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Synthesis, Characterization, and Reactivity of Ruthenium Diene/Diamine Complexes Including Catalytic Hydrogenation of Ketones

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Thermal reactions between $[RuCl_2(diene)]_n$ (diene = 2,5-norbornadiene, nbd; 1,5-cyclooctadiene, cod) with an excess of *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (tmeda) afforded derivatives $[RuCl_2(diene)(tmeda)]$ (diene = nbd, **1**; cod, **2**) as a mixture of cis and trans isomers. When thermolysis was performed under H_2 mixtures of hydride species [RuCl(H)(diene)(tmeda)] (diene = nbd, **3**; cod, **4**) and the bis-tmeda adduct *trans*-$[RuCl_2(tmeda)_2]$ (**5**) were obtained in different ratios depending upon the reaction conditions and reaction times. Heating polymeric Ru(II) precursors in toluene in the presence of a 5-fold excess of the bulkier *N*,*N*,*N*′,*N*′-tetraethylethylene diamine (teeda) resulted in a rare diamine dealkylation process with formation of *trans*-$[RuCl_2(nbd)(Et_2NCH_2CH_2NHEt)]$ (**6**) and *trans*-$[RuCl_2(cod)(EtHNCH_2CH_2NHEt)]$ (**7**) in high yields. The presence of N–H functionalities in the coordinated diamine ligands of **6** and **7** was unambiguously established by single-crystal X-ray diffraction studies. The dealkylation process of the teeda ligand seems to proceed intramolecularly as shown by solution NMR studies performed with the soluble Ru(II) precursors *trans*-$[RuCl_2(amine)_2(diene)]$ (diene = nbd, amine = morpholine, **9**; diene = cod, amine = Et_2NH, **10**). The above complexes $[RuCl_2(diene)(diamine)]$ have been tested as precatalysts in the hydrogenation of ketones both for transfer as well as direct hydrogenation, the latter route being the most effective.

Introduction

Hydrogenation is a core technology in fine chemical synthesis.[1] The catalytic reduction of polar C═O bonds can be achieved either by a transfer-hydrogenation process using organic sources of hydrogen or by direct hydrogenation with molecular hydrogen. Ruthenium compounds have proven to serve as very efficient catalysts for both types of transformations. Particularly, the most active precatalysts for the former reactions contain β-amino alcohols or 1,2-diamine attached to a ruthenium−arene fragment.[2] These precatalysts hardly react with H_2 but instead react with 2-propanol leading to transfer-hydrogenation catalytic systems. Although ruthenium diphosphine complexes have been described as homogeneous hydrogenation catalysts for decades,[3] the discovery of a highly efficient system for the direct hydrogenation of ketones by Noyori's group is more recent.[4] Noyori's type ruthenium−diphosphine/diamine[5] precatalysts react with H_2

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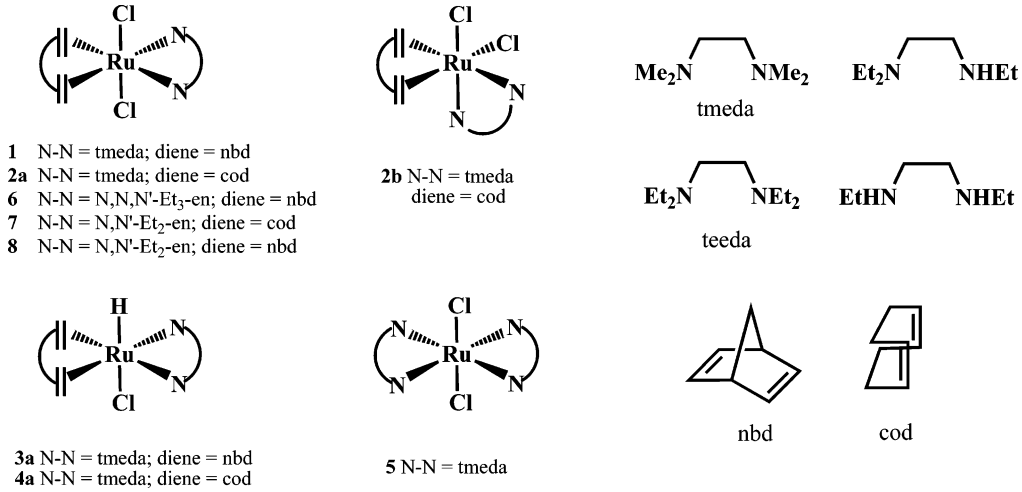
Chart 1. Complexes Prepared in This Work



in 2-propanol to generate active hydrogenation species. Recently, it has been reported that complexes of the type Cp*Ru(diamine),[6] which are isoelectronic to ruthenium−arene transfer-hydrogenation catalysts, perform the reduction of ketones with molecular hydrogen. These complexes constitute rare examples of hydrogenation catalysts without phosphine ligands.[7] These results prompted us to study the effect of a phosphane-free environment on the catalytic properties of Ru hydrogenation catalysts.

Different isomers of $[RuCl_2(amine)_2(diene)]$ were prepared by Potvin et al.[8b,c] by refluxing monodentate aliphatic or aromatic amines with $[RuCl_2(diene)_2]_n$. Recently, an improved synthesis of the complex *trans*-$[RuCl_2(nbd)(py)_2]$, a useful synthon for the preparation of ruthenium(diphosphine) hydrogenation catalysts has been reported.[5b,9] In this contribution, we present the synthesis and characterization of novel complexes $[RuCl_2(diene)(N-N)]$ prepared from $[RuCl_2(diene)_2]_n$, (diene = cycloocta-1,5-diene, cod, 2,5-norbornadiene, nbd), where *N*−*N* is *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (tmeda), *N*,*N*,*N*′-triethylethylene diamine, and *N*,*N*′-diethylethylene diamine (Chart 1). During the course of these studies, we have observed an unusual intramolecular dealkylation reaction on the *N*,*N*,*N*′,*N*′-tetraethylethylene diamine (teeda) to afford diamine ligands which contain one or two NH functionalities. We also describe herein the use of the complexes as catalyst precursors for the transfer and direct hydrogenation of ketones in basic 2-propanol solutions. Part of this work has been previously communicated.[10]

Experimental Section

General Methods. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and degassed before use. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teeda), *N*,*N*,*N*′-triethylethylenediamine, *N*,*N*′-diethylethylenediamine, and triethylamine (NEt_3) were purchased from Aldrich and used as received. $[RuCl_2(cod)]_n$ and $[RuCl_2(nbd)]_n$ were synthesized by following literature procedures.[11]

NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. ^1H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. All infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 884 spectrophotometer. Elemental analyses were performed in the Microanalytical Laboratory of the Instituto de Investigaciones Químicas Isla de la Cartuja.

***trans*-[RuCl$_2$(nbd)(tmeda)] (1).** tmeda (1.5 mL, 10 mmol) was added to a stirred suspension of $[RuCl_2(nbd)]_n$ (400 mg, 1.51 mmol) in toluene (20 mL). The mixture was heated at 80 °C over 12 h. The resulting brown solution was allowed to cool to room temperature and evaporated to dryness under vacuum. To eliminate an excess of tmeda, the crude product was washed with petroleum ether (2 × 5 mL) and dried under vacuum. Recrystallization from Et_2O/CH_2Cl_2 (5:1 mixture) at −20 °C afforded complex **1** as brown crystals. Yield: 80% (460 mg). Anal. Calcd

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for $C_{13}H_{24}Cl_2N_2Ru$: C, 41.05; H, 6.32; N, 7.77. Found: C, 41.23; H, 6.72; N, 7.86. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (br s, 4H, =C*H* for nbd), 3.89 (m, 2H, C*H* for nbd), 2.63 (s, 4H, NCH_2), 2.45 (br s, 12H, CH_3), 1.34 (m, 2H, CH_2 for nbd).[13] C {^{1}H} NMR (100 MHz, $CDCl_3$,): δ 74.6 (=*C*H for nbd), 60.8 (N*C*H$_2$), 60.4 (*C*H$_2$ for nbd), 52.9 (*C*H for nbd), 50.7 (s, *C*H$_3$).

