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Synthesis of Ruthenium(II) Complexes Containing Tridentate Triamine ('NNN') and Bidentate Diamine Ligands (NN'): as Catalysts for Transfer Hydrogenation of Ketones

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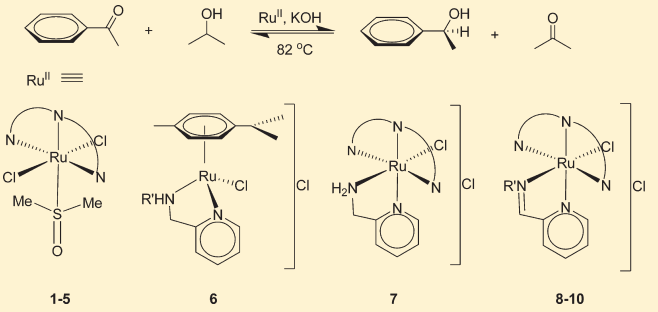
Supporting Information

ABSTRACT: A series of neutral and cationic Ru(II) complexes (**1**−**10**), bearing pyridine-based tridentate ('NNN'), pyridine-based bidentate (NN'), and mixed 'NNN' + NN' ligands, were synthesized by starting from $[RuCl_2(DMSO)_4]$ and $[RuCl_2(p\text{-cymene})]_2$ precursors. Solid-state structures of mixed-ligand complexes **9** and **10** were determined by single-crystal X-ray diffraction. Both complexes are unusual in that NN' ligands were spontaneously oxidized in air under base-free conditions to give imine-amine bidentate ligands upon replacement of *p*-cymene by meridional 'NNN'. The complexes **1**−**10** were screened for transfer hydrogenation (TH) of aryl ketones with 2-propanol. The highest catalytic activity was obtained with the complexes containing tridentate 'NNN' and **7**, which contain nonsulfonated 2-(aminomethyl)pyridine. However, for complexes $\mathbf{6}_{a-c}$, containing *p*-cymene (a facial tridentate ligand), a slower reaction rate was observed.



INTRODUCTION

Pyridine-based tridentate triamine compounds ('NNN') are very attractive ligands for coordination chemistry, and their transition-metal (TM) complexes have been successfully applied in homogeneous catalysis.[1−28] Although examples of the related Ru complexes are scarce, such complexes recently gained attention due to their use in catalysis and in other chemical applications.[29−48] For example, $_d$NNN$_d$-containing neutral Ru(II) complexes of the general formula $[RuCl_2(_dNNN_d)L]$ (L = monodentate ligands such as CH_3CN, PPh_3, and CO) are effective catalysts for the transfer hydrogenation (TH) of ketones.[29,32] During the preparation of this paper, a report on unsymmetrical and asymmetrical $[RuCl('NNN'')(PPh_3)_2]Cl$ complexes which showed excellent TH activity has appeared.[49]

On the other hand, Ru(II) complexes bearing chelating amine ligands such as N-sulfonated 1,2-diamines have been successfully used in the TH of acetophenone by Noyori and others.[50−63] However, in spite of these developments, there is still demand for stable and easily handled complexes prepared from cheap starting materials which make them preferred catalyst precursors. In comparison with the extensive chemistry of sulfonated 1,2-diamines, little research has been performed on pyridylsulfonamide compounds of the type $C_5H_4NCH_2NHSO_2Ar$, which are versatile bidentate ligands due to their ease of synthesis and variability of Ar groups.[64−68] Neutral sulfonamide ligands are expected to be poor ligands. Thus, the pyridyl-2-alkylsulfonamides generally coordinate to the metal center through the pyridyl nitrogen atom and the deprotonated nitrogen of the sulfonamide group.[69] However, Soltani et al. have recently shown that cationic Ir complexes containing neutral sulfonamide ligands are active catalysts for the TH of acetophenone derivatives in water.[70] More recently, Baratte and co-workers have shown that Ru(II) complexes containing nonsulfonated (2-aminomethyl)-pyridine ligands display excellent catalytic activity in the TH of ketones.[71] With the aim of contributing to the understanding of how geometric and electronic factors imposed by a combination of mixed tri- and bidentate ligands influence the catalyst performance, herein a series of novel Ru(II) complexes (**1**−**10**) were characterized and employed as catalysts for the TH of ketones.

EXPERIMENTAL SECTION

The manipulations were performed under air unless otherwise stated. All reagents and solvents were obtained from commercial suppliers and used without further purification. $[RuCl_2(p\text{-cymene})]_2$,[72] $[RuCl_2(DMSO)_4]$,[73] $_d$NNN$_d$;[74] $_b$NNN$_b$ (R = H),[75] $_p$NNN$_p$,[76] and

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$\widehat{NN}'_a$[66] were synthesized according to published procedures. NMR spectra were recorded at 297 K on a Bruker 300 MHz Ultrashield TM NMR spectrometer at 300 MHz (^{1}H) and 75.48 MHz (^{13}C) or at 297 K on a Varian Mercury AS 400 NMR spectrometer at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). Chemical shifts (δ) are given in parts per million and coupling constants (J) in hertz. The C, H, and N analyses were performed using a CHNS-932 (LECO) instrument. Infrared spectra were measured with a Perkin-Elmer Spectrum One FTIR system and recorded using a universal ATR sampling accessory within the range 550−4000 cm^{-1}. Melting points were determined in open capillary tubes on a digital Stuart SMP10 melting point apparatus or an Electrothermal 9100 melting point detection apparatus and are uncorrected. GC measurements for catalytic experiments were performed using a Younglin Acme 6100 GC instrument with an Optima 5MS capillary column or an Agilent 6890N GC instrument with a HP5 capillary column.

General Procedure for the Synthesis of $_b\widehat{NNN}_b$ Derivatives. A solution of 2,6-bis(benzimidazol-2-yl)pyridine (0.5 mmol) and KOH (1.15 mmol) in acetone (20 mL) was refluxed for 1 h under argon. Then benzyl halide (1.1 mmol) was added and the resulting solution was refluxed for a further 8 h. Volatiles were removed, and the residue was treated with CH_2Cl_2 (DCM) (10 mL) and filtered. The volume of the filtrate was reduced to ∼5 mL; *n*-hexane (10 mL) was added and cooled to obtain cream-colored crystals.

$_b\widehat{NNN}_b$ (R = $CH_2C_6H_5$). Yield: 83%. Mp: 240−242 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.51 (s, 4H, N-CH_2-Ar), 7.26 (m, 16H, Ar *H*), 7.81 (d, 2H, J = 7.9 Hz, *H*-8), 7.93 (t, 1H, J = 7.7 Hz, *H*-4), 8.41 (d, 2H, J = 7.9 Hz, *H*-3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 51.81, 110.01, 121.02, 122.61, 124.0, 127.03, 128.27, 129.66, 130.18, 135.51, 137.89, 139.85, 144.67, 151.01, 159.33.

$_b\widehat{NNN}_b$ (R = $CH_2C_6H_2Me_3$-2,4,6). Yield: 71%. Mp: 248−250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.19 (s, 6H, 4-*Me*-Ar), 6.26 (s, 4H, N-CH_2-Ar); 6.67 (d, 2H, J = 7.6 Hz, *H*-8), 6.71 (s, 4H, 3,5-*H*-Ar), 6.98 (t, 2H, J = 7.7 Hz, *H*-10), 7.19 (t, 2H, J = 7.6 Hz, *H*-9), 7.76 (d, 2H, J = 7.9 Hz, *H*-11), 8.07 (t, 1H, J = 7.8 Hz, *H*-4), 8.42 (d, 2H, J = 7.6 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.88, 46.83, 105.88, 115.03, 120.58, 121.08, 134.0, 135.07, 135.23, 142.02, 142.26, 149.0, 155.41, 163.18.

