Kinetic and Thermodynamic Products in the Reaction of $[RuCl_2(CO)_2]_n$ with Pyridinecarbaldimine Ligands and the Crystal Structure of *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine)

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The reaction of pyridinecarbaldehyde with the appropriate amines H_2NR (R = $CH_2CH_2OCH_3$, $CH_2CH_2CH_2OCH(CH_3)_2$) yielded the new pyridinecarbaldimine ligands $CH_3OCH_2CH_2$-Pyca (**b**) and *i*$PrOCH_2CH_2CH_2$-Pyca (**c**), respectively. The reaction of *n* equiv of R-Pyca ligand (*i*Pr-Pyca = **a**) with the polymer $[RuCl_2(CO)_2]_n$ led to the formation of monomeric ruthenium(II) complexes of composition $Ru(CO)_2Cl_2$(R-Pyca). The stereochemistry of these complexes could be controlled by altering the reaction conditions; i.e., in dichloromethane at ambient temperature the kinetic product *trans*-$Cl_2Ru(CO)_2$(R-Pyca) (**1**) is formed in 75–95% yield. Heating the kinetic product for 80 h in xylene or starting the reaction of the ligand with $[RuCl_2(CO)_2]_n$ in toluene at reflux temperature gave the thermodynamic *cis*-product (**2**) in high yields (90–95%). In the reaction of $[RuI_2(CO)_2]_n$ with the corresponding ligands only one isomer was formed: *trans*-$I_2Ru(CO)_2$(R-Pyca) (**3**). If the reaction of **c** with the polymer was carried out in methanol at room temperature, *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine) (**4c**) was obtained, in which a methanol molecule has added to the imine function of the ligand. The X-ray structure determination of the yellow crystals of **4c** ($C_{15}H_{22}N_2O_4Cl_2Ru$) was carried out. Crystal data for **4c**: monoclinic, space group $P2_1/c$ (No. 14) with a = 8.213(1) Å, b = 12.952(4) Å, c = 18.009(4) Å, β = 95.80(1)°, V = 1905.8(8) Å^3, and Z = 4. A special feature of the complex is the intramolecular N–H···O bridge, formed between the amine hydrogen and the ether oxygen of the ligand. The methanolysis is acid catalyzed. The reaction of **a** or **b** with $[RuCl_2(CO)_2]_n$ in methanol led to new, unidentified products, whose NMR and IR data showed that no methanolysis had taken place.

Introduction

In coordination chemistry the study of the influence of ligands on the geometry and reactivity of complexes is a topic of major importance. The finding that complexes with bidentate ligands have properties different from those containing two monodentate ligands (e.g. $Ph_2P(CH_2)_nPPh_2$ with n = 2–4 instead of two PPh_3) has resulted in the design of many new bidentate ligands.[1] Thus far, interest has been focused mainly on polydentate ligands with one type of donor atom. Exceptions are the hemilabile ether–phosphine ligands, which feature a phosphorus atom and an ether oxygen atom for strong and a weak coordination to the metal center, respectively.[2] Introduction of a hemilabile chain increases the potential reactivity of a metal center because vacant sites are easily available and can be protected intramolecularly.[2,3]

In our laboratory bidentate nitrogen ligands, and especially α-diimines, have been used as tuning ligands of mono- and/or dinuclear complexes of iron, ruthenium, palladium, and rhodium.[4] The interest in transition metal complexes with these ligands stems from (a) their σ-donor and π-acceptor properties, (b) their versatile coordination behavior and (c) the influence of easy-to-introduce substituents.[4] In Figure 1 examples of σN-coordinated *t*Bu-DAB (DAB = 1,4-diazabutadiene) (**A**),[5] σN, σN Ph-BIAN (Ph-BIAN = bis(phenylimino)acenaphthene) (**B**),[6] and σN, σN (**C**)[7] and σN, μ_2N′, η^2-C=N bonded (**D**)[8] *i*Pr-DAB are shown.

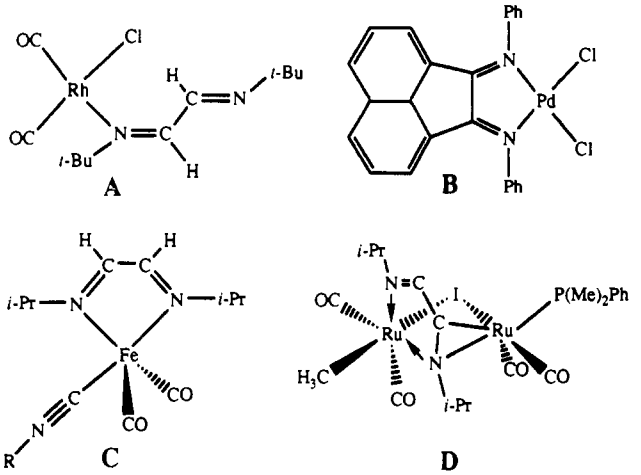

Figure 1. Examples of coordinated α-diimine ligands.

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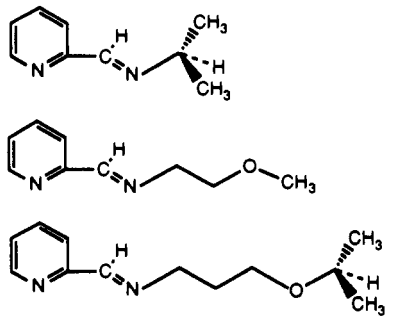

Figure 2. Ligands *i*Pr-Pyca (**a**), $CH_3OCH_2CH_2$-Pyca (**b**), and *i*$PrOCH_2CH_2CH_2$-Pyca (**c**).

To extend the chemistry of this type of ligand, we introduced an ether arm on the imine function of R-Pyca (R-pyridinecarbaldimine), creating a potential terdentate ligand. In our ether–Pyca ligands the ether arm consists of an alkyl chain with the ether oxygen atom on the fourth (ligand **b**) or fifth (ligand **c**) position with respect to the imine nitrogen atom. This variation was designed to investigate the influence of the length of the alkyl arm on metallocycle formation. Ligand **a** was used to compare these ligands with a non-ether-arm containing R-Pyca. Ligands **a**–**c** are shown in Figure 2.

We started our research on the monomeric ruthenium complexes with complexes $Ru(CO)_2Cl_2$(R-Pyca), analogous to the known $Ru(CO)_2I_2$(*p*-tolyl-DAB) complex.[9a] In this paper we report the selective formation of stereoisomers of $X_2Ru(CO)_2$-(R-Pyca) (with X = Cl or I) and the unexpected methanolysis of ligand **c** during complexation in methanol. The effect of the R group of the R-Pyca ligand on the reactivity of the complexes will be discussed.