[RuCl$_2$(cod)(tmeda)] (2a,b). The preparation was carried out in the same manner as that for **1** using tmeda (1.50 mL, 10 mmol) and [RuCl$_2$(cod)]$_n$ (400 mg, 1.43 mmol) in toluene (20 mL). The mixture was heated at 80 °C for 24 h. ^{1}H NMR (C_6D_6) analysis of the crude showed the presence of *trans*-**2a** and *cis*-**2b** isomers in ca. 2:3 ratio. The isomer *cis*-**2b** was separated from the mixture as orange-brown crystals by fractional crystallization from Et$_2$O/CH$_2$Cl$_2$ (5:1) mixtures. Yield for **2b**: 40% (230 mg). Increasing the reaction times from 24 h to 5 days allowed the isolation of **2b** in 75% yield. The isomer *trans*-**2a** could not be isolated from the reaction mixture by fractional crystallization and was spectroscopically characterized from the reaction mixture. Anal. Calcd for $C_{14}H_{28}Cl_2N_2Ru\cdot{}^1/_2H_2O$: C, 41.44; H, 7.15; N, 6.91. Found: C, 41.02; H, 7,01; N, 7,49. The NMR data for *trans*-**2a** has been previously reported.[13a]

cis-**2b**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.18 (m, 1H, =C*H* for cod), 4.10 (m, 1H, =C*H* for cod), 3.98 (m, 1H ,=C*H* for cod), 3.92 (m, 1H, =C*H* for cod), 3.28 (m, 1H, NCH_2), 2.96 (m, 1H, NCH_2), 2.73 (m, 4H, CH_2 for cod), 2.54 (1H, m, NCH_2), 2.46, 2.37, 2.19, 2.18 (s, 3H each, CH_3), 2.16 (m, 3H, CH_2 for cod), 2.04 (m, 1H, CH_2 for cod), 1.79 (m, 1H, NCH_2), 1.55 (m, 1H, CH_2 for cod), 1.45 (m, 1H, CH_2 for cod).[13] C {^{1}H} NMR (100 MHz, CD_2Cl_2,): δ 89.5 (=*C*H for cod), 88.3 s, (=*C*H for cod), 87.2 (=*C*H for cod), 85.6 (=*C*H for cod), 61.5 (N*C*H$_2$), 50.7 (N*C*H$_2$), 51.0, 50.7, 36.4 (*C*H$_3$), 31.5 (*C*H$_2$ for cod), 31.0 (*C*H$_2$ for cod), 28.6 (*C*H$_2$ for cod), 28.0 (*C*H$_2$ for cod).

[RuClH(nbd)(tmeda)] (3a, 3b). Method a. tmeda (1.5 mL, 10 mmol) was added to a suspension of [RuCl$_2$(nbd)]$_n$ (300 mg, 1.13 mmol) in toluene (20 mL). The reaction mixture was transferred to a pressure vessel and heated at 80 °C for 20 h under 2 bar of hydrogen. The reaction was allowed to cool at room temperature, and then the pressure was evacuated. The resulting suspension was filtered and evaporated to dryness, and the residue was analyzed by ^{1}H NMR, which showed the presence of *trans*-**3a** and *cis*-**3b** isomers in a ca. 9:1 ratio along with resonances due to complex **5** (see below). Complexes *trans*-**3a** and **5** were separated by fractional crystallization from Et$_2$O at −20 °C as pale yellow (yield ca. 35%) and reddish crystals (yield ca. 20%), respectively.

Method b. NEt$_3$ (0.10 mL, 0.71 mmol) was added to a solution of **1** (270 mg, 0.70 mmol) in toluene (20 mL). The solution was transferred to a pressure vessel and charged with 2 bar of hydrogen. The reaction mixture was heated at 80 °C for 8 h. The resulting suspension was filtered, the solvent was removed under vacuum, and the reaction crude was analyzed by ^{1}H NMR showing the presence of *trans*-**3a** and *cis*-**3b** isomers in a ca. 9:1 ratio. The major isomer *trans*-**3a** was isolated as pale yellow crystals by fractional crystallization from Et$_2$O. Yield 62% (150 mg). The minor isomer *cis*-**3b** could not be isolated by recrystallization and was characterized by NMR analysis of reaction mixture. Anal. Calcd for $C_{13}H_{25}ClN_2Ru$: C, 45.14; H, 7.23; N, 8.10. Found: C, 45.13; H, 7.34; N, 8.30.

trans-**3a**. ^{1}H NMR (400 MHz, C_6D_6): δ 4.35 (m, 1H, C*H* for nbd), 3.51 (m, 1H, C*H* for nbd), 3.48 (t, 2H, =C*H* for nbd, J_{HH} = 3.9 Hz), 3.13 (t, 2H, =C*H* for nbd, J_{HH} = 4.0 Hz), 2.14 (m, 2H, NCH_2), 2.05, 1.93 (s, 6H each, CH_3), 1.69 (m, 2H, NCH_2), 1.11 (t, 2H, CH_2 for nbd, J_{HH} = 1.7 Hz), −5.42 (s, 1H, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 61.0 (N*C*H$_2$), 56.2 (*C*H$_2$ for nbd), 55.3 (*C*H$_3$), 51.7 (*C*H for nbd), 51.3 (*C*H for nbd), 49.7 (*C*H$_3$), 47.1 (=*C*H for nbd), 47.0 (=*C*H for nbd). IR (Nujol): 2016 cm^{-1} (νRuH).

cis-**3b**; selected spectroscopic data. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.70 (m, 1H, =C*H* for nbd), 4.62 (m, 1H, =C*H* for nbd), 4.57 (m, 1H, =C*H* for nbd), 4.54 (m, 1H, =C*H* for nbd), 3.43, 2.92, 2.74, 2.62 (s, 3H each, CH_3), 0.97 (m, 2H, CH_2 for nbd), −5.38 (s, 1H, Ru−*H*).

[RuClH(cod)(tmeda)] (4a, 4b). Complexes **4a** and **4b** were obtained in 65% yield following the method described above for complexes **3a** and **3b**. Anal. Calcd for $C_{14}H_{29}ClN_2Ru$: C, 46.46; H, 8.08; N, 7.74. Found: C, 46.03; H, 7.66; N, 7.87. NMR data for *trans*-**4a** has been previously reported.[13a]

cis-**4b**; selected spectroscopic data. ^{1}H NMR (400 MHz, C_6D_6): δ 3.55−2.75 (m, 4H, =C*H* for cod), 2.66 (m, 2H, NCH_2) 2.51 (s, 3H, CH_3), 2.43 (m, 2H, NCH_2), 2.23, 2.19, 2.04 (s, 3H each, CH_3), −6.45 (s, 1H, Ru−*H*). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 70.6 (=*C*H for cod), 69.6 (=*C*H for cod), 65.5 (=*C*H for cod), 65.3 (=*C*H for cod), 60.3 (N*C*H$_2$), 53.5 (N*C*H$_2$, *C*H$_3$), 53.3, 48.7, 39.2 (*C*H$_3$), 35.6 (*C*H$_2$ for cod), 30.9 (*C*H$_2$ for cod), 29.5 (*C*H$_2$ for cod), 27.6 *C*H$_2$ for cod). IR (Nujol): 2032 cm^{-1} (νRuH).