$_b\widehat{NNN}_b$ (R = $CH_2C_6HMe_4$-2,3,5,6). Yield: 73%. Mp: 262−264 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.18 (s, 12H, 3,5-(*Me*)$_2$-Ar), 6.19 (s, 4H, N-CH_2-Ar), 6.63 (d, 2H, J = 7.6 Hz, *H*-8), 6.91 (s, 2H, 4-*H*-Ar), 7.01 (t, 2H, J = 7.5 Hz, *H*-10), 7.21 (t, 2H, J = 7.6 Hz, *H*-9), 7.81 (d, 2H, J = 7.6 Hz, *H*-11), 8.14 (t, 1H, J = 7.7 Hz, *H*-4), 8.52 (d, 2H, J = 7.8 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 21.18, 47.11, 111.97, 120.03, 122.91, 124.08, 126.0, 131.27, 134.21, 134.68, 138.07, 138.22, 142.11, 150.08.

$_b\widehat{NNN}_b$ (R = $CH_2C_6Me_5$). Yield: 82%. Mp: 270−272 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.13 (s, 12H, 3,5-(*Me*)$_2$-Ar), 2.21 (s, 6H, 4-(*Me*)-Ar), 6.18 (s, 4H, N-CH_2-Ar), 6.59 (d, 2H, J = 7.6 Hz, *H*-8), 7.01 (t, 2H, J = 7.5 Hz, *H*-10), 7.22 (t, 2H, J = 7.6 Hz, *H*-9), 7.81 (d, 2H, J = 7.6 Hz, *H*-11), 8.11 (t, 1H, J = 7.8 Hz, *H*-4), 8.72 (d, 2H, J = 7.8 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.94, 17.73, 19.92, 47.82, 112.0, 120.0, 122.51, 123.89, 126.07, 128.21, 133.41, 134.87, 136.03, 138.71, 142.38, 150.67.

General Procedure for the Synthesis of 1−5. $_b\widehat{NNN}_b$ (0.165 mmol) derivatives and $Ru(DMSO)_4Cl_2$ (0.080 mg, 0.165 mmol) were placed in the same Schlenk tube, and ethanol (5 mL) was added under argon. Then the mixture was stirred and heated under reflux for 1 day. The volatiles were removed under reduced pressure, and the residue was dissolved in $CHCl_3$ (5 mL). Diethyl ether (10 mL) was added to the solution to precipitate the complexes (**1**−**5**). The brown solid that formed was filtered off and dried under reduced pressure.

Complex ***1***. Yield: 62%. Mp: 318−320 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.61 (s, 6H, $(CH_3)_2SO$), 7.29 (d, 2H, J = 7.6 Hz, *H*-8), 7.43 (t, 2H, J = 7.4 Hz, *H*-10), 7.54 (t, 2H, J = 7.6 Hz, *H*-9), 8.19 (d, 2H, J = 7.8 Hz, *H*-11), 8.49 (t, 1H, J = 7.8 Hz, *H*-4), 8.65 (d, 2H, J = 8.0 Hz, *H*-3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 45.63, 110.03, 119.82, 123.11, 137.12, 143.91, 151.42, 152.13, 156.21.

Complex ***2***. Yield: 71%. Mp: 210−212 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 6H, $(CH_3)_2SO$), 6.23 (s, 4H, N-CH_2-Ar), 7.16−7.61 (m, 16H, *H*-8, *H*-9, *H*-10, and Ar-*H*), 7.82 (d, 2H, J = 7.9 Hz, *H*-11), 8.16 (t, 1H, J = 7.8 Hz, *H*-4), 8.53 (d, 2H, J = 8.0 Hz, *H*-3). ^{13}C NMR (100 MHz, DMSO-d_6): 45.58, 50.88, 111.28, 116.03, 118.05, 132.0, 134.13, 135.51, 135.71, 137.89, 144.67, 146.43, 151.01, 159.33.

Complex ***3***. Yield: 70%. Mp: 226−228 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 6H, 4-*Me*-Ar), 2.45 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.53 (s, 6H, $(CH_3)_2SO$), 6.18 (s, 4H, N-CH_2-Ar); 6.58 (d, 2H, J = 7.6 Hz, *H*-8), 6.84 (t, 2H, J = 7.8 Hz, *H*-10), 7.21 (s, 4H, 3,5-*H*-Ar) 7.51 (t, 2H, J = 7.7 Hz, *H*-9), 7.82 (d, 2H, J = 7.9 Hz, *H*-11), 8.26 (t, 1H, J = 7.8 Hz, *H*-4), 8.72 (d, 2H, J = 7.6 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.53, 20.01, 45.28, 50.17, 105.83, 116.03, 119.18, 120.32, 134.01, 134.86, 148.51, 151.63, 157.14, 165.91.

Complex ***4***. Yield: 77%. Mp: 244−246 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.24 (s, 12H, 3,5-(*Me*)$_2$-Ar), 2.79 (s, 6H, $(CH_3)_2SO$), 5.74 (s, 4H, N-CH_2-Ar), 6.33 (d, 2H, J = 7.7 Hz, *H*-8), 6.64 (s, 2H, 4-*H*-Ar), 7.03 (t, 2H, J = 7.6 Hz, *H*-10), 7.39 (t, 2H, J = 7.5 Hz, *H*-9), 7.81 (d, 2H, J = 7.7 Hz, *H*-11), 8.21 (t, 1H, J = 7.7 Hz, *H*-4), 8.92 (d, 2H, J = 7.8 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.02, 15.38, 45.39, 49.31, 112.06, 122.04, 124.08, 126.14, 142.18, 145.38, 150.17, 165.21, 168.09.

Complex ***5***. Yield: 78%. Mp: 260−262 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 12H, 2,6-(*Me*)$_2$-Ar), 2.19 (s, 12H, 3,5-(*Me*)$_2$-Ar), 2.23 (s, 6H, 4-(*Me*)-Ar), 2.65 (s, 6H, $(CH_3)_2SO$), 6.08 (s, 4H, N-CH_2-Ar), 6.38 (d, 2H, J = 7.6 Hz, *H*-8), 6.85 (t, 2H, J = 7.6 Hz, *H*-10), 7.21 (t, 2H, J = 7.7 Hz, *H*-9), 7.82 (d, 2H, J = 7.8 Hz, *H*-11), 8.18 (t, 1H, J = 7.8 Hz, *H*-4), 9.13 (d, 2H, J = 7.8 Hz, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.76, 18.02, 19.03, 45.23, 48.63, 108.03, 114.28, 120.07, 126.12, 137.03, 143.38, 144.47, 155.94, 159.07.

General Procedure for the Synthesis of $\widehat{NN}'_{a-c}$. 2-(Aminomethyl)pyridine ($\widehat{NN}'_a$) was used as supplied. The compound $\widehat{NN}'_b$ was prepared by modification of the published procedure.[77]

A solution of arylsulfonyl chloride (10 mmol) in 20 mL of dry tetrahydrofuran (THF) was added dropwise to a solution of (2-aminomethyl)pyridine (1.04 mL, 10 mmol) and triethylamine (2.82 mL, 20 mmol) in 50 mL of dry THF under argon. The reaction mixture was refluxed for 6 h, and then the volatiles were removed under reduced pressure. The residue was dissolved in DCM (20 mL) and washed with H_2O (3 × 50 mL) at room temperature. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was recrystallized from a DCM/hexane (1/3) mixture. The desired products were dried under reduced pressure at 50 °C for 1 h.