Experimental Section

Ruthenium trichloride trihydrate was a loan from Johnson Matthey, Inc. $[RuCl_2(CO)_2]_n$ and $[RuI_2(CO)_2]_n$ were prepared according to the literature.[10] *i*Pr-Pyca (**a**) was synthesized as described earlier.[11] Trimethylamine oxide was sublimed before use. All syntheses were carried out under nitrogen atmosphere, using standard Schlenk techniques. CH_2Cl_2 was dried over P_2O_5; all other solvents were dried over sodium wire. The solvents were distilled from the respective desiccants and stored under nitrogen. Column chromatography was performed using dried and activated silica gel (kieselgel 60, E. Merck, 70–238 mesh) as the stationary phase. ^1H and $^{13}C\{^1H\}$ NMR measurements were carried out on Bruker AC100, WM250, or AMX300 spectrometers. Chemical shifts (δ, ppm) are given relative to $SiMe_4$. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrometer connected to a Model 3600 data station. Field desorption (FD) mass spectra were obtained with a Varian MAT711 double-focussing mass spectrometer with a combined EI/FI/FD source, fitted with a 10-μm tungsten wire FD-emitter containing carbon microneedles with an average lenght of 30 μm, using emitter currents of 0–15 mA. Elemental analyses were carried out by the Elemental Analysis section of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. The obtained products have been identified by ^1H and $^{13}C\{^1H\}$ NMR, UV/vis (Table III), and IR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis of *i*$PrOCH_2CH_2CH_2$-Pyca (c). To 3.81 g (35.6 mmol) pyridinecarbaldehyde in 40 mL of diethyl ether was added 4.17 g (35.6 mmol) of (isopropoxypropyl)amine, together with 4 g of $MgSO_4$. After 18 h of stirring at RT (RT = room temperature), the $MgSO_4$ was filtered off and washed with two portions of 20 mL of diethyl ether. The collected filtrates were evaporated to dryness in vacuo. A light yellow oil resulted in quantitative yield (99%, 5.84 g). Anal. Found (calcd) for **c** $C_{12}H_{18}N_2O$: C, 69.82 (69.86); H, 8.59 (8.80); N, 13.37 (13.58). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 0.90 (6H, d, 6.1 Hz; *i*Pr Me), 1.76 (2H, quintet, 6.5 Hz; $CH_2CH_2CH_2$), 3.26 (2H, t, 6.5 Hz; NCH_2), 3.30 (1H, septet, 6.1 Hz; *i*Pr CH), 3.53 (2H, t, 6.5 Hz; OCH_2), 7.06 (1H, dd; H5), 7.49 (1H, dd; H4), 7.75 (1H, d, 7.9 Hz; H3), 8.17 (1H, s; N=CH), 8.40 (1H, d, 4.2 Hz; H6). ^{13}C NMR (APT, RT, 25.18 MHz): δ = 22.30 (*i*Pr Me), 31.16 ($CH_2CH_2CH_2$), 58.31 (NCH_2), 65.66 (OCH_2), 71.54 (*i*Pr CH), 121.35 (py C5), 124.73 (py C4), 136.60 (py C3), 149.56 (py C6), 154.61 (py C2), 162.26 (N=CH).

For the synthesis of $CH_3OCH_2CH_2$-Pyca (**b**) the same procedure as above was followed, using 2.53 g (23.6 mmol) of pyridinecarbaldehyde and 1.77 g (23.6 mmol) of (methoxyethyl)amine in 50 mL of diethyl ether. Yield: 100%. ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 3.27 (3H, s; OCH_3), 3.62 (2H, t, 5.7 Hz; NCH_2), 3.75 (2H, t, 5.7 Hz; OCH_2), 7.19 (1H, dd; H5), 7.62 (1H, dd; H4), 7.89 (1H, d, 8.1 Hz; H3), 8.31 (1H, s; N=CH), 8.53 (1H, d, 5.1 Hz; H6). ^{13}C NMR (APT, RT, 75.4 MHz): δ = 59.40 (NCH_2), 61.38 (OCH_2), 72.47 (OCH_3), 122.00 (py C5), 125.27 (py C4), 137.03 (py C3), 149.97 (py C6), 154.92 (py C2), 163.99 (N=CH).

Synthesis of *trans*-$Cl_2Ru(CO)_2$(R-Pyca) (1a–c). In a typical reaction, 363.4 mg of ligand **a** (2.45 mmol) in 10 mL of CH_2Cl_2 was added to a suspension of 556.3 mg of $[RuCl_2(CO)_2]_n$ (2.45 mmol) in 15 mL of CH_2Cl_2. The orange-yellow suspension was stirred at room temperature for 18 h. After evaporation of the solvent a brownish solid resulted, which was purified by column chromatography (column 1 × 20 cm; eluent dichloromethane/diethyl ether = 5/1). The first yellow fraction contained **1a** (yield 735 mg, 80%), the second orange fraction contained **2a** (yield 183 mg, 20%). Anal. Found (calcd) for **1a** ($C_{11}H_{12}N_2O_2Cl_2Ru$): C, 34.87 (35.12); H, 3.32 (3.22); N, 7.38(7.45). Selected IR data for **1a** (cm^{-1} in KBr): ν(CO) 2060 (vs) and 2000 (vs); ν(py C=N) 1632 (vw); ν(imine C=N) 1600 (m); ν(Ru–Cl) 340 (m) and 320 (m). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 1.65 (6H, d, 6.3 Hz; *i*Pr Me), 4.49 (1H, sept, 6.3 Hz; *i*Pr H), 7.69 (1H, dd; H5), 7.94 (1H, d, 7.5 Hz; H3), 8.10 (1H, dd; H4), 8.60 (1H, s; N=CH), 9.13 (1H, d, 6.6 Hz; H6). ^{13}C NMR (APT, 263K, 75.4 MHz): δ = 23.20 (*i*Pr Me), 65.52 (*i*Pr CH), 128.62 and 128.76 (py C4, py C5), 139.81 (py C3), 152.79 (py C6), 153.92 (py C2), 163.14 (N=CH), 195.13 and 195.64 (CO's).

Complex **1b** was obtained in analogous manner (ratio **1b**/**2b** = 3/1; yield = 75% for **1b**). Selected IR data for **1b** (cm^{-1} in KBr): ν(CO) 2063 (vs) and 1999 (vs); ν(py C=N) 1630 (vw); ν(imine C=N) 1597 (m). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 3.38 (3H, s; OCH_3), 4.02 (2H, t, 4.5 Hz; NCH_2), 4.40 (2H, t, 4.5 Hz; OCH_2), 7.70 (1H, dd; H5), 7.88 (1H, d, 5.1 Hz; H3), 8.12 (1H, dd; H4), 8.51 (1H, s; N=CH), 9.14 (1H, d, 5.1 Hz; H6). ^{13}C NMR (APT, RT, 62.9 MHz): δ = 54.63 (OCH_3), 63.41 and 67.36 (OCH_2 and NCH_2), 139.58 (py C5), 140.67 (py C4), 154.65 (py C3), 167.25 (py C6), 172.71 (py C2), 190.27 (N=CH), 213.94 and 221.57 (CO's).

Complex **1c** was obtained in analogous manner (ratio **1c**/**2c** = 4/1; yield = 80% for **1c**). Anal. Found (calcd) for **1c** ($C_{14}H_{18}N_2O_3Cl_2Ru$): C, 38.59 (38.72); H, 4.17 (4.18); N, 6.54 (6.45). Selected IR data for **1c** (cm^{-1} in KBr): ν(CO) 2050 (vs) and 1996 (vs); ν(py C=N) 1630 (vw); ν(imine C=N) 1600 (m); ν(Ru–Cl) 335 (m) and 320 (m). FD-mass: *m/e* 434 (M^+ = 434). ^1H NMR ($CDCl_3$, RT, 100.13 MHz): δ = 1.14 (6H, d, 6.1 Hz; *i*Pr Me), 2.31 (2H, quintet, 6.5 Hz; $CH_2CH_2CH_2$), 3.5 (2H + 1H, m; NCH_2 + *i*Pr CH), 4.34 (2H, t, 6.8 Hz; OCH_2), 7.70 (1H, m; H5), 7.91 (1H, d, 7.8 Hz; H3), 8.10 (1H, m; H4), 8.49 (1H, s; N=CH), 9.08 (1H, d, 5.2 Hz; H6). ^{13}C NMR (APT, 263 K, 25.18 MHz): δ = 22.50 (*i*Pr Me), 28.95 ($CH_2CH_2CH_2$), 61.63 (NCH_2), 63.99 (OCH_2), 71.77 (*i*Pr CH), 128.57 (py C5), 129.05 (py C4), 140.24 (py C3), 153.36 (py C6), 153.91 (py C2), 166.63 (N=CH), 195.44 and 195.60 (CO's).