***trans*-[RuCl$_2$(tmeda)$_2$] (5).** tmeda (1.5 mL, 10 mmol) was added to a suspension of [RuCl$_2$(nbd)]$_n$ (400 mg, 1.51 mmol) in toluene (20 mL). The mixture was transferred to a pressure vessel and charged with hydrogen (2 bar). The reaction was heated at 80 °C for 4 days. The reaction was allowed to cool to room temperature, and the pressure was evacuated. The resulting red suspension was filtered, the solvent was pumped off, and the residue recrystallized from Et$_2$O/CH$_2$Cl$_2$ (2:1 mixture) at −20 °C. Yield: 70% (430 mg). Complex **5** can also be prepared by using [RuCl$_2$(cod)]$_n$ as the metal precursor. The hydrogenation reaction took 5 days to completion, and the reaction yield was quantitative as shown by ^{1}H NMR analysis of the crude. Anal. Calcd for $C_{12}H_{32}Cl_2N_4Ru$: C, 35.63; H, 7.92; N,13.86. Found: C, 35.49; H, 7.80; N, 14.15. NMR data for **5** has been previously reported.[13a]

***trans*-[RuCl$_2$(nbd)(Et$_2$NCH$_2$CH$_2$NHEt)] (6). Method a.** teeda (1 mL, 4.73 mmol) was added to a suspension of [RuCl$_2$(nbd)] (250 mg, 0.95 mmol) in toluene (10 mL). The mixture was heated at 80 °C for 24 h affording a dark orange solution. After cooling at room temperature, the solvent was evaporated to dryness. The ^{1}H NMR spectrum of the reaction crude showed complex **6** as the only Ru-containing species formed in the reaction. Recrystallization from Et$_2$O/CH$_2$Cl$_2$ (6:1 mixture) at −20 °C gave orange crystals of **6**. Yield: 73% (290 mg).

Method b. *N*,*N*,*N*′-triethylethylene diamine (0.40 mL, 2.30 mmol) was added to a suspension of [RuCl$_2$(nbd)]$_n$ (200 mg, 0.76 mmol) in toluene (10 mL). The resulting mixture was heated at 80 °C for 5 h, affording a dark orange solution. The solution was taken to dryness, and complex **6** was obtained in quantitative yield and needed no further purification. Anal. Calcd for $C_{15}H_{28}Cl_2N_2Ru$: C, 44.12; H, 6.86; N, 6.91. Found: C, 43.80; H, 6.89; N, 7.03. ^{1}H NMR (400 MHz, C_6D_6): δ 4.79 (m, 2H, =C*H* for nbd), 4.72 (m, 2H, =C*H* for nbd), 3.91 (br s, 2H, C*H* for nbd), 3.63 (m, 1H, CH_2(Et)), 3.57 (m, 1H, CH_2(Et)), 3.18 (br s, N−*H*), 3.08 (td, 1H, Et$_2$NCH_2, J_{HH} = 13 Hz, J_{HH} = 2.3 Hz), 2.60 (qd, 1H, EtHNCH_2, J_{HH} = 12.8 Hz, J_{HH} = 13 Hz, J_{HH} = 2.3 Hz), 2.33 (m, 3H, CH_2-(Et)), 2.08 (da, 1H, EtHNCH_2, J_{HH} = 13 Hz), 1.76 (m, 1H,

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Table 1. Crystal Data and Structure Refinement Details for Complexes **4a** and **6**

	4a	**6**
formula	$C_{14}H_{29}ClN_2Ru$	$C_{15}H_{28}Cl_2N_2Ru$
fw	361.91	408.36
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	14.158(5)	7.302(5)
b, Å	9.341(4)	18.162(5)
c, Å	13.755(5)	13.562(5)
β, deg	117.75(3)	103.89(5)
V, Å^3	1609.9(11)	1746.0(14)
Z, D_{calcd}, g cm^{-3}	4, 1.493	4, 1.554
F(000)	752	840
μ, cm^{-1}	11.27	11.97
reflns collected	4803	26 184
reflns unique	4644 [R_{int} = 0.0329]	5209 [R_{int} = 0.0269]
obsd reflns [$I > 2\sigma(I)$]	3132	4020
params	188	199
final R indices [$I > 2\sigma(I)$]	R1 = 0.0428; wR2 = 0.1114	R1 = 0.0283; wR2 = 0.0688
Final R indices [all data]	R1 = 0.0675; wR2 = 0 1224	R1 = 0.0430; wR2 = 0.0745

CH_2(Et)), 1.56 (da, 1H, Et$_2$NCH_2, J_{HH} = 12.7 Hz), 1.28 and 1.21 (ABq, 2H, CH_2 for nbd, J_{AB} = 8.9 Hz), 0.78 (t, 3H, CH_3, J_{HH} = 6.8 Hz), 0.46 (t, 3H, CH_3, J_{HH} = 6.9 Hz), 0.44 (t, 3H, CH_3, J_{HH} = 6.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 75.6 (=C*H* for nbd), 73.5 (=C*H* for nbd), 73.0 (=C*H* for nbd), 70.0 (=C*H* for nbd), 60.8 (CH_2 for nbd), 57.0 (Et$_2$NCH_2), 52.9 (C*H* for nbd), 52.2 (C*H* for nbd), 49.0 (EtHNCH_2), 47.0, 46.7, 43.9 (CH_2(Et)), 13.2, 10.8, 7.0 (CH_3). IR (Nujol): 3220 cm^{-1} (νN−H).

***trans*-[RuCl$_2$(cod)(EtHNCH$_2$CH$_2$NHEt)] (7).** The preparation was carried out in the same manner as that described above using teeda (0.75 mL, 3.60 mmol) and [RuCl$_2$(cod)]$_n$ (200 mg, 0.71 mmol) in toluene (10 mL). Recrystallization from Et$_2$O/CH_2Cl_2 (3:1 mixture) at −20 °C gave orange crystals of **7**. Yield: 75% (210 mg). Additionally, complex **7** could also be prepared in quantitative yield by following the procedure described in method b (see above) using either *N*,*N*,*N*′-triethylethylene diamine or *N*,*N*′-diethylethylene diamine and [RuCl$_2$(cod)]$_n$. Anal. Calcd for $C_{14}H_{28}Cl_2N_2Ru$: C, 42.42; H, 7.07; N, 7.12. Found: C, 42.09; H, 6.89; N, 7.15. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.21 (td, 2H, =C*H* for cod, J_{HH} = 8.5 and 5.6 Hz), 4.00 (t, 2H, =C*H* for cod, J_{HH} = 8 Hz), 3.61 (br s, 2H, N−*H*), 2.92 (m, 4H, NCH_2), 2.84 (m, 2H, CH_2 for cod), 2.74 (m, 2H, CH_2(Et)), 2.42 (dq, 2H, CH_2(Et), J_{HH} = 14.3 and 7.1 Hz), 2.25 (m, 4H, CH_2 for cod), 1.69 (m, 2H, CH_2 for cod), 1.12 (t, 6H, CH_3, J_{HH} = 7.2 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 89.7 (=C*H* for cod), 88.9 (=C*H* for cod), 49.9 (NCH_2), 45.9 (CH_2(Et)), 33.1 (CH_2 for cod), 30.1 (CH_2 for cod), 15.7 (CH_3). IR (Nujol): 3200 cm^{-1} (νN−H).