$\widehat{NN}'_b$. Yield 66%. Mp: 68−70 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.03 (d, 2 H, J = 6.0 Hz, H_f), 7.24 (t, 1 H, J = 7.5 Hz, Ph-H_p), 7.35 (d, 1 H, J = 7.5 Hz, H_d), 7.54−7.66 (m, 2 H, Ph-H_o), 7.72 (t, 1 H, J = 7.8 Hz, H_b), 7.79−7.83 (m, 2 H, Ph-H_m), 8.30 (t, J = 6.0 Hz, 1 H, H_c), 8.43 (d, J = 4.8 Hz, 1 H, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.4, 122.1, 122.9, 127.0, 129.6, 132.9, 137.2, 141.0, 149.2, 157.6. IR (cm^{-1}): 3060, 2973, 2936, 2858, 2846, 1596, 1576, 1479, 1463, 1479, 1463, 1444, 1436, 1328; 1298, 1229, 1157, 1090, 1071, 1052, 1008, 851, 830, 750, 733, 690.

$\widehat{NN}'_c$. Yield: 67%. Mp: 89−91 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.19 (s, 6 H, SO_2-Ar-$(CH_3)_2$), 2.44 (s, 6 H, SO_2-Ar-$(CH_3)_2$), 4.09 (d, J= 6.3 Hz, 2 H, H_f), 7.15 (s, 1 H, SO_2−Ar-H_p), 7.27 (d, J= 8.1 Hz, 1 H, H_d), 7.66 (t, J = 8.1 Hz, 1 H, H_b), 8.10 (t, 1 H, J = 6.3 Hz, H_c), 8.39 (d, 1 H, J = 4.8 Hz, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 17.6, 20.5, 47.2, 121.4, 122.2, 134.2, 134.9, 135.3, 136.4, 138.7, 148.5, 157.2. IR (cm^{-1}): 3091, 3007, 2973, 2943, 2853, 1597, 1572, 1479, 1458, 1442, 1386, 1376,

Table 1. Crystal Data and Structure Refinement Parameters for Complexes 9 and 10

param	9	10
CCDC deposition no.	785422	785421
color/shape	black/plate	black/prism
chem formula	$[RuCl(C_{19}H_{13}N_5)(C_{12}H_{10}N_2O_2S)]\cdot Cl$	$[RuCl(C_{11}H_9N_5)(C_{12}H_{10}N_2O_2S)]\cdot Cl\cdot H_2O$
formula wt	729.59	647.50
temp (K)	296	296
wavelength (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
cryst syst	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
unit cell params		
a, b, c (Å)	8.1576(5), 18.6367(9), 10.1442(7)	8.3674(2), 16.1181(3), 10.4014(3)
α, β, γ (deg)	90, 91.002(6), 90	90, 106.616(2), 90
V (Å^3)	1541.99(16)	1344.22(6)
Z	2	2
D_{calcd} (Mg/m^3)	1.571	1.600
μ (mm^{-1})	0.791	0.899
abs cor	integration (X-RED32)	integration (X-RED32)
T_{min}, T_{max}	0.7815, 0.9854	0.6149, 0.8677
F_{000}	736	652
cryst size (mm^3)	0.52 × 0.25 × 0.01	0.62 × 0.38 × 0.16
diffractometer/measurement method	STOE IPDS II/rotation (ω scan)	STOE IPDS II/rotation (ω scan)
index ranges	$-10 \le h \le 10, -23 \le k \le 23, -12 \le l \le 12$	$-10 \le h \le 10, -20 \le k \le 20, -13 \le l \le 13$
θ range for data collecn (deg)	$2.01 \le \theta \le 26.77$	$2.04 \le \theta \le 27.55$
no. of rflns collected	10616	22438
no. of indep /obsd rflns	6478/3411	6098/5518
R_{int}	0.1534	0.0456
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	6478/1/397	6098/4/340
goodness of fit on F^2	1.121	1.012
final R indices ($I > 2\sigma(I)$)	R1 = 0.0876, wR2 = 0.1568	R1 = 0.0291, wR2 = 0.0620
R indices (all data)	R1 = 0.1605, wR2 = 0.1783	R1 = 0.0339, wR2 = 0.0632
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.748, −0.783	0.725, −0.626

1320, 1255, 1205, 1142, 1093, 1069, 1008, 879, 849, 834, 810, 761, 724, 675.

General Procedure for the Synthesis of 6_{a-c}. An ethanolic solution (15 mL) of 1.10 mmol of $\widetilde{NN}'_{a-c}$ was mixed with $[RuCl_2(p\text{-cymene})]_2$ (0.306 g, 0.50 mmol). The reaction mixture was heated under reflux for 6 h. The volatiles were removed under reduced pressure, and then the residue was dissolved in DCM (15 mL) and precipitated by addition of diethyl ether (30 mL). The solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

Complex ***6a***. Yield: 64%. Mp: 140−142 °C dec. Anal. Calcd for $C_{16}H_{22}Cl_2N_2Ru$: C, 46.38; H, 5.35; N, 6.76. Found: C, 47.38; H, 5.86; N, 6.39. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.12 (d, 6H, J = 6.9 Hz, H_k), 1.97 (s, 3H, H_g), 2.69−2.78 (m, 1H, H_j), 4.11−4.21 (m, 2H, H_f), 4.31−4.39 (m, 2H, $-NH_2$), 5.78 (t, 2H, J_1 = 6.9 Hz, J_2 = 6.6 Hz, H_i), 5.99 (d, 1H, J = 6.0 Hz, H_h), 6.04 (d, 1H, J = 5.7 Hz, H_h), 7.50−7.58 (m, 2H, $H_d + H_b$), 7.97 (t, 1H, J = 7.8 Hz, H_c), 9.15 (d, 1 H, J = 5.4 Hz, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.17, 21.95, 22.90, 30.70, 52.52, 82.28, 82.87, 83.50, 85.25, 98.37, 103.45, 121.63, 125.28, 139.54, 155.05, 161.94. IR (cm^{-1}): 3375, 3209, 3061, 2965, 2926, 2873, 1608, 1471, 1441, 1386, 1321, 1282, 1252, 1199, 1155, 1105, 1091, 1057, 1033, 1015, 946, 880, 804, 768, 728, 672.

Complex ***6b***. Yield: 69%. Mp: 187−189 °C dec. Anal. Calcd for $C_{22}H_{26}Cl_2N_2O_2RuS$: C, 47.65; H, 4.73; N, 5.05; S, 5.78; found: C, 47.70; H, 4.86; N:5.85; S, 5.39. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.17 (d, 6 H, J = 6.6 Hz, H_k), 2.25 (s, 3 H, H_g), 2.78−2.87 (m, 1H, H_j), 4.23 (d, 2H, J = 6.0 Hz, H_f), 7.09 (d, 2H, J = 6.6 Hz, H_i), 7.54−7.66 (m, 6H, Ph-H + H_d), 7.79−7.85 (d, 2H, J = 6.6 Hz, H_h), 8.09 (t, J = 7.5 Hz, 1H, H_b), 8.47 (t, 1H, J = 6.0 Hz, H_c), 8.61 (d, 1H, J = 6.0 Hz, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.0, 24.5, 33.5, 45.8, 126.1, 126.6, 127.1, 129.3, 132.3, 133.3, 135.0, 140.3, 142.8, 145.8, 158.2. IR (cm^{-1}): 3077, 2968, 2938, 2924, 2874, 2845, 2830, 1626, 1611, 1583, 1569, 1543, 1473, 1448, 1365, 1345, 1287, 1234, 1165, 1053, 1033, 1002, 935, 884, 850, 756, 727, 686.

