogen donor atoms to coordinate to the metal center in a rather flexible coordination mode. The structural feature of five-coordination results in the formation of coordinatively unsaturated ruthenium(II) complexes containing the **NN'N** ligand and makes these complexes interesting from the viewpoint of potential application in homogeneously ruthenium(II)-catalyzed reactions. The presence of a labile dinitrogen ligand makes complex **8** potentially interesting as a precursor for the synthesis of a variety of ruthenium(II) complexes of type RuCl$_2$(**NN'N**)L, where L is a neutral ligand. We have already found that the dinitrogen can be readily replaced by small molecules like ethylene,[45] and we are currently investigating this reactivity further.

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