***trans*-[RuCl$_2$(nbd)(EtHNCH$_2$CH$_2$NHEt)] (8).** *N*,*N*′-Diethylethylene diamine (0.35 mL, 2.44 mmol) was added to a suspension of [RuCl$_2$(nbd)]$_n$ (215 mg, 0.81 mmol) in toluene (10 mL). The mixture was heated at 80 °C for 1 h, resulting in an orange solution. After cooling at room temperature, the volatiles were removed under vacuum to give a brown solid. Recrystallization from Et$_2$O/CH_2Cl_2 (2:1 mixture) at −20 °C afforded orange crystals. Yield: 60% (180 mg). Anal. Calcd for $C_{13}H_{24}Cl_2N_2Ru$: C, 41.04; H, 6.32; N, 7.37. Found: C, 40.87; H, 6.29; N, 7.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64 (m, 2H, =C*H* for nbd), 4.57 (m, 2H, =C*H* for nbd), 3.79 (m, 2H, C*H* for nbd), 3.11 (br s, N−*H*), 2.79 (m, 4H, NCH_2), 2.58, 2.44 (m, 2H each, CH_2(Et)), 1.41 (t, 2H, CH_2 for nbd, J_{HH} = 1.5 Hz), 0.91 (t, 6H, CH_3, J_{HH} = 7.3 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 76.0 (=CH for nbd), 73.1 (=CH for nbd), 61.5 (CH_2 for nbd), 51.9 (CH for nbd), 49.3 (NCH_2), 44.8 (CH_2(Et)), 13.6 (CH_3). IR (Nujol): 3220 cm^{-1} (νN−H).

***trans*-[RuCl$_2$(nbd)(morpholine)$_2$] (9).** The complex was prepared according to a published method[8] for the piperidine analogue. Morpholine (1 mL, 11.5 mmol) was added to a suspension of [RuCl$_2$(nbd)]$_n$ (500 mg, 2.27 mmol) in acetone (3 mL). The mixture was stirred at room temperature for 15 h to give a pale yellow solid and a brown solution. The solid was filtered, washed with petroleum ether, and dried under vacuum. Yield: 90% (890 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.42 (br s, 4H, =C*H* for nbd), 3.82 (br s, 2H, C*H* for nbd), 3.82 (m, 4H, OCH_2), 3.45 (m, 4H, OCH_2), 2.62−2.90 (m, 4H, NCH_2), 2.48 (m, 4H, NCH_2), 1.51 (br s, 2H, CH_2 for nbd). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 71.1 (=CH for nbd), 68.3 (CH_2−O), 60.5 (CH for nbd), 51.4 (CH_2 for nbd), 47.4 (NCH_2).

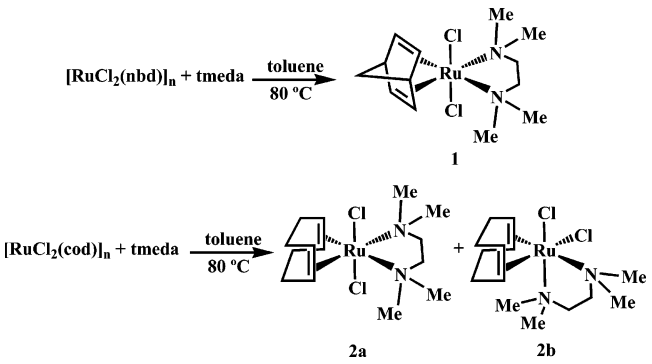
***trans*-[RuCl$_2$(cod)(NEt$_2$)$_2$] (10).** The preparation was carried out following the same procedure as that for **9** using NHEt$_2$ (1 mL, 9.5 mmol) and [RuCl$_2$(cod)]$_n$ (285 mg, 1.01 mmol) in acetone (10 mL). Complex **10** was isolated as a pale yellow material. Yield: 45% (140 mg). Selected NMR data: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (br s, 4H, =C*H* for cod), 2.65 (m, 8H, CH_2 for cod), 3.02 (q, 8H, CH_2(Et), J_{HH} = Hz) 2.55 (m, 4H, N−*H*), 1.46 (t, 12H, CH_3, J_{HH} = Hz. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 88.1 (=CH for cod), 43.0 (CH_2(Et)), 11.5 (CH_3).

General Procedure for the Catalytic Reduction of Acetophenone. The transfer-hydrogenation experiments were carried out using standard Schlenk glassware. Acetophenone (3.5 mL, 30 mmol) was added to a solution of the catalyst (0.05 mmol) and KOH (2 mL, 0.1 M in 2-propanol) in 2-propanol (10 mL). The reaction mixture was heated at 60 °C for 1 h and allowed to warm to room temperature. Conversions were determined by ^{1}H NMR spectrum of the reaction crude after removal of the volatiles under vaccum.

For the direct hydrogenation of the ketone, the substrate (30 mmol), catalyst (0.05 mmol), base (0.2 mmol), and 2-propanol (10 mL) were placed inside the glovebox in a 50 mL Parr autoclave reactor. The reactor was filled with H_2 to a given hydrogen pressure. The reaction mixture was heated at 60 °C for 1 h and allowed to warm to room temperature. The pressure was the released, and conversions were determined by analysis of the ^{1}H NMR spectrum of the reaction crude after removal of the volatiles under vacuum.

X-ray Structure Determination. The intensity data of complexes **4a** and **6** were collected at room temperature on a Bruker AXS Smart 1000 diffractometer, equipped with an area detector, and on a Philips PW 1100 (**6** and **4a**, respectively) single-crystal diffractometer using graphite monochromated Mo Kα radiation. Crystallographic and experimental details for the structures are summarized in Table 1. When necessary, a correction for absorption was made. The structures were solved by Patterson and Fourier

Scheme 1. Preparation of Complexes **1**−**2b**



methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.[12] The two carbon atoms C1 and C2 of the tmeda ligand in **4a**, as well as the carbon atoms C7 and C8 of one of the three ethylene groups of the *N*,*N*,*N*′-Et_3−en ligand in **6**, were found disordered in two positions. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms, expecting the hydride H1 in **4a**, which was found in the ΔF and refined isotropically.

Results and Discussion

Synthesis and Characterization of tmeda Complexes. The compound **1** is prepared by the reaction of $[RuCl_2(nbd)]_n$ (2,5-norbornadiene) with an excess of tmeda in toluene at 80 °C (Scheme 1). Its ^{1}H NMR spectrum shows resonances at δ 4.69, 3.89, and 1.34 for nbd. The presence of a singlet for the methyl groups of tmeda at δ 2.45 supports a structure in which the chlorides are occupying mutually trans positions. The $^{13}C\{^1H\}$ NMR spectrum of **1** is also consistent with the proposed stereochemistry (see Experimental Section). By following the same methodology but using $[RuCl_2(cod)]_n$ as the metal precursor, two isomeric products of composition $[RuCl_2(cod)(tmeda)]$ (**2a** and **2b**) are obtained in a 2:3 ratio.

The major isomer *cis*-**2b** is isolated by fractional crystallization from the reaction mixture. Its ^{1}H NMR spectrum, in CD_2Cl_2, displays four sets of multiplets at δ 4.18, 4.10, 3.98, and 3.92 for the olefinic protons and individual resonances for all methylene protons of the cod ligand. Also, the methyl groups of the diamine are not equivalent, appearing as singlets at δ 2.46, 2.37, 2.19, and 2.18. The lack of symmetry observed for this ruthenium species is indicative of a mutually cis position for the chlorides in the molecules of **2b**. The isomer *trans*-**2a** has been prepared in a different route by Kirchner et al.[13a] The characterization of the minor isomer *trans*-**2a** is made by comparison with the data already reported.