Synthesis of *cis*-$Cl_2Ru(CO)_2$(R-Pyca) (2a–c). A typical procedure is as follows: To a solution of 136.4 mg of ligand **b** (0.83 mmol) in 20 mL of xylene was added 190 mg of $[RuCl_2(CO)_2]_n$ (0.83 mmol). The yellow-brownish suspension was refluxed for 20 h in the dark. After cooling, the brown precipitate was collected on a glass filter and washed twice with 10 mL of hexanes. The solid was purified by column chromatography as described above, yielding 264 mg (85%) of **2a** and 47 mg (15%) of **1a**. Anal. Found (calcd) for **2a** ($C_{11}H_{12}N_2O_2Cl_2Ru$): C, 35.08 (35.12); H, 3.34 (3.22); N, 7.41 (7.45). Selected IR data for **2a** (cm^{-1} in KBr): ν(CO) 2060 (vs) and 1995 (vs); ν(py C=N) 1625 (vw); ν(imine C=N) 1595 (m); ν(Ru–Cl) 320 (m). FD-mass: *m/e* 376 (M^+ = 375). ^1H

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NMR ($CDCl_3$, RT, 300.13 MHz): δ = 1.51, 1.54 (3H, d, 6.3 Hz; *i*Pr Me 2x); 4.22 (1H, sept, 6.3 Hz; *i*Pr H), 7.77 (1H, dd; H5), 8.07–8.20 (2H, m; H3 and H4), 8.63 (1H, s; N=CH), 9.60 (1H, d, 5.1 Hz; H6). ^{13}C NMR (APT, 263 K, 75.4 MHz): δ = 23.21 and 23.28 (*i*Pr Me), 67.22 (*i*Pr CH), 127.90 and 128.50 (py C4, py C5), 140.00 (py C3), 150.68 (py C6), 154.00 (py C2), 164.78 (N=CH), 188.56 and 194.97 (CO's).

Complex **2b** was obtained in 95% crude yield (based on NMR). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 3.38 (3H, s; OCH_3), 3.86 (2H, m; NCH_2), 4.19 (2H, m; OCH_2), 7.77, 8.05, 8.16, 8.45 (H3–H5 and N=CH, not resolved), 9.62 (1H; H6). $^{13}C\{^1H\}$ NMR (RT, 75.4 MHz): δ = 59.42 (OCH_3), 66.73 and 69.98 (OCH_2 and NCH_2), 128.62 (py C5), 129.65 (py C4), 140.92 (py C3), 151.11 (py C6), 154.86 (py C2), 170.00 (N=CH), 189.12 and 195.33 (CO's). It was not possible to obtain **2b** in pure form because the complex decomposed during working up. Therefore, no IR and UV/VIS spectra were measured.

Complex **2c** was obtained in 90% yield. Selected IR data for **2c** (cm^{-1} in KBr): ν(CO) 2060 (s) and 1995 (vs); ν(py C=N) 1630 (vw); ν(imine C=N) 1600 (m); ν(Ru–Cl) 318 (w). FD-mass: *m/e* 434 (M^+ = 434). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 1.12 (6H, d, 6.0 Hz; *i*Pr Me), 2.05–2.30 (2H, m; $CH_2CH_2CH_2$), 3.35–3.70 (2H + 1H, m; NCH_2 + *i*Pr CH), 4.05–4.30 (2H, m; OCH_2), 7.79 (1H, dd; H5), 8.02 (1H, d, 7.5 Hz; H3), 8.16 (1H, dd; H4), 8.46 (1H, s; N=CH), 9.62 (1H, d, 5.3 Hz; H6). ^{13}C NMR (APT, 263 K, 25.18 MHz): δ = 22.22 and 22.34 (*i*Pr Me), 29.79 ($CH_2CH_2CH_2$), 64.29 (NCH_2), 65.04 (OCH_2), 71.93 (*i*Pr CH), 128.10 (py C5), 128.62 (py C4), 140.10 (py C3), 151.26 (py C6), 154.40 (py C2), 167.45 (N=CH), 188.71 and 194.50 (CO's).

Conversion of 1 to 2. For **1a**, a solution of 50 mg of **1a** in 20 mL of xylene was refluxed for 20 h. After evaporation of the solvent an orange solid was obtained, containing 70% of the starting complex and 30% of **2a** as revealed by ^1H NMR. No other products were observed.

For **1b** (300 mg in 30 mL of xylene) and **1c** (60 mg in 20 mL of xylene), the same procedure resulted in mixtures of identical composition, i.e. 30% **1b/c** and 70% **2b/c**.

Refluxing 2a in Xylene. A solution of 10 mg of **2a** in 10 mL of xylene was refluxed for 18 h. After evaporation of the solvent 100% of the starting material was recovered.

Synthesis of $Cl_2Ru(CO)_2$(R-Pyca) via $Ru(CO)_3$(R-Pyca) (Mixture of 1 and 2). A suspension of 127.0 mg of **a** (0.86 mmol) and 104.1 mg of $Ru_3(CO)_{12}$ (0.16 mmol) in 20 mL of hexane was refluxed for 10 min. When Cl_2(g) was bubbled through the red-brown solution of $Ru(CO)_3$(*i*Pr-Pyca), a dark solid separated immediatly. After cooling down of the mixture to RT, the dark-lilac solid was filtered out on a G4 glass filter, washed with 10 mL of hexane, and dried *in vacuo*. The solid was dissolved in 10 mL of dichloromethane, and the solution was exposed to sunlight for 10 min. The solution turned yellow, and after evaporation of the solvent, 170 mg of yellow powder resulted (93% yield), containing **1a** and **2a** in a 1:1 ratio (according to ^1H NMR). The isomers were separated by column chromatography as described above.

Synthesis of *trans*-$I_2Ru(CO)_2$(R-Pyca) (3a–c). To a solution of 264 mg of $[RuI_2(CO)_2]_n$ (0.63 mmol) in 20 mL of dichloromethane was added 175 mg of **c** (0.85 mmol). The reaction mixture was stirred for 30 h in the dark. After evaporation of the solvent, the red-lilac solid was purified by column chromatography (column 1 × 20 cm; eluent dichloromethane/diethyl ether = 1/1). The only fraction obtained contained **3c** in 80% yield (483 mg). Selected IR data for **3c** (cm^{-1} in KBr): ν(CO) 2049 (vs) and 1992 (vs); ν(imine) 1599 (w). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 1.17 (6H, d, 6.0 Hz; *i*Pr Me), 2.37 (2H, quintet, 6.0 Hz; $CH_2CH_2CH_2$), 3.50–3.64 (2H + 1H, m; NCH_2 + *i*Pr CH), 4.38 (2H, t, 6.6 Hz; OCH_2), 7.60 (1H, dd; H5), 7.92 (1H, d, 7.8 Hz; H3), 8.06 (1H, dd; H4), 8.34 (1H, s; N=CH), 9.12 (1H, d, 5.4 Hz; H6). ^{13}C NMR (APT, RT, 75.4 MHz): δ = 22.75 (*i*Pr Me), 30.49 ($CH_2CH_2CH_2$), 62.89 (NCH_2), 64.54 (OCH_2), 71.98 (*i*Pr CH), 128.44 (py C5), 129.39 (py C4), 140.01 (py C3), 153.98 (py C6), 154.20 (py C2), 166.30 (N=CH), 197.76 and 198.05 (CO's).

Using the same procedure, complex **3b** was obtained in 90% yield. Selected IR data for **3b** (cm^{-1} in KBr): ν(CO) 2048 (vs) and 1998 (vs); ν(C=N) 1597 (vw). ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 3.41 (3H, s; OCH_3), 4.03 (2H, t, 4.8 Hz; NCH_2), 4.35 (2H, t, 4.8 Hz; OCH_2), 7.60 (1H, dd; H5), 7.85 (1H, d, 7.5 Hz; H3), 8.05 (1H, dd, H4), 8.35 (1H, s; N=CH), 9.10 (1H, d, 7.5 Hz; H6). ^{13}C NMR (APT, RT, 75.4 MHz): δ = 59.25 (OCH_3), 65.36 and 68.86 (OCH_2 and NCH_2), 128.55 (py C5), 129.41 (py C4), 139.76 (py C3), 154.46 (py C6), 154.56 (py C2), 167.11 (N=CH), 197.83 and 198.17 (CO's).