Complex ***6c***. Yield: 82%. Mp: 201−203 °C dec. Anal. Calcd for $C_{26}H_{34}Cl_2N_2O_2RuS$: C, 51.14; H, 5.61; N, 4.59; S, 5.25. Found: C, 50.23; H, 6.02; N, 4.82; S, 4.95. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.17 (d, 6 H, J = 7.2 Hz, H_k), 2.19 (s, 6H, SO_2-Ar-$(CH_3)_2$), 2.26 (s, 3 H, H_g), 2.43 (s, 6H, SO_2-Ar-$(CH_3)_2$), 2.79−2.88 (m, 1H, H_j), 4.17 (d, 2H, J= 6.3 Hz, H_f), 7.07−7.14 (m, 4H, H_i), 7.18 (s, 1H, SO_2-Ar-H_p), 7.39−7.47 (m, 1H, H_d), 7.99 (t, 1H, J = 7.2 Hz, H_b), 8.20 (t, 1H, J = 6.3 Hz, H_c), 8.52 (d, 1H, J = 4.5 Hz, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.1, 20.9, 22.0, 24.5, 33.5, 45.4, 124.4, 124.6, 126.6, 129.3, 134.8, 135.0, 135.6, 136.0, 138.6, 142.2, 145.1, 145.7, 155.4. IR (cm^{-1}): 3121, 3086, 2967, 2931, 2875, 1627, 1611, 1571, 1543, 1465, 1447, 1388, 1361, 1340, 1285, 1250, 1206, 1163, 1052, 1032, 934, 884, 848, 830, 751, 723, 674.

General Procedure for the Synthesis of 7−10. An ethanolic solution (15 mL) of 1.10 equiv of $'\widetilde{NNN}'$ was mixed with **6** (1 mmol).

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The reaction mixture was heated under reflux for 10 h. The volatiles were removed under reduced pressure, and then the residue was dissolved in DCM (15 mL) and precipitated by addition of diethyl ether (30 mL). The brown-black solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

Complex ***7***. Yield: 187 mg, 64%. Mp: >280 °C. Anal. Calcd for $C_{27}H_{27}Cl_2N_5Ru$: C, 54.64; H, 4.59; N, 11.80. Found: C, 53.88; H, 4.21; N, 12.26. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.71 (d, 6H, J = 4.2 Hz, *H*-6), 3.93 (t, 1H, J_1 = 6.0 Hz, J_2 = 5.7 Hz, H_f), 4.95 (t, 1H, J_1 = 6.3 Hz, J_2 = 6.0 Hz, H_f), 6.65 (d, 1H, J = 5.7 Hz, H_d), 7.02−7.61 (m, 13H, Ar-*H* + −N*H*$_2$), 7.91 (t, 1H, J_1 = 8.4 Hz, J_2 = 7.8 Hz, H_c), 8.01 (t, 1H, J_1 = 8.1 Hz, J_2 = 7.8 Hz, *H*-4), 8.33 (d, 1H, J = 7.8 Hz, *H*-3), 8.46 (d, 1H, J = 8.1 Hz, *H*-3), 8.91 (d, 1H, J = 7.5 Hz, H_a). ^{13}C NMR (75 MHz, DMSO-d_6): δ 17.84, 17.97, 49.79, 120.08, 120.98, 121.91, 123.17, 124.66, 125.08, 126.07, 126.33, 127.28, 128.63, 128.91, 129.17, 135.83, 136.69, 149.10, 149.43, 150.15, 151.54, 160.91, 161.63, 161.76, 164.04, 173.30, 173.87. IR (cm^{-1}): 3382, 3226, 3130, 3044, 2922, 1622, 1608, 1591, 1498, 1482, 1471, 1437, 1386, 1374, 1307, 1289, 1226, 1209, 1154, 1101, 1070, 1028, 1020, 865, 800, 782, 757, 736, 700, 671.

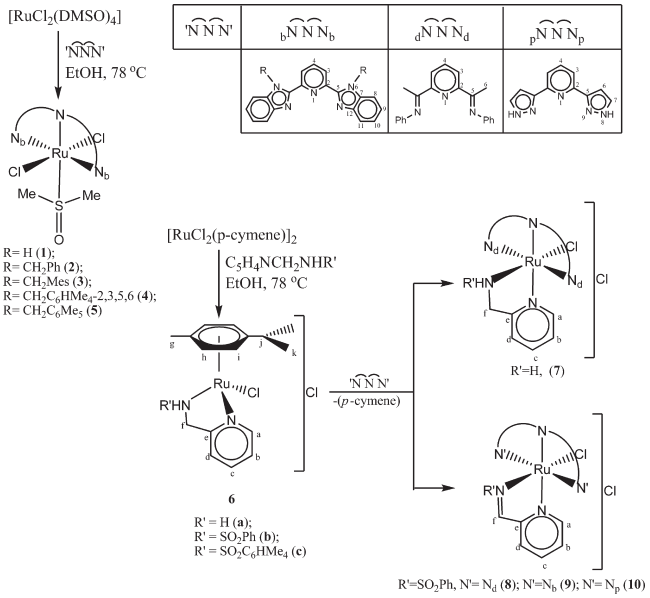
Complex ***8***. Yield: 65%. Mp: >280 °C. Anal. Calcd for $C_{33}H_{29}Cl_2N_5O_2RuS$: C, 54.17; H, 4.00; N, 9.57; S, 4.38. Found: C, 52.83; H, 4.25; N, 8.24; S, 3.96. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.44 (s, 6H, *H*-6), 6.96−7.09 (m, 10H, Ph-*H*), 7.49 (d, 2H, J = 7.2 Hz, SO_2-Ar-*H*), 7.60 (t, 1H, J_1 = 7.5 Hz, J_2 = 7.2 Hz, *H*-4), 7.66 (t, J = 8.1 Hz, 2 H, SO_2-Ar-*H*), 7.84−7.92 (m, 2H, $\widehat{NN}'$-*H* + SO_2-Ar-*H*), 8.26−8.32 (m, 2H, $\widehat{NN}'$-*H*), 8.51 (d, 2H, J = 8.4 Hz, *H*-3), 9.28 (d, J = 5.1 Hz, 1 H, H_a), 9.74 (s, 1H, H_f). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.0, 126.9, 127.2, 128.7, 129.0, 129.3, 131.0, 133.6, 134.7, 134.8, 135.6, 136.5, 146.4, 152.1, 152.7, 159.5, 174.7, 175.8. IR (cm^{-1}): 3074, 2960, 2874, 1695, 1630, 1601, 1484, 1463, 1448, 1425, 1407, 1377, 1359, 1271, 1235, 1169, 1136, 1052, 1034, 927, 903, 866, 844, 807, 753, 721, 689.

Complex ***9***. Yield: 0.46 g; 63%. Mp: >280 °C. Anal. Calcd for $C_{31}H_{23}Cl_2N_7O_2RuS$: C, 51.03; H, 3.18; N, 13.44; S, 4.40. Found: C, 49.34; H, 3.89; N, 12.94; S, 3.89. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.85−6.95 (m, 5 H, SO_2-Ar-*H*), 7.06 (t, 2 H, J_1 = 8.1 Hz, J_2 = 7.2 Hz, *H*-10), 7.35 (t, 2 H, J = 8.1 Hz, *H*-9), 7.46 (t, 1 H, J_1 = 6.9 Hz, J_2 = 7.2 Hz, H_b), 7.63 (d, 2 H, J = 8.4 Hz, *H*-11), 8.28 (t, 1 H, J_1 = 6.9 Hz, J_2 = 6.3 Hz, H_c), 8.36 (t, 1 H, J_1 = 7.5 Hz, J_2 = 7.8 Hz, *H*-4), 8.56 (d, 2 H, J = 7.8 Hz, *H*-8), 8.74 (d, 1 H, J = 7.8 Hz, H_d), 9.05 (d, 1 H, J = 7.8 Hz, *H*-3), 9.12 (d, 1 H, J = 7.8 Hz, *H*-3), 10.14 (s, 1 H, H_f), 10.49 (d, 1 H, J = 5.1 Hz, H_a), 15.06 (br, 2H, N-*H*). ^{13}C NMR (75 MHz, DMSO-d_6): δ 101.8, 114.2, 115.5, 121.9, 124.7, 125.7, 126.6, 128.8, 129.4, 133.6, 134.5, 135.2, 136.4, 136.8, 141.1, 150.9, 152.2, 157.1, 175.0. IR (cm^{-1}): 3038, 3013, 2943, 1608, 1592, 1547, 1526, 1480, 1455, 1413, 1351, 1320, 1290, 1249, 1234, 1184, 1172, 1148, 1086, 1056, 1033, 1014, 980, 906, 894, 845, 811, 804, 779, 763, 735, 722, 680.