It is worth mentioning that the distribution of *trans*-**2a** and *cis*-**2b** (2:3) observed in the ^{1}H NMR spectrum of the reaction extract after 24 h of stirring seems to be the result of a kinetic control. Actually, a thermodynamic equilibrium mixture is achieved by heating (80 °C) a solution of **2a** and **2b** in a 2:3 molar ratio for 5 days in the presence of tmeda. The progress of the transformation is followed by ^{1}H NMR spectroscopy. Resonances due to *trans*-**2a** isomer decreased in intensity whereas those due to *cis*-**2b** increased to yield an equilibrium mixture of about 17% **2a** and 83% **2b**, with *cis*-**2b** therefore being the thermodynamically more stable product. Conversely, as described above, complex **1** exists only as the *trans*-dichloro isomer. Similar results have been reported by James et al. for complexes of the type $[RuCl_2(P-P)(N-N)]$. For the DPPF ligand (DPPF = 1,1′-bis(diphenylphosphino)-ferrocene), the bidentate diimine ligands afforded only the *cis*-dichloro species whereas the bidentate diamine ligands generated the *trans*-dichloro isomer.[5j] But when the less bulkier and more flexible DPPB phosphine ligand (DPPB = 1,4-bis(diphenylphosphino)butane) was used instead, the bipyridine or phenanthroline bidentate ligands generated both the cis and trans isomers, the former being the thermodynamic product.[14]

Attempts to displace the diene ligand in **1** and **2a** and **2b** by a second tmeda molecule proved unsuccessful, even when performing reactions in neat tmeda as the solvent. A similar behavior has been observed for complexes TpRu(cod)X,[15a] which contains the homoscorpionate ligand, hydrotris-(pyrazolyl)borate, Tp. However, the Cp analogue CpRu(cod)-Cl[15b] (Cp = C_5H_5) easily dissociated the cod molecule in the presence of different donors ligands. The authors attributed such behavior to the coligand electronic effect. When coligands are σ-donors (as the N atoms of the pyrazolyl rings in the Tp ligand), the diene becomes substitutionally inert, being easily displaced when σ-donor and π-acceptor ligands (such as C_5R_5) are attached to the metal center. In this regard, Braunstein et al.[16] in a recent paper have described the synthesis of complexes $[RuCl_2-(PCH_2-oxazoline)_2]$ by refluxing $[RuCl_2(cod)]_n$ with the chelating P,N ligand in EtOH. The bis-chelate derivative is the only product isolated even when the reaction is performed with a 1:1 P,N/Ru ratio.

Synthesis of the Hydrido Derivatives. In order to remove the diene molecule in **1** and **2**, the procedures described in Scheme 1 are performed under 2 bar of hydrogen. Reactions produce a mixture of hydride species **3** and **4** as major products and the desired complex **5** as the minor product (Scheme 2). Alternatively, the hydride derivatives **3** and **4** can be synthesized in good yields by heating a toluene solution of complexes **1** and **2** with equimolar amount of NEt_3 in the presence of hydrogen.

The method described in Scheme 2, using $[RuCl_2(diene)-(tmeda)]$(**1** and **2**) as the starting material, also produces small amounts of **5** (5−10%) depending on the reaction time. The hydride **3** is obtained as a mixture of trans and cis isomers in a ratio of 9:1. The isomers are identified by NMR spectroscopy. The four methyl groups of tmeda in *trans*-**3a** lead to two singlets at 2.03 and 1.90 ppm in the ^{1}H NMR spectrum, consistent with a structure that has a hydride trans

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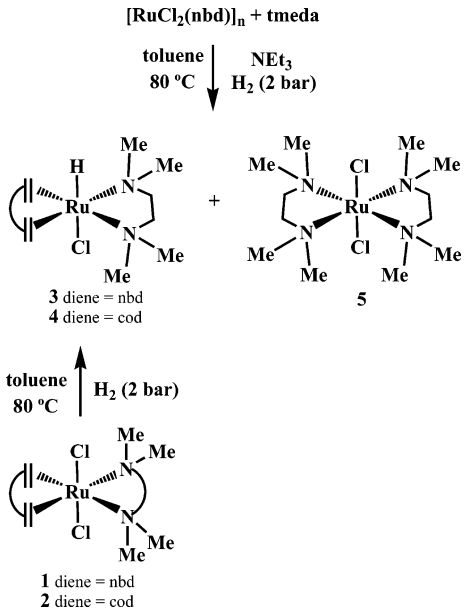
Scheme 2. Synthesis of Hydrido Derivatives



to chloride. The hydride region of the spectrum shows a singlet at −5.42 ppm in good agreement with other ruthenium−hydride species containing nitrogen donor ligands.[7c,17] The methyl groups of tmeda are not equivalent in *cis*-**3b** due to the lower symmetry of this isomer, and, consequently, four singlets of three protons each are seen in the δ 3.5−2.6 range. Also, a distinctive singlet at −5.38 due to the hydride ligand appears in the high-field region of the ^{1}H NMR spectrum. The hydride is also observed in the IR spectrum of **3a** that shows a Ru−H vibration at 2016 cm^{-1}.

The complex [RuCl(H)(cod)(tmeda)] also exists as a mixture of *trans*- and *cis*-chloro species, the former being the major product. The isomer **4a** has been obtained previously[13a] by the reaction of [RuCl$_2$(cod)] with 2 equiv of tmeda in refluxing MeOH. The minor isomer *cis*-**4b** cannot be isolated in a pure form, and its complete characterization is made on the basis of NMR spectrum of the reaction mixture. The lack of symmetry of this isomer is shown by the appearance of different sets of signals for all hydrogen atoms of cod and tmeda ligands (see Experimental Section). The hydride region of the ^{1}H NMR spectrum shows a singlet at−6.45 ppm.

The structure proposed for *trans*-**4a** has been confirmed by a single-crystal X-ray diffraction study (Figure 1). Selected bond distances and angles are listed in Table 2. The coordination around ruthenium is slightly distorted octahedral, with the midpoints of the double bonds of the cod ligand and the nitrogen atoms of the diamine ligand in the equatorial positions, and the chlorine and hydrogen atoms at the apexes. The trans Cl1−Ru1−H1 bond angle is 171.5(11)°. The Ru1−H1 distance, 1.58(3) Å, is in the range found for the already reported ruthenium−hydride complexes.[5c,h,8c,17a] Ru1−N1 and Ru1−N2 bond distances are similar at 2.257(3) and 2.263(3) Å, respectively. The Ru−Cl distance is 2.5610(14) Å, in the range found for similar Ru complexes.[5c,h]

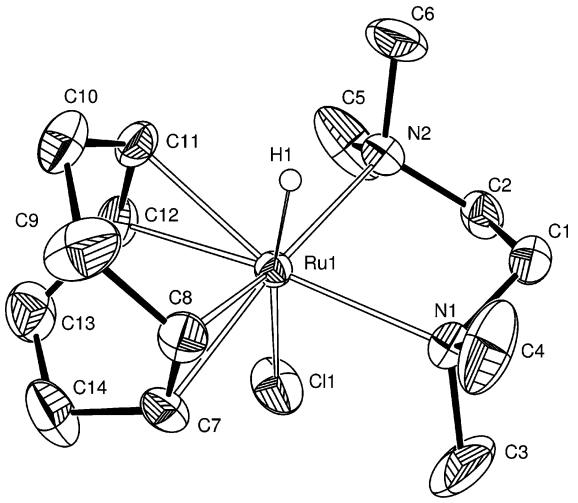


Figure 1. ORTEP view of the structure of **4a** together with the atomic numbering scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **4a**[a]