Using the same procedure, complex **3a** was obtained in 90% yield. IR and NMR data agree with literature values.[12]

Synthesis of *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine) (4c). A 182.4-mg amount of **c** (0.88 mmol) in 5 mL of methanol was added at −30 °C to a suspension of 206.3 mg of $[RuCl_2(CO)_2]_n$ (0.905 mmol) in 25 mL of methanol in the dark. After stirring for 4 h at −30 °C the solution was evaporated to circa 10 mL, and the pink-yellow solution was stored at −30 °C. After 18 h yellow crystals were obtained in 25% yield. Repeated evaporation of the mother liquid and recrystallization resulted in a total yield of 336 mg (80%) of **4c**. Anal. Found (calcd) for **4c** ($C_{15}H_{22}N_2O_4Cl_2Ru$): C, 38.53 (38.63); H, 4.63 (4.76); N, 6.14 (6.01). Selected IR data (cm^{-1} in KBr): ν(N–H) 3200 (m); ν(CO) 2060 (vs) and 2000 (vs); ν(py C=N) 1605 (vw); ν(Ru–Cl) 323 (m). ^1H NMR ($CDCl_3$, RT, 100.13 MHz): δ = 1.23 and 1.29 (6H, d, 2.4 Hz; *i*Pr Me 2x), 1.5–2.6 (2H, m; $CH_2CH_2CH_2$), 2.7–3.1 (2H, m; NCH_2), 3.67 (3H, s; OCH_3), 3.5–3.9 (2H + 1H, m; OCH_2 + *i*Pr CH), 6.21 (1H, d, 5.5 Hz; $NCH(OCH_3)$), 6.62 (1H, s broad; NH), 7.45 (1H, dd; H5), 7.61 (1H, d, 7.3 Hz; H3), 7.91 (1H, dd; H4), 8.82 (1H, d, 5.5 Hz; H6). ^{13}C NMR (APT, 263 K, 75.4 MHz): δ = 22.30 and 22.56 (*i*Pr Me), 27.56 ($CH_2CH_2CH_2$), 41.35 (NCH_2), 56.93 (OCH_3), 69.96 (OCH_2), 73.03 (*i*Pr CH), 90.93 (N–CH(OCH_3)–), 123.80 (py C5), 126.07 (py C4), 139.61 (py C3), 153.10 (py C6), 158.65 (py C2), 194.31 and 195.57 (CO's).

Reaction of $[RuCl_2(CO)_2]_n$ with a and b in Methanol. A 156.2-mg amount of $[RuCl_2(CO)_2]_n$ (0.68 mmol) was stirred in 15 mL of methanol until a clear yellow solution was formed (ca. 2 days). After addition of 113.3 mg of *i*Pr-Pyca (**a**) (0.76 mmol), the solution turned light-pink. The solution was evaporated after 3 days, and a brown sticky solid remained. Selected IR data (cm^{-1} in KBr): ν(CO) 2140 (s), 2070–2080 (vs), 1980 (vs), 1710 (w); ν(C=N) 1640 (m), 1595 (m). Main signals in ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 1.24 (3H, d, 6.0 Hz), 1.40 (3H, d, 6.0 Hz), 1.45 (3H, d, 6.0 Hz), 3.29 (5H, s), 3.35 (2H, s), 3.41 (1H, s), 3.50 (1H, s), 3.62 (1H, s), 4.0–4.4 (2H, m), 7.2–7.4 (1H, m), 7.6–8.1 (4H, m), 8.61 (1H, s), 8.79 (1H, d, 4.8 Hz). Column chromatography resulted in decomposition of the products. Recrystallization (CH_2Cl_2/Et_2O) was not successful.

The same procedure for **b** (192.4 mg of $[RuCl_2(CO)_2]_n$ (0.85 mmol) and 154.2 mg of **b** (0.94 mmol)) yielded a dark brown solid. Selected IR data (cm^{-1} in KBr): ν(CO) 2140 (vs), 2050 (vs), 1985 (vs), 1965 (shoulder); ν(C=N): 1635 (m), 1605 (m). Main signals in ^1H NMR ($CDCl_3$, RT, 300.13 MHz): δ = 3.27, 3.29, 3.30, and 3.36 (all singlets, total 9H), 3.6–3.7 (2H, m), 3.7–3.9 (2H, m), 7.5–7.6 (1H, m), 7.7–8.0 (3H, m), 8.60 (1H, s), 8.81 (1H, d, 5.1 Hz). Column chromatography resulted in decomposition of the products. Recrystallization (CH_2Cl_2/Et_2O) was not successful.

Reaction of $[RuCl_2(CO)_2]_n$ with a in Toluene at RT. To a suspension of 13.1 mg (0.057 mmol) of $[RuCl_2(CO)_2]_n$ in 10 mL of toluene was added 12.3 mg (0.083 mmol) of ligand **a**. The suspension was stirred for 2 days at RT, but no clear solution was formed. After evaporation of the solvent, the residue was washed twice with 10 mL of hexane. ^1H NMR revealed that a mixture of products was formed (not containing either **1a** or **2a**).

Attempts To effect CO Abstraction in 1 and 2. (i) By Me_3NO. To a solution of 10 mg of **1** or **2** in 10 mL of THF or 10 mL of CH_2Cl_2 was added 1 equiv of Me_3NO. The solution turned purple within 5 min, and IR spectroscopy showed the disappearance of the CO frequencies of **1** or **2** and appearance of one broad signal at 1960 cm^{-1}. It was not possible to isolate the product by evaporation of the solvent or crystallization.

(ii) By Irradiation. Irradiation (high-pressure Hg lamp, λ > 320 nm) of 10 mg of **1** or **2** in 30 mL of THF or 25 mL of CH_2Cl_2 led to a purple solution after 2 h (IR: ν(CO) = 1960 cm^{-1}). It was not possible to isolate the product by evaporation of the solvent or crystallization.

Reaction of 1 and 2 with AgOTf. A typical experiment is as follows: To a solution of 116.5 mg (0.27 mmol) of **2c** in 10 mL of CH_2Cl_2 was added a solution of 69 mg (0.27 mmol) of AgOTf in 10 mL of CH_2Cl_2 with the exclusion of light. After being stirred at RT for 1 h, the yellow suspension was filtered and evaporated to dryness. ^1H NMR showed several new signals (no starting material left). Recrystallization was tried from CH_2Cl_2/hexane mixtures. The products decomposed after several hours in solution.

Crystal Structure Determination of *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine) (4c). A yellowish, plate-shaped crystal (0.18 × 0.20 × 0.95 mm) was glued to the tip of a glass

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Table I. Crystallographic Data for **4c**

formula	$C_{15}H_{22}N_2O_4Cl_2Ru$
space group	$P2_1/c$
cryst system	monoclinic
Z	4
a, Å	8.213(1)
b, Å	12.952(4)
c, Å	18.009(4)
β, deg	95.80(1)
V, Å^3	1905.8(8)
D_{calcd}, g cm^{-3}	1.625
μ_{calcd}, cm^{-1}	11.1
radiation (Mo Kα), Å	0.710 73
T, K	100
R_F[a]	0.078
R_{wF}[b]	0.105

[a] $R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_{wF} = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2\}^{1/2}$.

fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-F diffractometer. Broad, highly-structured reflection profiles of varying width were observed, which is indicative of a crystal consisting of several slightly miss-aligned individuals. The *A*-vector method was used to calculate for each reflection the ψ angle for which the minimal profile width can be expected.[13] Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range $14.3° < \theta < 19.6°$. Reduced-cell calculations did not indicate higher lattice symmetry.[14] Crystal data and details on data collection and refinement are presented in Table I. Data were collected at 100 K in the $\omega/2\theta$ mode with scan angle $\Delta\omega = 0.79 + 0.35 \tan\theta°$. Intensity data of 4649 reflections were collected in the range $1.1° < \theta < 27.5°$, of which 4123 are independent. Data were corrected for *Lp* effects and for a linear decay of 4% of the three periodically measured reference reflections ($\bar{2}22$, $22\bar{2}$, 232) during 68 h of X-ray exposure time. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.09I)^2$.[15] The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86[16]). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76[17]). Hydrogen atoms (including the amine hydrogen H24) were included in the refinement on calculated positions (C,N–H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two overall isotropic thermal parameters with values of 0.030(15) and 0.025(8) Å^2 for the methyl hydrogen atoms of the isopropyl group and the other hydrogen atoms, respectively. Weights were introduced in the final refinement cycles. Convergence was reached at $R = 0.078$, $R_w = 0.105$, unit weights, and $S = 5.11$, for 228 parameters and 3359 reflections with $I > 2.5\sigma(I)$. A final difference Fourier map showed no residual density outside –3.80 and 1.67 e Å^{-3}, probably absorption artifacts. Neutral-atom scattering factors were taken from Cromer and Mann;[18] anomalous dispersion corrections, from Cromer and Liberman.[19] Geometrical calculations and illustrations were performed with PLATON.[20] All calculations were performed on a Micro VAX-II. Positional parameters are listed in Table II.