Complex ***10***. Yield: 84%. Mp: >250 °C. Anal. Calcd for $C_{23}H_{19}Cl_2N_7O_2RuS$: C, 43.88; H, 3.04; N, 15.58; S, 5.09. Found: C, 45.07; H, 3.76; N, 14.47; S, 4.65. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.93−6.96 (m, 4H, *H*-6 + *H*-7), 7.25 (t, 1H, J_1 = 7.8 Hz, J_2 = 8.1 Hz, H_c), 7.58 (t, 1 H, J_1 = 7.2 Hz, J_2 = 7.5 Hz, *H*-4), 7.69 (d, 2 H, J = 2.4 Hz, *H*-3), 7.97−8.08 (m, 5H, SO_2-Ph-*H*), 8.30 (t, 1 H, J_1 = 7.8 Hz, J_2 = 7.5 Hz, H_b), 8.87 (d, 1 H, J = 8.1 Hz, H_d), 10.05 (d, J = 5.4 Hz, 1 H, H_a), 10.11 (s, 1H, H_f), 13.48 (s, 2H, $_p\widehat{NNN}_p$(N-*H*)). ^{13}C NMR (75 MHz, DMSO-d_6): δ 105.5, 118.6, 126.8, 128.6, 130.0, 132.6, 134.0, 134.9, 135.4, 136.4, 153.2, 154.2, 154.9, 157.1, 175.9. IR (cm^{-1}): 3062, 3032, 2973, 2943, 2924, 2830, 1699, 1638, 1591, 1483, 1462, 1449, 1427, 1395, 1374, 1354, 1314, 1298, 1253, 1233, 1184, 1169, 1139, 1082, 1053, 1033, 1019, 930, 901, 787, 760, 751, 736, 724, 690.

X-ray Crystallography. The single-crystal X-ray data of **9** and **10** were collected on a STOE diffractometer with an IPDS(II) image plate detector. All diffraction measurements were performed at room temperature (296 K) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in ω-scanning mode. The structures were solved by direct methods using SHELXS-97[78] and refined through full-matrix least-squares methods using SHELXL-97[79] implemented in the WinGX[80] program suite. All NH and CH hydrogen atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.86 and 0.93 Å, respectively. For complex **10**, the coordinates of the water H atoms were determined from a difference map and were refined isotropically subject to a DFIX restraint of O−H = 0.82 Å. The displacement parameters of the NH and CH hydrogen atoms were constrained to U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for water) of their parent atoms. Data collection: X-AREA.[81] Cell refinement: X-AREA. Data reduction: X-RED32.[81] A summary of the crystal data, experimental details, and refinement results are given in Table 1. The general purpose crystallographic tool PLATON[82] was used for the structure analysis and presentation of the results.

Scheme 1. Synthesis of Ru(II) Complexes 1−10 and Numbering Scheme for the Ligands $'\widehat{NNN}'$ and $\widehat{NN}'$



RESULT AND DISCUSSION

Synthesis of Compounds. The ligands used and the synthesis and reaction routes of the novel Ru(II) complexes are presented in Scheme 1. Synthesized compounds were characterized by elemental analysis and NMR and IR spectra. The structures of **9** and **10** were confirmed by X-ray crystallography.

$\widehat{NN}'_{b,c}$, $_d\widehat{NNN}_d$, $_b\widehat{NNN}_b$ (R = H), and $_p\widehat{NNN}_p$ were synthesized according to a modified literature procedure in good yield.[66,74−77] $_b\widehat{NNN}_b$ derivatives were obtained via alkylation of the $_b\widehat{NNN}_b$ (R = H) with benzyl chloride, 2,4,6-trimethylbenzyl chloride, 2,3,5,6-tetramethylbenzyl bromide, and 2,3,4,5,6-pentamethylbenzyl bromide in the presence of KOH in acetone at reflux. The mononuclear six-coordinate Ru(II) complexes **1**−**5** were synthesized by reaction of $RuCl_2(DMSO)_4$ with $_b\widehat{NNN}_b$ derivatives in ethanol. On the other hand, $\widehat{NN}'_{a,b}$ ligands were obtained by the reaction of arylsulfonyl chloride with (2-aminomethyl)pyridine in the presence of triethylamine in THF at reflux. The monocationic chloro complexes $\mathbf{6}_{a-c}$ are accessible in good yield by treatment of the $[RuCl_2(p\text{-cymene})]_2$ with $\widehat{NN}'_{a-c}$ at 78 °C in ethanol solution. The reaction of $\mathbf{6}_a$ with

$_{d}\widehat{NNN}_{d}$ in boiling ethanol gives complex **7**. On the other hand, the replacement reaction of $\mathbf{6_b}$ with $_{d}\widehat{NNN}_{d}$, $_{b}\widehat{NNN}_{b}$, and $_{p}\widehat{NNN}_{p}$ in ethanol at 78 °C unexpectedly resulted in the cationic six-coordinate Ru(II) imine complexes **8**−**10**. As a matter of fact, a number of ruthenium complexes with multidentate ligands are known to give oxidative dehydrogenated ligands which remain coordinated to the metal center.[83] Furthermore, the oxidation of amine complexes to imine complexes by molecular oxygen is base-catalyzed and is strongly dependent on the ancillary ligands coordinated to Ru(II).[84] However, to our knowledge, there has been no report on the metal-prompted oxidation of *N*-(2-methylpyridyl)arenesulfonylamide.

All complexes are air- and moisture-stable both in the solid state and in solution. **1**−**5** and $\mathbf{6_{a-c}}$ are soluble in chlorinated solvents, DMSO, DMF, and MeOH, while **7**−**10** are soluble in DMSO, DMF, and MeOH.

In ^{1}H NMR spectra for the $_{b}\widehat{NNN}_{b}$ derivatives, the H-3 and H-4 protons were observed as doublets and triplets in a 2:1 ratio at around δ 8.11−8.56 ppm. The protons of the phenyl rings of each ligand appear as eight-proton multiplets around δ 6.6−7.8 ppm. Upon coordination of Ru(II) (**1**−**5**), the ^{1}H NMR spectra of complexes showed some differences from their respective ligands ($_{b}\widehat{NNN}_{b}$), especially the pyridine backbone. H-3 and H-4 protons for complexes **1**−**5** were observed as doublets and triplets in a 2:1 ratio with a general shift toward lower fields as compared to their respective ligands. Moreover, ^{13}C NMR signals shifted to higher fields. **1**−**5** gave ^{1}H and ^{13}C NMR spectra corresponding to the proposed formulation. With reference to previous X-ray diffraction and DFT studies on other related $[RuCl_2(\widehat{NNN}')(DMSO)]$ systems,[85] we tentatively assigned an S-bonded trans structure to **1**−**5**.