Ru1−Cl1	2.5610(14)	H1−Ru1−Cl1	171.5(11)
Ru1−H1	1.58(3)	H1−Ru1−CT1	86.70(12)
Ru1−N1	2.257(3)	H1−Ru1−CT2	85.64(12)
Ru1−N2	2.263(3)	H1−Ru1−N1	86.5(12)
Ru1−CT1	2.038(4)	H1−Ru1−N2	86.4(11)
Ru1−CT2	2.039(4)	Cl1−Ru1−CT1	100.49(13)
		CT1−Ru1−CT2	85.80(15)
Cl1−Ru1−CT2	99.36(13)	N1−Ru1−N2	81.04(12)
Cl1−Ru1−N1	88.36(10)	CT1−Ru1−N1	95.84(15)
Cl1−Ru1−N2	86.11(9)	CT2−Ru1−N2	96.35(15)

[a] CT1 and CT2 are the midpoints of the C7−C8 and C11−C12 double bonds.

Synthesis of Bis-tmeda Complex. As mentioned above, the bis-chelated **5** has been obtained as a minor product by the method given in Scheme 2. Extended heating (4−5 days) under those conditions produced quantitative yields of **5**, which could be isolated as reddish crystals from Et$_2$O/CH$_2$Cl$_2$ mixtures. Unlike the analogous complex *trans*-[FeCl$_2$(tmeda)$_2$],[18] which is air- and moisture-sensitive and stable in solution only in an excess of tmeda, complex **5** is remarkably air-stable both in solution and in the solid state. Its ^{1}H NMR spectrum in CD$_2$Cl$_2$ is very simple, showing only two singlets at 2.69 and 2.57 ppm for the methyl and methylene protons of tmeda, respectively. The preparation of this complex has also been reported by Kirchner and coworkers,[13a] and its X-ray structure has been recently described by Ernst et al.[13b]

Reactions of [RuCl$_2$(diene)]$_n$ with teeda. Upon exchanging the tmeda ligand with the more sterically demanding teeda ligand, unexpected transformations are observed. When [RuCl$_2$(diene)]$_n$ are heated in toluene with 5 equiv of teeda for 24 h, the formation of *trans*-[RuCl$_2$(diene)(EtHNCH$_2$CH$_2$N(X)Et)], (diene = nbd, X = Et, **6**; diene = cod, X = H, **7**) is observed in high yields (eq 1).

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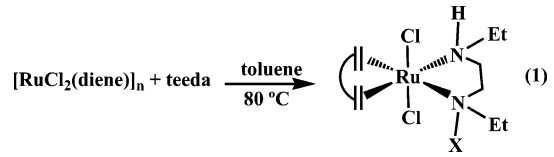

6 diene = nbd; X = Et
7 diene = cod; X = H

Unexpectedly, diamine ligands bonded to Ru in **6** and **7** bear N−H functionalities as the result of the formal loss of one or two C_2H_4 fragments of the parent teeda and the subsequent conversion of the tertiary into secondary amine. Compelling evidence for the presence of N−H groups in the diamine ligands is provided by IR and NMR spectroscopy. Thus, the IR spectrum of **6** exhibits a sharp absorption at 3220 cm^{-1} and its ^1H NMR spectrum in benzene-d_6 (Figure 2) shows a broad resonance at δ 3.18 and only three sets of ethyl signals for the diamine ligand. In addition, the ethylenic chain protons of the diamine are not equivalent, giving rise to four multiplets at 3.08, 2.60, 2.08, and 1.56 ppm. The resonance at 2.60 ppm is coupled (J_{HH} = 13 Hz) to that due to N−H, as can be inferred by selective irradiation experiments.

The structure of compound **6** has been determined by X-ray methods as well as that of **7**, which has been previously reported by us.[10] An ORTEP view of the complex **6** is shown in Figure 3, and a list of selected bond distances and angles is collected in Table 3. The distorted-octahedral environment of Ru1 involves the nitrogen atoms from the diamine ligand and the midpoints of the C9−C10 and C12−C13 double bonds from the nbd molecule in the equatorial positions and the chlorine atoms at the apexes. The Cl1−Ru1−Cl2 bond angle deviates significantly from linearity with a value of 164.74(3)°. The Ru1−N1 bond distance involving the tertiary nitrogen atom is much longer, 2.305(2) Å, than the Ru1−N2 one of 2.179(3) Å, involving the secondary nitrogen atom, which is comparable to that observed in the structure of **7**.[10]

Complex **7** exhibits a relatively simple ^1H NMR spectrum compared with that of **6** due to the presence of a more symmetric diamine ligand in its molecule. Consequently, only one set of signals for the ethyl protons of the chelating diamine appears in the spectrum, and the two N−H protons, which are in an equivalent environment, give rise to a broad resonance at 3.61 ppm.

Complexes **6** and **7** can be prepared directly and quantitatively from the commercially available diamines $Et_2NCH_2CH_2NHEt$ and $EtHNCH_2CH_2NHEt$. The thermal reaction of $[RuCl_2(nbd)_n]$ with $EtHNCH_2CH_2NHEt$ leads to the formation of a new species **8** that is not formed by the previous route. The NMR features of **8** are very similar to those of **7,** in good agreement with a trans geometry of the chloride ligands.

Transition-metal-assisted C−N bond activation of amines and N-heterocycles constitutes a crucial step in the catalytic hydrodenitrogenation[19] of crude oil as well as in the metabolism of amines by enzymes such as cytochrome P-450.[20] In addition, processes involving C−N single bond cleavage have found important synthetic applications such as the metal-catalyzed synthesis of unsymmetrical amines[21] or N-heterocycles.[22] James et al. has reported the stoichiometric conversion of a secondary amine to a primary amine by a dinuclear ruthenium(II)−phosphine species.[23] The transformations described herein constitute an unique example regarding the N-dealkylation of tertiary chelating diamines by a mononuclear phosphine-free Ru(II) complex. The exchange of alkyl groups between primary and/or secondary amines catalyzed by $RuCl_2(PPh_3)_3$[21b,24] involves the formation of imine hydride species, which react further with nucleophiles such as additional amine to give intermediates from which the exchange of amines is produced. Since the reactions shown in eq 1 require an excess of teeda ligand, a similar pathway could be invoked to account for these processes. However, we have collected some mechanistic information that enforces the proposition of an *intramolecular* pathway for the observed N-dealkylation reactions. Due to the insolubility of $[RuCl_2(diene)]_n$ precursors in toluene, we have developed an alternative procedure for the synthesis of complexes **1** and **2** in the homogeneous phase. Thus, we have prepared the complexes **9** and **10**, soluble Ru(II) precursors, following a procedure similar to that described in the literature[8] for other ruthenium−amine derivatives. The geometries proposed for complexes **9** and **10** are unequivocally inferred from their NMR features. The ^1H NMR spectrum of **9** shows three groups of resonances for the three different types of hydrogens of the nbd ligand at δ 4.42 (4 H), 3.82 (2 H), and 1.51 (2 H) and the morpholine protons give rise to a set of four multiplets (4 H each) in the range of δ 3.9−2.5. As expected for a *trans*-dichloro species, the number of ^{13}C resonances is lower than that for the less symmetrical cis arrangement, and only five resonances are observed for all the carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum of **9**.