Results

The reaction of equivalent molar amounts of (methoxyethyl)-amine or (isopropoxypropyl)amine with pyridinecarbaldehyde led to the formation of the new ligands methoxyethyl-Pyca (**b**) and isopropoxypropyl-Pyca (**c**), respectively. The reaction of *n* equiv of R-Pyca (**a**–**c**) with $[RuCl_2(CO)_2]_n$ in CH_2Cl_2 at room temperature led to the products *trans*-$Cl_2Ru(CO)_2$(R-Pyca) (**1**) and *cis*-$Cl_2Ru(CO)_2$(R-Pyca) (**2**) in 75–80% and 20–25% yield, respectively. These isomers were also formed at reflux temperature in toluene in respective yields of 5–15% and 85–95%. When $[RuCl_2(CO)_2]_n$ was reacted with **a** in toluene at RT, a mixture of compounds was formed (not containing either **1a** or **2a**). Heating of this mixture did not result in the formation of **1a** or **2a**. The reaction of $Ru(CO)_3$(*i*Pr-Pyca), synthesized in situ from $Ru_3(CO)_{12}$ and *i*Pr-Pyca, with Cl_2(g) led to the formation of **1a** and **2a** in a one to one ratio. Isomers **1** were converted into isomers **2** by refluxing in xylene. Yields of **2** and **1** after 20 h of refluxing were 70 and 30%, respectively, for all three ligands, and no side products were observed. Pure **2a** did not change upon refluxing in xylene for 18 h. The isomers with ligands **a** and **c** could be separated by column chromatography on silica, using $CH_2Cl_2/Et_2O = 5/1$ as eluent. Complex **2b** decomposed during workup.

In the reaction of *n* equiv of R-Pyca (**a**–**c**) with $[RuI_2(CO)_2]_n$ in CH_2Cl_2 at RT, *trans*-$I_2Ru(CO)_2$(R-Pyca) (**3**) was formed in 80–90% yield. When the reaction of $[RuCl_2(CO)_2]_n$ with isopropoxypropyl-Pyca was carried out in methanol at RT, yellow crystals of *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine) (**4c**) were isolated in high yield, in which the imine bond of the ligand is methanolyzed. If this reaction was carried out in methanol in the presence of a base, products **1c** and **2c** were formed in a 3 to 1 ratio. The solid-state structure of **4c** has been elucidated by a single-crystal structure determination. A PLUTO drawing is shown in Figure 3, together with a schematic presentation of the complex. Fractional coordinates and selected bond distances and angles are shown in Tables II and III, respectively. Details of the crystal structure will be discussed below.

Carrying out the reaction of $[RuCl_2(CO)_2]_n$ with ligands **a** or **b** in methanol led to a mixture of complexes, as could be deduced from ^{1}H NMR and IR spectra of the crude product. Due to decomposition during column chromatography, these complexes could not be analyzed.

Irradiation of **1** and **2** or reaction with Me_3NO in THF or CH_2Cl_2 led to purple solutions with an IR absorption at 1960 cm^{-1}. It was not possible to isolate the product because it decomposed on evaporation of the solvent or on crystallization. The purple product did not react with CO at RT.

The reaction of **1** and **2** with silver triflate (silver trifluoromethanesulfonate; AgOTf) resulted in the formation of a

Table II. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **4c** (Esd's in Parentheses)

	x	y	z	U_{eq}, Å^2
Ru	0.20426(9)	0.21646(7)	0.43256(5)	0.0165(2)
Cl(1)	0.0756(3)	0.0761(2)	0.36376(15)	0.0228(7)
Cl(2)	0.3155(3)	0.3591(2)	0.50483(16)	0.0260(8)
O(1)	0.2731(8)	0.4027(7)	0.2664(4)	0.024(2)
O(2)	–0.1625(8)	0.4465(6)	0.3820(4)	0.020(2)
O(3)	0.3702(10)	0.0622(8)	0.5396(5)	0.034(3)
O(4)	0.5016(9)	0.2124(8)	0.3469(5)	0.035(3)
N(1)	–0.0142(9)	0.2262(8)	0.4862(5)	0.017(2)
N(2)	0.0651(10)	0.3322(7)	0.3654(5)	0.018(3)
C(1)	–0.0668(12)	0.1557(9)	0.5301(6)	0.020(3)
C(2)	–0.2120(12)	0.1666(9)	0.5629(6)	0.021(3)
C(3)	–0.3038(12)	0.2532(10)	0.5462(6)	0.024(3)
C(4)	–0.2544(12)	0.3273(10)	0.4981(6)	0.022(3)
C(5)	–0.1063(11)	0.3110(9)	0.4672(6)	0.018(3)
C(6)	–0.0366(12)	0.3870(9)	0.4174(6)	0.017(3)
C(7)	–0.0305(12)	0.3002(9)	0.2952(6)	0.021(3)
C(8)	0.0809(12)	0.2669(9)	0.2362(6)	0.021(3)
C(9)	0.1773(13)	0.3550(10)	0.2059(6)	0.024(3)
C(10)	0.3770(13)	0.4850(10)	0.2439(7)	0.027(3)
C(11)	0.4002(17)	0.5568(12)	0.3070(8)	0.042(5)
C(12)	0.5369(13)	0.4392(12)	0.2235(8)	0.035(4)
C(13)	–0.1058(14)	0.5401(10)	0.3527(7)	0.027(3)
C(14)	0.3080(12)	0.1229(10)	0.4976(7)	0.023(3)
C(15)	0.3887(13)	0.2146(10)	0.3781(6)	0.025(3)

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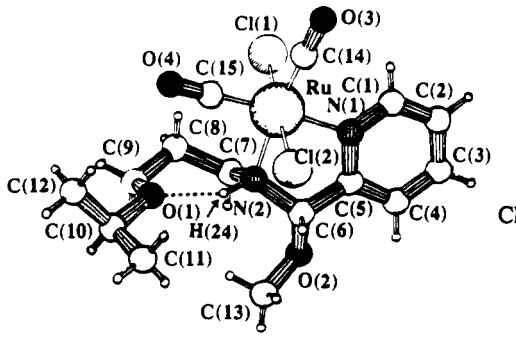


Figure 3. PLUTO[20] plot and schematic presentation of **4c**.

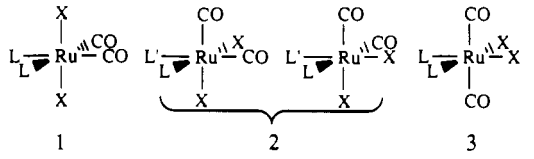


Figure 4. Possible isomers of complex $RuX_2(CO)_2(L_2)$.