Similarly, from the ^{1}H NMR spectra, the effect of coordination of the Ru(II) to the $\widehat{NN}'$ ligand through the sulfonamide nitrogen and pyridyl nitrogen for $\mathbf{6_{b,c}}$ could clearly be seen. The H_f protons of $\widehat{NN}'_{b,c}$ appear as a doublet at δ 4.03 and 4.09 ppm, respectively. Upon coordination to Ru(II) ($\mathbf{6_{b,c}}$), the signals of H_f moved further downfield and appeared as a doublet at δ 4.23 and 4.17 ppm, respectively. Also, the protons of the pyridine ring of $\mathbf{6_{b,c}}$, especially H_a, are shifted downfield compared to those of free ligands ($\widehat{NN}'_{b,c}$). Similarly, aromatic protons of the *p*-cymene group (H_h and H_i) on $\mathbf{6_{b,c}}$ are shifted downfield in comparison to the $[RuCl_2(p\text{-cymene})]_2$ dimer. Moreover, in the ^{13}C NMR spectra, the sulfonamide ligands ($\widehat{NN}'_{b,c}$) exhibited a singlet at δ 48.4 and 47.2 ppm, which can be assigned to the methylene carbons ($\widehat{NN}'_{b,c}$ (Py-CH_2-NH)). Upon coordination to Ru(II) ($\mathbf{6_{b,c}}$), those peaks moved further upfield and appeared at δ 45.8 and 45.4 ppm, respectively.

The main points of interest in the NMR spectra of **8**−**10** are the loss of the peaks assignable to methylene protons (H_f) on the sulfonamide group and the appearance of a new singlet around δ 9.74−10.15 ppm. This suggested that the sulfonamide was converted to a sulfonimine group ($\widehat{NN}'_{b}$ (Py-*CH*=N−). The H-3 and H-4 protons arising from $_{d}\widehat{NNN}_{d}$, $_{b}\widehat{NNN}_{b}$, and $_{p}\widehat{NNN}_{p}$ were observed as doublets and a triplet in a 2:1 ratio at around δ 7.58−9.12 ppm. From ^{13}C NMR spectra of **8**−**10**, −*C*H=N− peaks appeared at 175.0−175.9 ppm.

In the IR spectra, NH stretching frequencies shift from 3060 and 3091 cm^{-1} in $\widehat{NN}'_{a,b}$ to 3077 and 3121 cm^{-1} in $\mathbf{6_{b,c}}$, respectively. Also, the SO_2 stretches shift from 1157 and 1328 cm^{-1} in $\widehat{NN}'_{a}$ and 1142 and 1320 cm^{-1} in $\widehat{NN}'_{b}$ (for the asymmetric and symmetric stretches, respectively) to 1165 and 1345 cm^{-1} in $\mathbf{6_b}$, 1163 and 1340 cm^{-1} in $\mathbf{6_c}$, 1169 and 1359 cm^{-1} in **8**, 1172 and 1351 cm^{-1} in **9**, and 1169 and 1354 cm^{-1} in **10**.

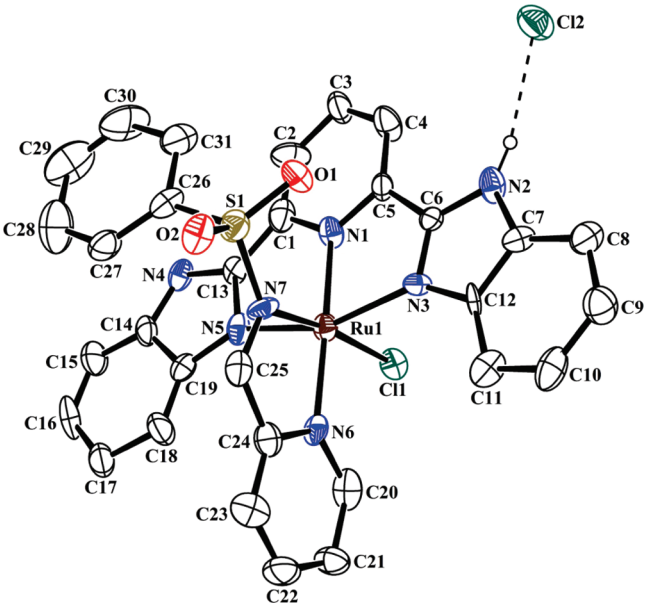


Figure 1. View of complex **9** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only the H atom involved in hydrogen bonding has been included.

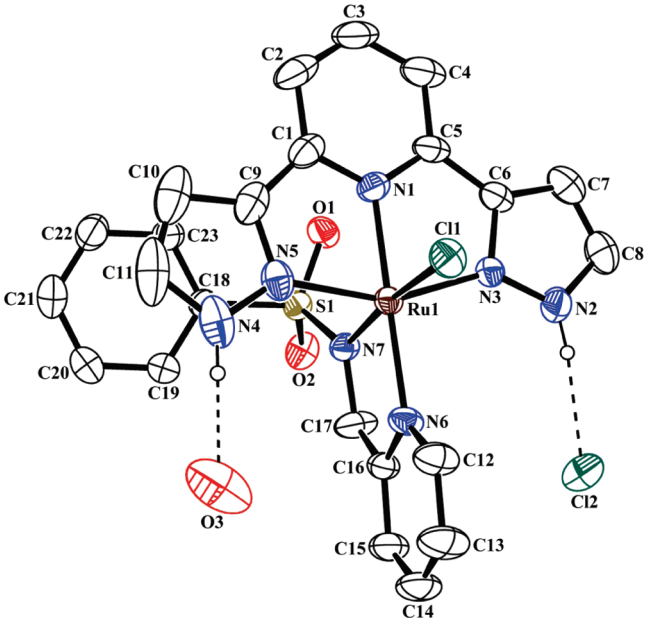


Figure 2. View of the complex **10** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only H atoms involved in hydrogen bonding have been included.

In the ^{1}H NMR spectra of $\mathbf{6_a}$, H_f protons belonging to (2-aminomethyl)pyridine were observed as multiplets around 4.11−4.39 ppm. Upon coordination to Ru(II) (**7**), those peaks were observed as two triplets at 3.93 and 4.95 ppm and H-6 protons were observed as doublets at 2.71 ppm. In the ^{13}C NMR spectra of **7**, −N=C(CH_3) peaks were observed at 17.84 and

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Table 2. Selected Geometric Parameters for Complexes 9 and 10

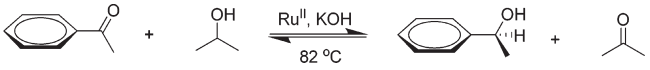
param	9	10	param	9	10
		Bond Lengths (Å)			
Ru1−Cl1	2.387(4)	2.3741(8)	N3−C6	1.286(17)	1.355(4)
Ru1−N1	1.971(11)	2.002(3)	N3−C12	1.435(16)	
Ru1−N3	2.062(11)	2.051(2)	N4−C11		1.341(7)
Ru1−N5	2.093(11)	2.042(3)	N4−C13	1.383(17)	
Ru1−N6	2.053(13)	2.078(2)	N4−C14	1.31(2)	
Ru1−N7	2.022(12)	2.014(2)	N5−C9		1.363(5)
S1−O1	1.427(10)	1.420(2)	N5−C13	1.331(17)	
S1−O2	1.420(11)	1.437(3)	N5−C19	1.349(17)	
S1−N7	1.676(11)	1.653(2)	N7−C17		1.406(4)
S1−C18		1.769(3)	N7−C25	1.325(18)	
S1−C26	1.754(14)		C6−C7		1.386(5)
N2−N3		1.342(4)	C7−C8		1.351(6)
N4−N5		1.331(4)	C9−C10		1.382(6)
N2−C6	1.391(18)		C10−C11		1.365(8)
N2−C7	1.395(18)		C16−C17		1.447(5)
N2−C8		1.354(5)	C24−C25	1.47(2)	
		Bond Angles (deg)			
Cl1−Ru1−N1	86.2(4)	86.06(8)	N1−Ru1−N7	101.8(4)	101.17(10)
Cl1−Ru1−N3	89.8(3)	88.72(8)	N3−Ru1−N5	156.6(4)	155.88(11)
Cl1−Ru1−N5	88.4(3)	88.82(8)	N3−Ru1−N6	104.2(4)	101.38(10)
Cl1−Ru1−N6	94.8(3)	94.08(8)	N3−Ru1−N7	91.9(4)	93.36(10)
Cl1−Ru1−N7	172.0(3)	172.74(7)	N5−Ru1−N6	99.2(4)	102.73(12)
N1−Ru1−N3	77.1(4)	77.96(10)	N5−Ru1−N7	93.1(4)	92.09(10)
N1−Ru1−N5	79.5(5)	77.93(12)	N6−Ru1−N7	77.2(4)	78.70(10)
N1−Ru1−N6	178.4(5)	179.33(12)			

17.97 ppm and −N=C(CH$_3$) peaks were observed at 173.30 and 173.87 ppm.