The addition of 1 equiv of $Et_2NCH_2CH_2NHEt$ to a solution of **9** in $CDCl_3$ affords complex **6** in quantitative yield upon stirring at room temperature for 1 h (Scheme 3). NMR monitoring of the reaction shows the clean conversion of **9** into **6**. In contrast, the reaction of **9** with 1 equiv of tmeda proceeds quite slowly at room temperature. Upon heating at 80 °C for 3 h, a 70:30 mixture of **1**/**9** is formed. Further heating (15 h) does not produce any change in the product ratio, as a clear indication of the existence of a thermody-

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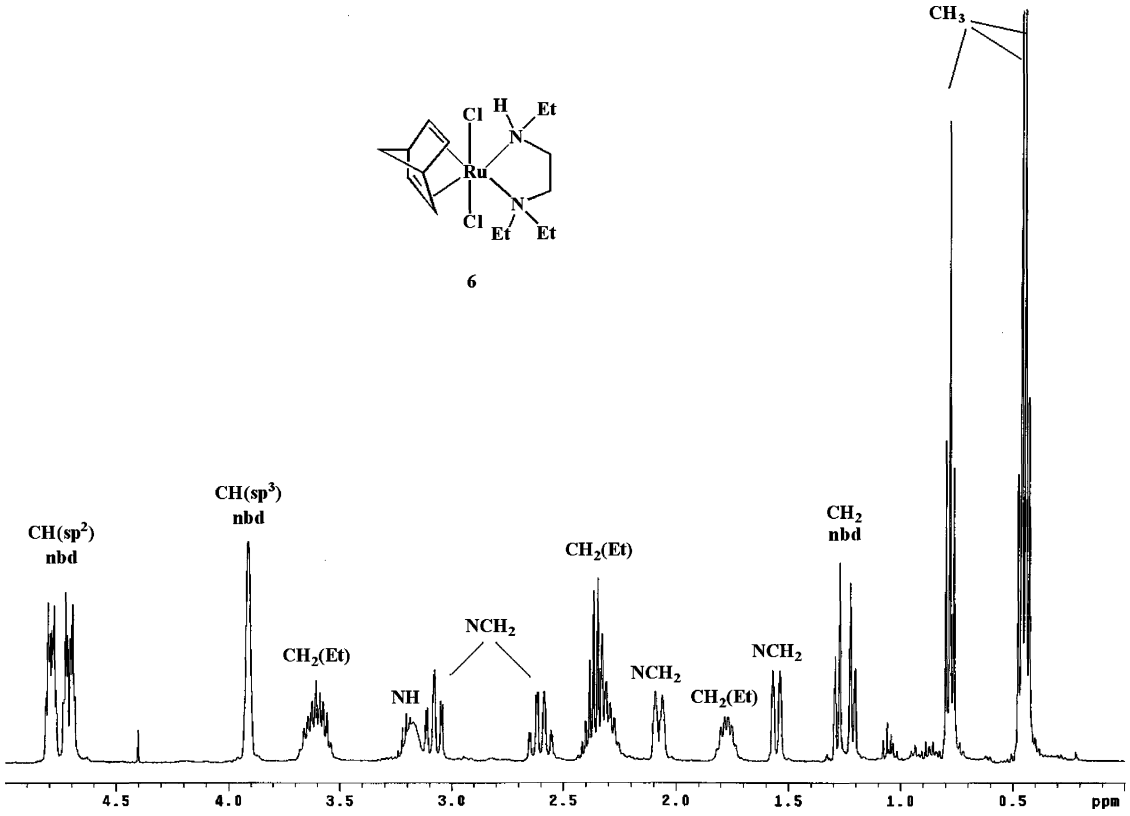


Figure 2. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

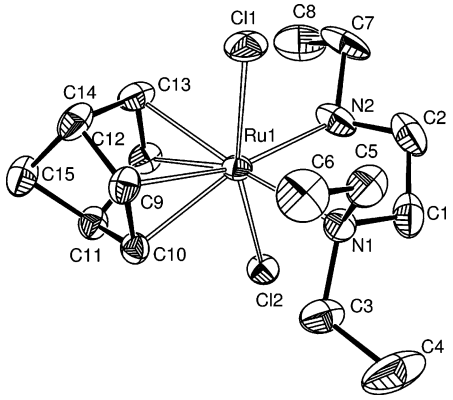


Figure 3. ORTEP view of the structure of complex **6** together with the atomic numbering scheme.

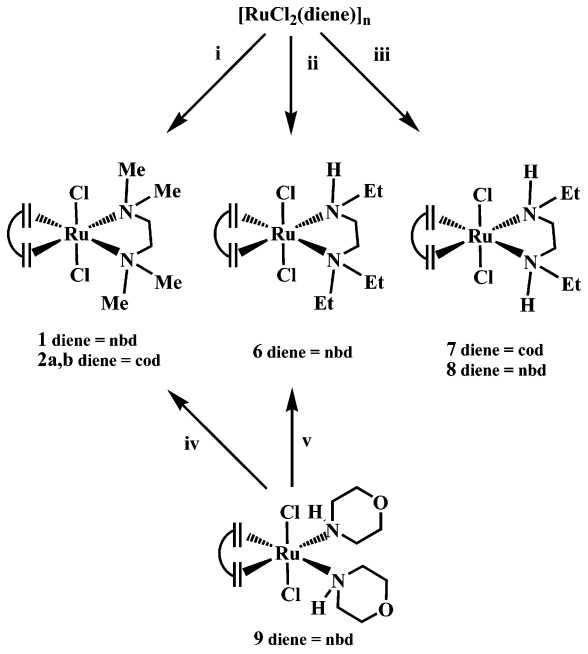
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **6**[a]

Ru1−Cl1	2.431(2)	Cl1−Ru1−Cl2	164.74(3)
Ru1−Cl2	2.444(2)	Cl1−Ru1−N1	87.22(5)
Ru1−N1	2.305(2)	Cl1−Ru1−N2	86.01(8)
Ru1−N2	2.179(3)	Cl1−Ru1−CT1	98.65(7)
Ru1−CT1	2.084(2)	Cl1−Ru1−CT2	94.34(7)
Ru1−CT2	2.089(2)	Cl2−Ru1−N1	86.14(5)
		N1−Ru1−N2	81.42(9)
Cl2−Ru1−N2	79.42(8)	CT1−Ru1−CT2	68.66(9)
Cl2−Ru1−CT1	96.31(7)	N1−Ru1−CT1	104.52(9)
Cl2−Ru1−CT2	93.87(7)	N2−Ru1−CT2	105.31(9)

[a] CT1 and CT2 are the midpoints of the C9−C10 and C12−C13 double bonds.

namic equilibrium under those conditions. The addition of an slight excess of tmeda provides quantitative conversions. Moreover, the thermal reaction of **9** with 1 equiv of teeda is slower than that with tmeda and leads to complex **6** in quantitative yield after 15 h of heating. In all experiments

Scheme 3. Thermal Reactions of $[RuCl_2(diene)]_n$ and $[RuCl_2(nbd)(morpholine)_2]$ with Various Diamines[a]



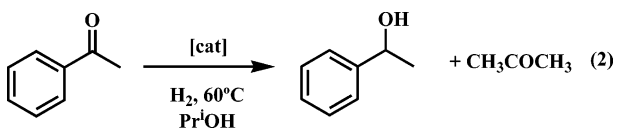
[a] Reactions conditions: (i) toluene, 80 °C, excess tmeda; (ii) toluene, 80 °C, excess teeda or $Et_2NCH_2CH_2NHEt$; (iii) for cod, toluene, 80 °C, excess teeda, $Et_2NCH_2CH_2NHEt$, or $EtHNCH_2CH_2NHEt$; for nbd, only with $EtHNCH_2CH_2NHEt$; (iv) $CDCl_3$, 1 equiv tmeda, 80 °C, 3 h, 70%; (v) $CDCl_3$, 1 equiv $Et_2NCH_2CH_2NHEt$, room temperature, 1 h, 100% or dichloroethane, 1 equiv teeda, 80 °C, 15 h, 90%.