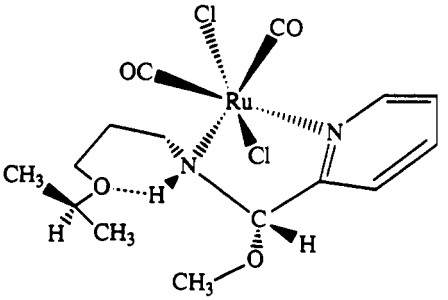
Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **4c** (Esd's in Parentheses)

Ru–Cl(1)	2.386(3)	C(8)–C(9)	1.521(16)
Ru–Cl(2)	2.388(3)	C(9)–O(1)	1.419(15)
Ru–C(14)	1.834(12)	N(1)–C(5)	1.358(15)
Ru–C(15)	1.886(11)	C(5)–C(6)	1.485(15)
Ru–N(1)	2.126(8)	C(6)–O(2)	1.392(13)
Ru–N(2)	2.176(9)	O(2)–C(13)	1.419(15)
N(2)–C(6)	1.495(14)	N(2)–H(24)	0.981(12)
N(2)–C(7)	1.479(14)	O(1)–H(24)	1.865(11)
C(7)–C(8)	1.532(15)		
Cl(1)–Ru–Cl(2)	176.05(9)	Cl(2)–Ru–C(14)	92.0(4)
Cl(1)–Ru–C(14)	88.9(4)	Cl(2)–Ru–C(15)	90.6(4)
Cl(1)–Ru–C(15)	93.3(4)	Cl(2)–Ru–N(1)	90.0(3)
Cl(1)–Ru–N(1)	86.1(3)	Cl(2)–Ru–N(2)	85.4(2)
Cl(1)–Ru–N(2)	93.2(2)	Ru–N(2)–C(7)	119.1(7)
Ru–N(1)–C(5)	114.1(7)	N(2)–C(7)–C(8)	111.7(8)
C(5)–C(6)–N(2)	109.7(9)	C(7)–C(8)–C(9)	114.0(1.0)
C(5)–C(6)–O(2)	109.3(8)	C(8)–C(9)–O(1)	108.6(9)
C(6)–N(2)–C(7)	112.7(8)	C(9)–O(1)–C(10)	113.7(8)

mixture of cationic complexes, as shown by ^1H NMR. It was not possible to identify the products or to obtain one isomer in pure form.

Discussion

Selective Syntheses of *cis*- and *trans*-$X_2Ru(CO)_2$(R-Pyca) Complexes. The reaction of $[RuX_2(CO)_2]_n$ with n equiv of bidentate ligands L_2 can in principle lead to the formation of three stereoisomers, as depicted in Figure 4.[21] Only a few complexes of configuration 3 (and then only for monodentate phosphine ligands) have been reported,[22] presumably because of the thermodynamically unfavorable trans position of both carbonyl ligands. Indeed the reaction of $[RuX_2(CO)_2]_n$ with R-Pyca has led to complexes with configurations 1 and 2 (**1** and **2**, respectively). The reaction of $[RuCl_2(CO)_2]_n$ with n equiv of R-Pyca in CH_2Cl_2 at RT led to the kinetic product *trans*-Cl_2-$Ru(CO)_2$(R-Pyca) (**1**: *OC*-6-32)[23] in high yields. In refluxing toluene or xylene *cis*-$Cl_2Ru(CO)_2$(R-Pyca) (**2**) was formed as the main product. **1** isomerized in refluxing xylene to the thermodynamic product *trans*-$Cl_2Ru(CO)_2$(R-Pyca) (**2**). The selective synthesis of these complexes and the isomerization are schematically depicted in Figure 5.



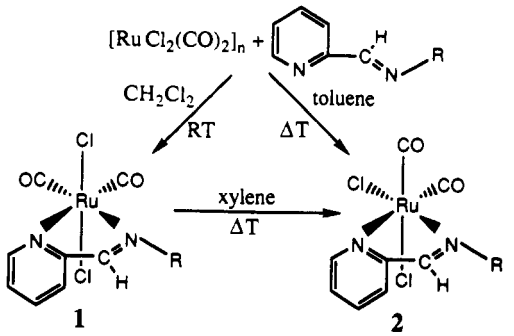


Figure 5. Selective syntheses and isomerization of **1** and **2**.

With the asymmetric ligand R-Pyca, in principle two diastereoisomeric forms of complex **2** are possible (*OC*-6-42 or *OC*-6-43, both consisting of two enantiomers).[23] NMR data reveal that only one diastereomer of **2** is present, as only one set of resonances is seen for the pyridine moiety of the ligand. We suggest that this is diastereomer *OC*-6-43, in which the carbonyl ligand in the plane of the R-Pyca ligand coordinates trans to the pyridine function and the chloride trans to the imine function, because of the better π-acceptor properties of the latter.[24]

The structure of complexes **1** and **2** was deduced from ^1H and $^{13}C\{^1H\}$ NMR data. In **1** the $Cl_2Ru(CO)_2$ fragment has C_{2v} symmetry, and therefore, a simple pattern is expected for the prochiral protons of the R group of the R-Pyca ligand. Complexes **2** lack this symmetry, and the protons of the R-groups show diastereotopicity in the ^1H NMR spectra. Another striking difference between the spectra of **1** and **2** is the frequency of H6 (for atom numbering, cf. Figure 6). In complexes **1a–c** H6 is observed at 9.13, 9.14, and 9.08 ppm, respectively. For **2a–c** the H6 resonance is seen at 9.60, 9.62, and 9.62 ppm, respectively, showing a downfield shift of circa 0.5 ppm. This shift is most probably due to the through-space interaction of the chloride atom, which is in a cis position to and in the plane of the pyridine moiety of the R-Pyca ligand in complexes **2**. Apparently the trans influence of the chloride atom is comparable with that of the carbonyl ligand, as the imine proton H7 does not change much from going from conformation **1** to **2**.[25] The $^{13}C\{^1H\}$ NMR spectra of complexes **1** show two slightly different resonances for the carbonyl carbon atoms at circa 195 ppm. In $RuCl_2(CO)_2$(bpy) (conformation 1) both CO's show the same resonance at 197.38 ppm (CH_3CN).[26] The CO frequencies of complexes **2** are 188.56, 194.97 (**2a**), 189.12, 195.33 (**2b**), and 188.71, 194.50 (**2c**), respectively. Clearly the carbonyl carbon atoms differ more in this case, as one coordinates trans to an imine carbon atom and one trans to a chloride atom. For **2b** double resonances were

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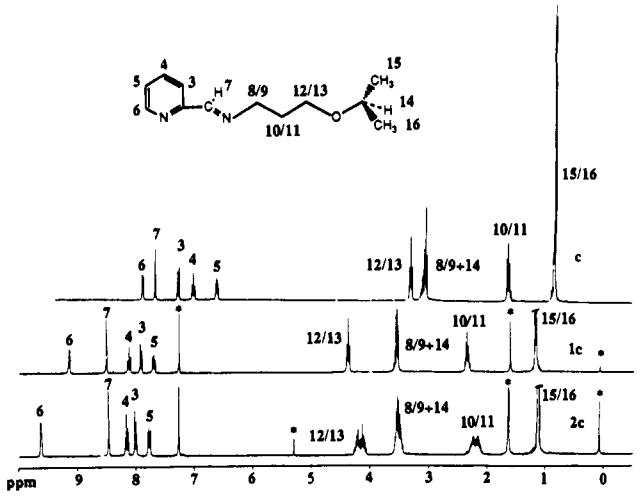

* δ = 0.05 ppm silicon grease; 1.69 ppm H_2O; 5.17 ppm CH_2Cl_2; 7.27 ppm $CHCl_3$

Figure 6. ^1H NMR spectra ($CDCl_3$, RT) of **c**, **1c**, and **2c** and numbering scheme of ligand **c**.

Table IV. UV/vis Data (nm) of Complexes **1a**, **2a**, **1c**, and **2c** in CH_2Cl_2 (Extinction Coefficient in Parentheses)

1a	382 (1.4×10^2), 277 (7×10^3)
1c	386 (1.6×10^2), 277 (8×10^3)
2a	386 (1.5×10^2), 327 (1.7×10^2), 268 (6×10^3)
2c	386 (1.9×10^2), 331 (1.9×10^2), 277 (7×10^3)

Table V. Solvatochromic Behavior of **1a** and **2a** (Absorption Maximum in nm)

	C_6H_{12}	CH_2Cl_2	CH_3OH
1a	387	382	363
2a	*a*	386	365

[a] Not soluble in hexanes.

observed for the prochiral isopropyl carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum, as a result of diastereotopicity. In Figure 6 the ^1H NMR spectra of the free ligand **c** and complexes **1c** and **2c** are shown.