Crystal Structures of 9 and 10. The solid-state structures of compounds **9** and **10** were verified by single-crystal X-ray analysis. The perspective ORTEP-3[86] views of **9** and **10** with the adopted atomic numbering scheme are depicted in Figures 1 and 2. Selected bond lengths and angles are given in Table 2. Complexes **9** and **10** contain a bidentate $\widehat{NN}'_a$ ligand with a Ru(II) metal center and one Cl ligand. The two complexes differ from each other in the symmetrical $\widehat{NNN}$-tridentate triamine ligand: 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine ($_b\widehat{NNN}_b$) in complex **9** and 2,6-bis(1*H*-pyrazol-3-yl)pyridine ($_p\widehat{NNN}_p$) in complex **10**. However, the crystallization characteristics of the two cations are the same, with both crystallizing in the monoclinic space group $P2_1$. In the complexes, the charge is neutralized by a Cl anion, and complex **10** also includes a water molecule in the asymmetric unit.

The local structure around the Ru(II) ions is that of an octahedron, the equatorial plane of which (N1/N3/N5/N6) is formed by three nitrogen atoms from the tridentate ligand (N1, N3, and N5) and one nitrogen atom of the bidentate ligand (N6). The axial positions in the octahedron are occupied by one chlorine ligand (Cl1) and one nitrogen atom of the bidentate ligand (N7). As can be seen from the trans angles, which vary from 156.6(4) to 178.4(5)° for **9** and from 155.88(11) to 179.33(12)° for **10**, and the cis angles, which vary from 77.1(4) to 104.2(4)° for **9** and from 77.93(12) to 102.73(12)° for **10**, the coordination octahedron around the Ru(II) ions is rather deformed, the major distortion arising via the N3−Ru1−N5 angle. This angle is considerably smaller than the ideal angle of 180°. In each complex, the Ru−N$_{pyridine}$ bond length of the tridentate ligand is shorter than those of the other Ru−N bonds. This is probably due to the geometric requirements of the $\widehat{NNN}$-tridentate ligand and the fact that the pyridine N atom donor occupies the central position of the tridentate ligand. Thus, the Ru−N$_{pyridine}$ bond becomes shorter than other Ru−N bonds because of the restraints of the two chelating arms on either side of the coordinating atom. In contrast to that formed by the tridentate triamine ligands, the five-membered chelate rings formed by the bidentate ligand deviate from planarity. This nonplanar chelate ring has a twist conformation in complex **9**, with Ru1 and N6 displaced by 0.048(4) and −0.067(6) Å above and below the N7−C25−C24 plane, while it has an envelope conformation in complex **10**, with N7 atom displaced from the Ru1−N6−C16−C17 mean plane by 0.065(2) Å (puckering parameters: Q = 0.104(2) Å and φ = 136.02(14)°).[87]

Table 3. Catalytic Activity for Transfer Hydrogenation of Acetophenone Catalyzed by Ru(II) Complexes [a]



entry	cat.	conversn (%)	time (min)
1	**1**	74	10
2	**2**	13	
3	**3**	22	
4	**4**	33	
5	**5**	47	
6	**1**	91	30
7	**2**	58	
8	**3**	72	
9	**4**	80	
10	**5**	86	
11	**1**	94	60
12	**2**	89	
13	**3**	92	
14	**4**	94	
15	**5**	97	

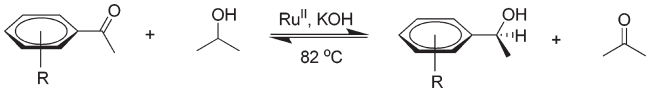
[a] Reactions were carried out at 82 °C using 10 mmol acetophenone with 0.1 mol % Ru(II) in 20 mL of 2-propanol for 1 h.

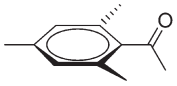
The bond lengths and bond angles of the phenyl and pyridine rings are similar to those found in related pyridylarenesulfonamide ligands.[88−92] The fact that the imine N7=C25 bond distance in **9** is significantly shorter than the corresponding bond in **10** can be considered as possible evidence of the conjugation of the imine N7=C17 bond with the sulfonyl S=O bonds in **10**. The dihedral angle between the two coordinated pyridine rings is 86.42(5)° in **9** and 88.53(4)° in **10**, indicating a nearly perpendicular orientation. In both complexes, the benzene ring of the sulfonamide ligand is almost parallel to the five-membered ring of the tridentate ligand. This disposition allows an intramolecular $\pi-\pi$ stacking interaction with an interplanar spacing of 3.640(4) Å for **9** and 3.625(4) Å for **10** between the ring centroids.

The two complexes show some similarities in hydrogen-bonding interactions. In the molecular structure of the complexes, there is one intramolecular hydrogen-bonding interaction of the type C−H···Cl, forming the five-membered ring $S(5)$.[93] The crystal structures are stabilized by N−H···Cl, O−H···Cl, N−H···O, C−H···Cl, and C−H···O intermolecular interactions (see the Supporting Information for details).

Catalytic Studies. TH has been studied extensively in the past decade, and catalysts that combine known metal complexes with

Table 4. Catalytic Activity for Transfer Hydrogenation of Ketones Catalyzed by Ru(II) Complexes[a]



Entry	Substrate	Catalyst	Conversion (%)
1		$\mathbf{6_a}$	3[d]
2		$\mathbf{6_b}$	73
3		$\mathbf{6_c}$	44
4		**7**	100 (100)[d] (84)[e]
5		**8**	94
6		**9**	97 (85)[b] (12)[c]
7		**10**	72
8		$\mathbf{6_b}$	77
9		$\mathbf{6_c}$	51
10		**7**	78[d]
11		**8**	99 (89)[b]
12		**9**	99 (95)[b]
13		**10**	81
14		$\mathbf{6_b}$	69
15		$\mathbf{6_c}$	46
16		**7**	73[d]
17		**8**	94
18		**9**	99 (90)[b]
19		**10**	70
20		$\mathbf{6_b}$	77
21		$\mathbf{6_c}$	48
22		**7**	76[d]
23		**8**	97
24		**9**	99 (91)[b]
25		**10**	73
26		$\mathbf{6_b}$	61
27		$\mathbf{6_c}$	34
28		**7**	82[d]
29		**8**	82
30		**9**	84
31		**10**	49
32		$\mathbf{6_b}$	24
33		$\mathbf{6_c}$	8
34		**7**	54 (11[d])
35		**8**	38
36		**9**	43
37		**10**	33

[a] Reactions were carried out at 82 °C using 1 mmol of substrate with 0.01 mmol of Ru(II) in 5 mL of 2-propanol for 1 h. [b] Carried out at 82 °C using 1 mmol of substrate with 0.01 mmol of Ru(II) in 5 mL of 2-propanol for 30 min. [c] Carried out at 25 °C using 1 mmol of substrate with 0.01 mmol of Ru(II) in 5 mL of 2-propanol for 1 h. [d] Carried out at 82 °C using 1 mmol of substrate with 0.01 mmol of Ru(II) in 5 mL of 2-propanol for 15 min. [e] Carried out at 82 °C using 10 mmol of substrate with 0.01 mmol of Ru(II) in 5 mL of 2-propanol for 1 h.

new ligands are reported continuously. In this work, we described the synthesis of a series of novel Ru(II) complexes (**1**−**10**) employed as catalysts for the TH of ketones.