(Scheme 3), free morpholine is observed in the ^{1}H NMR spectrum of reaction mixtures. Similar experiments have been carried out with complex **10** as the starting material, although these substitution reactions require longer reaction times and

a slight excess of the diamine to achieve similar conversions. According to the available data, the conversion of **9** into **6** using the $Et_2NCH_2CH_2NHEt$ ligand takes place almost instantaneously at room temperature. When 2 equiv of morpholine are added to the mixture, the reaction rate decreases considerably. The observation that, at room temperature, tmeda reacts more slowly than $Et_2NCH_2CH_2NHEt$ is a good indication that coordination of the latter to the Ru(II) center must occur initially through the NHEt arm, which provides less steric hindrance than the NEt_2 counterpart. Attempts to isolate or detect a teeda adduct have failed, probably due to steric reasons. We believe such an effect also accounts for the observed double N-dealkylation of the diamine ligand when cod is bonded to the Ru(II) center. The high steric demand of the cod moiety is reflected by the deviation of the Cl1−Ru−Cl1′ angle (159.19(4) °) from linearity in **7**.[10] The almost quantitative yields of products observed when using 1 equiv of the chelating diamines unambiguously establish the intramolecular nature of this transformation, in contrast to the previously reported intermolecular alkyl group exchange catalyzed by ruthenium.

Catalytic Hydrogenation of Ketones. As mentioned above, complexes of the type $[RuCl_2(P-P)(N-N)]$ have been used as precatalysts for the reduction of ketones to alcohols.[4,5] The high catalytic activity shown by some of these systems is attributed to the presence of N−H groups in the diamine ligand. The reduction of the ketone is achieved by metal−ligand bifunctional catalysis in which the Ru−H and N−H bonds play an important role.[4e,25] Since some of the compounds described in this work contain diamine ligands with N−H groups, we have decided to evaluate their activity as catalytic precursors for the hydrogenation of ketones.

In a first set of experiments (entries 1−4, Table 4), under typical conditions for transfer hydrogenation, a 2-propanol solution of acetophenone containing the catalyst precursors **1**, **2b**, **7**, or **8** (0.16% with respect to the substrate) and a 4-fold excess of KOH heated for 1 h give low to moderate conversions into the corresponding alcohol (eq 2) that reach the maximum with **7** as the precatalyst and a 57% ratio of conversion with a turnover frequency value of 343 h^{-1}. Blank experiments in the absence of Ru complexes give no conversion of acetophenone under the same conditions. The use of K^{t}BuO as the base affords similar yields whereas NEt_3 results were unsuccessful for this transformation.



(2)

A second series of experiments have been performed using the same array of catalyst precursors and reaction conditions, but under 2 atm of H_2. The results (entries 5−8 in Table 4) indicate that there is an effect of the presence of hydrogen gas in the reaction mixture that exerts a distinct influence in the conversions into the desired alcohol. Thus, the reaction carried out with **1** as the catalyst precursor is not affected by the hydrogen atmosphere whereas in the case employing **8**, conversion (entry 8, 82%) nearly doubles that of the experiment performed under N_2 (entry 4, 43%). Although complexes **1** and **2b** seem to induce a lower level of hydrogenation than **7** or **8**, the use of a higher pressure of hydrogen, up to 10 atm, makes the catalytic activity of **2b** similar to those of **7** and **8**, **1** being less active under those conditions. Even the bis-tmeda complex **5** catalyzes this hydrogenation reaction, under 10 atm of H_2, with a 44% yield. We have also studied the hydrogenation of cyclohexanone using complexes **2a** and **7** under 10 bar of H_2 at 60 °C (entries 14 and 15). Quantitative conversions are achieved in only 30 min of reaction, showing that the activity of these catalysts is much greater toward cyclohexanone than that of acetophenone. A similar feature has been observed when using phosphine-free complexes [Tp*RuH(cod)][7b] (Tp* = hydrotris(3,5-dimethyl-pyrazolyl)borate) and [RuHCl(bpzm)(cod)][7c] (bpzm = bis(pyrazolyl)methane) as catalysts in such transformations.

Table 4. Hydrogenation of Ketones Catalyzed by Ruthenium Complexes[a]

Entry	Catalyst precursor	Substrate	Conv (%)	P H_2(atm)	TOF[a]
1	**1**		33	0	196
2	**2b**		16		100
3	**7**		57		343
4	**8**		43		256
5	**1**		36	2	216
6	**2b**		42		251
7	**7**		67		402
8	**8**		82		492
9	**1**		65	10	393
10	**2b**		86		519
11	**7**		90		545
12	**8**		86		518
13	**5**		44		263
14	**2a**		>95%	10	1140
15	**7**		>95%		1140

[a] Experimental conditions (see Experimental Section): 60 °C, 1 h, cat/base/S = 1:4:600.

These results can be interpreted in the following manner. Under transfer-hydrogenation conditions, it seems clear that the presence of the N−H group in these Ru(II) systems could facilitate the reduction of acetophenone via the bifunctional mechanism in which the "RuH−NH" unit plays an important role. Since the catalytic activity of **2b**, **7**, and **8** is quite similar, under high pressure of H_2, the transfer-hydrogenation mechanism must be overcome by the direct-hydrogenation pathway in which the N−H group in the diamine ligand does not seem crucial for the catalytic performance of these Ru-

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(II) species.[26] In good agreement with that result previously reported,[5a,d,i] the monohydride complexes **3** and **4** are inactive for the reduction of acetophenone under transfer-hydrogenation conditions in the absence of base. Therefore, the catalytic species in such transformations could be dihydride complexes formed in the presence of a strong base under hydrogen.

Conclusions

We have prepared new phosphine-free ruthenium−diamine species of type $[RuCl_2(diene)(N-N)]$, where diene = nbd, cod, and $N-N$ = tmeda, *N*,*N*,*N*′-triethylethylene diamine, and *N*,*N*′-diethylethylene diamine. Reactions of the polymeric $[RuCl_2(diene)]_n$ with H_2 in the presence of tmeda produce mixtures of hydrido chloro complexes *trans*-[RuHCl(diene)(tmeda)] and *trans*-$[RuCl_2(tmeda)_2]$ in different ratios depending upon the reaction conditions. When a more sterically demanding diamine, teeda, is used N-dealkylation processes of the parent diamine are observed affording Ru(II) complexes in which the N−N ligand coordinated to the metal center has one or two N−H functionality depending on the nature of the diene molecule. Crystal structures for *trans*-[RuHCl(cod)(tmeda)] and *trans*-$[RuCl_2(nbd)(Et_2NCH_2CH_2NHEt)]$ are presented. The catalytic activity of these phosphine-free complexes in the reduction of acetophenone has been evaluated under transfer-hydrogenation and direct-hydrogenation conditions. The data indicate the systems are reasonably efficient under high pressure H_2 and that under these conditions the H_2 hydrogenation mechanism dominates that of hydrogen transfer.

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Supporting Information Available: Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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