The IR spectra of complexes **1** and **2** show two terminal ν(CO) absorptions at circa 1995 and 2060 cm^{-1}. These absorptions do not allow a differentiation between conformations 1 and 2. An indication for the configuration of the complexes would be the Ru–Cl absorption that is generally observed between 280 and 340 cm^{-1}.[9,27-30] For complexes **1** and **2** described in this paper, two (320 and 340 cm^{-1}) absorptions and one (335 cm^{-1}) absorptions have been observed in the IR spectrum, respectively. These values do not agree with data of similar Cl_2Ru octahedral complexes. Usually one absorption is observed for the antisymmetrical stretching vibration for *trans*-dichloride compounds,[9,27-30] whereas in the *cis*-dichloride both the symmetrical and antisymmetrical stretches are IR active, leading to two absorptions in this region.[9b,25] Another exception has been reported for the complexes *cis*-$Cl_2Ru(bpy)_2$ and *trans*-$Cl_2Ru(bpy)_2$ with bpy = 2,2′-bipyrimidine. Both isomers show only one absorption in the Ru–Cl stretching area at 322 and 342 cm^{-1}, respectively.[30] These results suggest that one should be careful when ascribing a *cis*- or *trans*-dichloride conformation to complexes on the basis of ruthenium–chloride frequencies. For the recently published complex $RuCl_2(CO)_2(bpy)$, with two trans coordinating chloride atoms, no ν(Ru–Cl) was reported.[26]

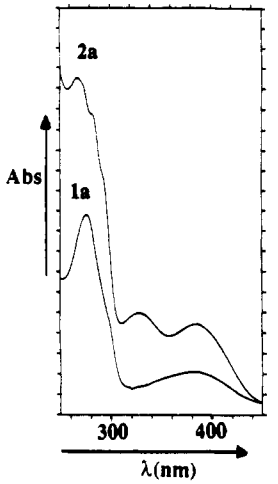

Figure 7. UV/vis spectra (CH_2Cl_2, RT) of **1a** and **2a**.

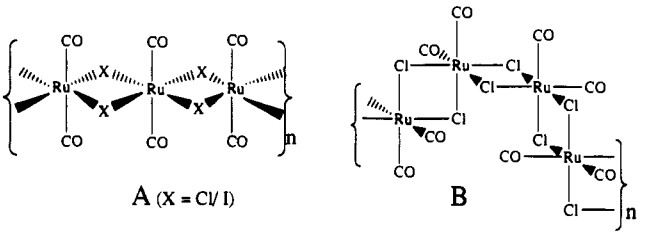

Figure 8. Three-dimensional structure of $[RuCl_2(CO)_2]_n$.

UV/vis spectra of **1** and **2** with ligands **a** and **c** (complex **2b** could not be obtained in pure form) show two absorption bands at circa 380 and 270 nm (isomer **1**) and three bands at circa 386, 330, and 270 nm (isomer **2**) (see Table IV). The band at longest wavelength extending into the visible region is the metal to ligand charge transfer (MLCT), as shown by the dependence on solvent polarity for **1a** and **2a** (see Table V).[24] The electronic spectra of **1a,c** are almost identical, as are the spectra of **2a,c**. Obviously the R group of the ligand has no influence on the energy of the π^* level of the ligand, which determines the energy of the MLCT absorption band. However, the difference in the absorption spectra of isomer **1** and **2** is remarkable (Figure 7). The *cis*-Cl_2 isomer shows two absorption bands between 300 and 400 nm, whereas the more symmetric *trans*-Cl_2 isomer features one absorption only. The difference in the UV/vis spectra can be attributed to a decrease in symmetry of complex **2** as compared to **1**, which reduces the degeneracy of the metal d-orbitals. The d-orbitals are no longer degenerate, and two MLCT's are seen. The energy difference between the two weak bands is too small to originate from a MLCT to the second π^* orbital of the R-Pyca ligand.[24] With resonance Raman spectroscopy (KNO_3 pellets) we tried to obtain more information about the origin of the two bands of isomer **2**, but unfortunately the complexes decomposed during measurement.

Formation of the Kinetic Product. Conformation 1 in Figure 4 with both chloride ligands trans to each other has been reported as the kinetic product in similar reactions of the polymer with bidentate ligands.[29,31] The question arises why isomer 1 (and not isomer 2) is the kinetic product of the reaction of $[RuCl_2(CO)_2]_n$ with a bidentate ligand. This must have its origin in the structure of the polymer.

Irving suggested a polymeric structure with bridging halides and trans coordinated carbonyls for $[RuX_2(CO)_2]_n$[32] with X = Cl or I (see A in Figure 8). We found that the IR spectra (KBr pellets) of $[RuCl_2(CO)_2]_n$ made in different batches differed, although always strong absorptions were present in the 2020–

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2040- and 2070–2080-cm^{-1} regions and weak absorptions were found in the 2130–2140-cm^{-1} region. This suggests that the structure of the polymer in the solid state varies. In solution (MeOH) the spectra of the different batches were almost identical: ν(CO) 1995 (s), 2050–2070 (s), and 2130 (w) cm^{-1}. The IR (KBr) spectra support the idea of a structure with bridging halides,[32] because no bridging carbonyls (expected at 1800–1900 cm^{-1}) or end-on coordinated chlorides (circa 320 cm^{-1}) are present. As only a weak absorbtion above 2100 cm^{-1} (trans coordinating CO's) is observed, we propose a 3-dimensional polymeric structure with the bulk of the carbonyl ligands terminal and cis-coordinated toward each other (see B in Figure 8). If we assume that the structure of the polymer resembles B (Figure 8), we can account for the fact that isomer 1 is the kinetic isomer. It is known that carbonyls have a larger trans influence than halides in square planar (platinum) complexes.[25] Although ligands with π-accepting capacities do not have high trans-effects in octahedral complexes, the trans effect order in octahedral complexes parallels the trans-influence order in square planar complexes.[25] This means that CO will have a larger trans effect than chloride and that the chloride atoms trans to the carbonyl ligands will be replaced first on addition of a new ligand.[25] As the carbonyl ligands are in a cis position toward each other, and the incoming ligand will coordinate trans to both carbonyl ligands, isomer 1 will be formed as the kinetic product.

To check whether the formation of the product is solvent dependent, the reaction at RT was also carried out in toluene. Reaction of $[RuCl_2(CO)_2]_n$ with **a** in toluene at RT led to the formation of a mixture of compounds (not containing either **1a** or **2a**), and subsequent heating did not alter the reaction mixture, indicating that the products formed are no intermediates in the formation of complexes **1a**/**2a**. The poor solubility of the polymer in toluene at low temperature can be the cause of this (not further investigated) observation.

Isomerization. The kinetic isomer **1** isomerized in refluxing xylene to isomer **2** (70% conversion in 20 h). The isomerization is very clean, as no side products could be observed by ^1H NMR spectroscopy. Refluxing of pure **2a** in xylene for 18 h did not result in the formation of any **1a**. This shows that the equilibrium **1**/**2** lies very far or completely on the side of complex **2** under these conditions. The isomerization is very likely intramolecular as no intermediates or loss of CO was observed, and the rate of isomerization was independent of the concentration. In the literature some studies on the mechanisms of rearrangements in complexes of type $RuX_2(CO)_2L_2$ have been reported.[21,22,31,33] It is conceivable that the R-Pyca ligand acts as a monodentate ligand in the transition state, thus creating a five-coordinated unsaturated ruthenium center, which can isomerize. Monodentate coordinating R-DAB ligands have been observed in palladium, platinum, and rhodium complexes.[5,34] Another possible mechanism for intramolecular isomerisation is the Bailar twist. Starting from isomer 1, rotation around an axis through the planes of two carbonyl ligands and one chloride atom and the plane through the R-pyca ligand and the other chloride atom can result in the formation of isomers 2 (both diastereomers) and 3.[22] We see the formation of only one diastereomer on heating; obviously only the thermodynamically more favorable complex is formed (*vide infra*). Breuer reported the isomerization of *trans*-$Cl_2Ru(CO)_2$(R-DAB) (isomer 1) to occur in acetone, acetonitrile, and methanol at high temperatures (>120 °C in a sealed NMR tube; R = *i*Pr, *t*Bu).[33] In these cases a mixture of isomers 1 and 2 is formed, as a result of opposing steric and electronic effects. The *all-cis* structure (2) is electronically more favorable because of an axial Cl–Ru–CO fragment, which provides more π-back-bonding to the carbonyl ligand, but there is steric repulsion of the R-group on the DAB ligand with the halide within the DAB-Ru plane.[33] In the case of the $Cl_2Ru(CO)_2$(R-Pyca) complexes the halide in the R-Pyca–Ru plane can coordinate cis to the less sterically demanding pyridine function, thereby minimizing sterical congestion. This would account for the fact that for the latter complexes isomer 2 (*OC*-6-43) is formed in quantitative yield: the π-back-bonding to both carbonyls is maximal (CO trans to pyridine and trans to Cl), and the steric repulsion of the halide within the R-Pyca–Ru plane is not so strong.

The corresponding iodide complexes were formed in a reaction of $[RuI_2(CO)_2]_n$ with *n* equiv of ligand **a**, **b**, or **c**. In this case isomer 1 was formed exclusively, which could not be isomerized to 2 at high temperatures. The fact that *trans*-$I_2Ru(CO)_2$(R-Pyca) (**3**) is the only isomer observed is most probably due to the larger steric interactions of the iodide ligands in cis position to each other as compared to the chloride ligands. The same isomer has been found for the analogous $I_2Ru(CO)_2$(R-DAB) complexes (R = *i*Pr, *t*Bu, *p*tolyl).[9a]

Enhanced Reactivity of the Coordinated Imine Linkage of Ligand c. Synthesis and Crystal Structure of *trans*-$Cl_2Ru(CO)_2$(N-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine) (4a). Reaction of $[RuCl_2(CO)_2]_n$ with **c** in methanol led to the formation of *trans*-$Cl_2Ru(CO)_2$(*N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)amine), in which one molecule of methanol has added to the imine function of the ligand. Evidence for this methanolysis stems from the ^1H and $^{13}C\{^1H\}$ NMR spectra, which show signals at 3.67 and 6.62 ppm for the methoxy and amine hydrogen atoms and at 90.93 and 56.93 ppm for the former imine and the methoxy carbon atom, respectively. In the IR spectrum of **4c** a sharp absorption band at 3200 cm^{-1} indicates the presence of a N–H group.[35]

The X-ray structure, depicted in Figure 3, shows a σN, σN′-coordinating *N*-(pyrid-2-ylmethoxymethyl)(3-isopropoxypropyl)-amine and the two chloride and carbonyl ligands trans and cis coordinated, respectively. Selected bond distances and bond angles are shown in Table III. The N(2)–C(6) bond length of 1.495(14) Å clearly indicates a single N–C bond, as N–C distances in imine fuctions are generally between 1.23 and 1.28 Å.[35,36] The sp^3 carbon atom C(6) causes the N(1)–C(5)–C(6)–N(2) torsion angle to be 32.4(1.3)°. For the similar ligand *t*BuN=CHCH-(CH_2COCH_3)N(H)*t*Bu coordinating to Mn a torsion angle of 14.75° (no esd reported) has been observed.[35] In the latter complex, *cis,trans*-$[Mn(CO)_2(CN\text{-}tBu)_2$(*t*BuN=CHCH($CH_2$-$COCH_3$)N(H)*t*Bu)$][ClO_4]$, the small torsion angle most probably results from the steric congestion between the *t*Bu groups and the group on the former imine carbon atom. A special feature of complex **4c** is the intramolecular hydrogen bond N(2)–H(24)···O-(1) between the oxygen atom of the ether arm and the hydrogen atom attached to the former imine nitrogen atom. Although the hydrogen atom could not be located on the electron density maps, the N···O distance of 2.747(11) Å and the general conformation of this part of the molecule strongly suggests its presence. Introduction of the hydrogen atom at an idealized sp^3 position (N–H = 0.98 Å) results in an H···O distance of 1.865(11) Å and an N–H···O angle of 148.2(1.0)°. The six-membered ring is thought to exist also in solution, as the ^1H NMR spectrum shows a complicated, constant pattern for the ether arm of the ligand at both high and low temperatures.

Hydrolysis of imine bonds is a common reaction that is known to be acid or base catalyzed[37] but which can also be accelerated by metal ions, such as Cu(II), Zn(II), and Ni(II), in alcohol/

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water mixtures.[38] We had not expected the solvolysis of the imine bond, because methanol has often been used in similar reactions of $[RuCl_2(CO)_2]_n$ with R-DAB.[33] The reaction can, however, be explained as an acid-catalyzed hydrolysis. As the synthesis of $[RuCl_2(CO)_2]_n$ is carried out in concentrated acid, it is possible that traces of acid are still present in the polymer. Consequently, the reaction in methanol was carried out in the presence of triethylamine, and only **1c** and **2c** were formed. Solvolysis of **1c** or **2c** in methanol in the presence of acid, however, did not lead to **4c**; nor did the free ligand react with methanol under acidic conditions. This indicates that the methanolysis takes place during complexation of **c** to $[RuCl_2(CO)_2]_n$. The methanolysis is not stereoselective, as both enantiomers of **4c** are present in the X-ray structure.

Methanolysis was not observed when carrying out the reaction in methanol with ligands **a** or **b**. Under the same conditions a mixture of products was formed. Attempts to isolate the products failed, as column chromatography led to decomposition. ^1H NMR and IR spectra of the crude products revealed, however, that no methanolysis had taken place (no signals of methoxy or amine groups in the NMR; no absorption around 3200 cm^{-1} in the IR). The methanolysis of ligand **c** during complexation to $[RuCl_2(CO)_2]_n$ and the failure in the case of ligands **a** and **b** may therefore be rationalized by the stabilization of the amine hydrogen by the internal O–H bridge and the formation of a six-membered ring, prior to the attack of the methoxy group on the imine carbon atom.

Attempts to obtain an intramolecular coordination of the ether arm by the formation of an unsaturated ruthenium complex unfortunately failed. Abstraction of a carbonyl ligand led to new complexes (IR $\nu(CO)$ = 1960 cm^{-1}) which could not be isolated. For $I_2Ru(CO)_2$(*i*Pr-DAB) irradiation in CH_3CN yielded $I_2Ru(CO)(CH_3CN)$(*i*Pr-DAB) ($\nu(CO)$ = 1975 cm^{-1}),[39] whereas irradiation of $Cl_2Ru(CO)_2$(R-DAB) (R = *i*Pr, *t*Bu) in THF led to formation of a red polymer $[Ru(CO)Cl_2(R\text{-}DAB)]_n$ ($\nu(CO)$ = 1972 cm^{-1}).[33] This polymer reacted only under high CO pressure back to the monomer. Because the product of irradiation of $Cl_2Ru(CO)_2$(R-Pyca) did not react with CO (1.5 bar) and could not be isolated properly, we suggest that this product too is a polymer.

The reaction of **1** and **2** with silver triflate resulted in the formation of a mixture of cationic complexes (as revealed by ^1H NMR). Because no preferred isomer was found, which is expected if a stable intramolecular ether coordination is present, we think that the ether arm does not coordinate in these cationic complexes. Thus far we have not been able to obtain a complex in this series that shows the intramolecular coordination of the ether arm to the ruthenium center. The fact that complex **2b** is not stable (in contrast to complexes **2a,c**) and that methanolysis only takes place in the reaction of $[RuCl_2(CO)_2]_n$ with ligand **c**, and not with ligand **a** or **b**, clearly indicates that a (small) variation in the R group of R-Pyca can result in a change in reactivity. On the other hand, the formation of isomers, the rate of isomerization (**1** to **2**), and the IR and electronic spectra do not depend on the R-group of the R-Pyca ligand.

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Supplementary Material Available: Tables containing further details of the structure determination, atomic coordinates, bond lengths and angles, isotropic thermal parameters, and anisotropic thermal parameters for **4c** (7 pages). Ordering information is given on any current masthead page.

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