Catalytic studies with complexes of type **1**−**5** were performed for the transfer hydrogenation of acetophenone in the presence of KOH by 2-propanol. Reactions were performed under identical conditions to allow comparison of results. In a typical experiment, **1** (0.01 mmol) and acetophenone (10 mmol) was dissolved in 2-propanol (19 mL). This mixture was stirred at 82 °C for 10 min. After the mixture was cooled to room temperature, 1 mL of 0.1 M KOH (0.1 mmol) solution in 2-propanol was then introduced and the mixture was stirred at 82 °C. Reactions were monitored by GC. The results are summarized in Table 3.

Similarly, the TH of ketones with 2-propanol catalyzed by the cationic Ru(II) complexes **6**−**10** were carried out under identical conditions to allow comparison of results (Table 4). Preliminary studies were performed using $\mathbf{6_b}$ as catalyst and acetophenone as a model substrate. In a typical experiment, $\mathbf{6_b}$ (0.01 mmol) and acetophenone (1 mmol) were dissolved in 2-propanol (4 mL). This mixture was stirred at 82 °C for 10 min. After the mixture was cooled to room temperature, the base (0.1 mmol) was added and the mixture was stirred at 82 °C. Reactions were monitored by GC. Very rapid conversions were achieved at 82 °C. When the temperature was decreased, the catalytic conversion became noticeably slower.

On the basis of these results, the neutral Ru(II) complexes **1**−**5** are more active catalysts than the cationic complexes **6**−**10**. For the neutral complexes **1**−**5**, time dependence is also noticeable. For example, for the 10 and 30 min periods **1** is the best. In other words, complexes with N-alkyl substitution show lower activities than the complexes with N−H. However, for a 60 min period the catalytic activity increases in the order **2** < **3** < **4**, **1** < **5**.

For cationic half-sandwich Ru(II) arene complexes, interestingly, the sulfonamide-containing complexes $\mathbf{6_{b,c}}$ are more active catalysts than the (2-aminomethyl)pyridine-containing complex $\mathbf{6_a}$. On the other hand, $\mathbf{6_b}$ is a more active catalyst than $\mathbf{6_c}$ for all ketones. These results might be related to the steric hindrance of the sulfonamide ligands. Complexes **8**−**10** are generally more active than $\mathbf{6_b}$. However, unexpectedly, $\mathbf{6_b}$ is more active than **10** except for 4′-Cl-acetophenone and 4′-F-acetophenone. The catalytic activities of complexes containing NNN ligands increase in the following order for all ketones: **10** < **8** < **9**. Complex **7** is a more efficient catalyst than the other cationic Ru(II)-NNN complexes (**8**−**10**). Ru(II) complexes are generally more efficient catalysts for electron-withdrawing substituents such as F, Cl, and Br on the para position of the aryl ring of the ketone. When an electron-donating group is introduced in the aryl ring of the ketone, the catalytic activity decreases.

CONCLUSIONS

In this work, we reported the preparation and characterization of a series of neutral and cationic Ru(II) complexes bearing tridentate and bidentate ligands and their catalytic activities for the hydrogen transfer reaction of acetophenone derivatives with the use of 2-propanol in the presence of KOH. When cationic Ru(II) arene complexes containing sulfonamide ligands ($\mathbf{6_{b,c}}$) were treated with NNN ligands, unexpectedly, a facile oxidative dehydrogenation of sulfonamides (C_5H_4N-CH_2-NH-SO_2-Ph) took place under base-free and mild conditions (0.2 atm of O_2 at 78 °C) and in each case (**8**−**10**) the oxidized ligand remained coordinated in the metal center. To our knowledge, this is the first report of amine oxidation from the coordinated sulfonamide ligands to the corresponding sulfonimine ligands on an Ru(II) metal center. Catalytic experiments showed that the neutral Ru(II) complexes **1**−**5** are more active catalysts than the cationic complexes **6**−**10**. On the other hand, cationic Ru(II) complexes **7**−**10**, containing NNN ligands, are more active than the cationic half-sandwich Ru(II) complexes $\mathbf{6_{a-c}}$, bearing a *p*-cymene group. **7** is a more active complex than the other cationic Ru(II) complexes (**6**, **8**−**10**) for all ketones. The efficiency of the catalyst seems to

depend not only on the ligands of the complex but also on the substituent on the aromatic ketones. Electron-withdrawing groups introduced into the para position of the acetophenone increased the yield, whereas electron-donating groups at the para position of the acetophenone decreased the yield. Moreover, when 2′,4′,6′-trimethylacetophenone was used as a substrate, a constant decrease in the catalytic yield was observed, which was probably due to steric effects.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 785421 and 785422 also contain the supplementary crystallographic data (excluding structure factors) for the structures reported in this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223-336033).

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■ REFERENCES

(1) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745–1776and references therein.
(2) Guangyong, X.; Tingcheng, L.; Aiqing, Z. *Inorg. Chem. Commun.* **2010**, *10*, 1199–1202.
(3) Brown, C. C.; Stephan, D. W. *Dalton Trans.* **2010**, *31*, 7211–7213.
(4) Dayan, O.; Doğan, F.; Kaya, I.; Çetinkaya, B. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2010**, *5*, 337–344.
(5) Lang, J. R. V.; Denner, C. E.; Alt, H. G. *J. Mol. Catal. A* **2010**, *322*, 45–49.
(6) Guo, L.; Gao, H.; Zhang, L.; Zhu, F.; Wu, Q. *Organometallics* **2010**, *9*, 2118–2125.
(7) Russell, S. K.; Darmon, J. M.; Lobkovsky, E. *Inorg. Chem.* **2010**, *6*, 2782–2792.
(8) Liu, P.; Yan, M.; He, R. *Appl. Organomet. Chem.* **2010**, *2*, 131–134.
(9) Long, Z.; Wu, B.; Yang, P.; Li, G.; Liu, Y.; Yang, X. J. *J. Organomet. Chem.* **2009**, *23*, 3793–3799.
(10) Semikolenova, N. V.; Zakharov, V. A.; Echevskaja, L. G.; Matsko, M. A.; Bryliakov, K. P.; Talsi, E. P. *Catal. Today* **2009**, *144*, 334–340.
(11) Hanton, M. J.; Tenza, K. *Organometallics* **2008**, *21*, 5712–5716.
(12) Tondreau, A. M.; Lobkovsky, E.; Chirik, P. J. *Org. Lett.* **2008**, *13*, 2789–2792.
(13) Özdemir, N.; Dinçer, M.; Dayan, O.; Çetinkaya, B. *Acta Crystallogr., Sect. C* **2008**, *64*, m224–m227.
(14) Goerl, C.; Alt, H. G. *J. Organomet. Chem.* **2007**, *21*, 4580–4592.
(15) Trivedi, M.; Pandey, D. S.; Xu, Q. *Inorg. Chim. Acta* **2007**, *7*, 2492–2498.
(16) Ceniceros-Gomeza, A. E.; Barba-Behrensa, N.; Quiroz-Castro, M. E.; Bernes, S.; Noth, H.; Castillo-Blum, S. E. *Polyhedron* **2000**, *15*, 1821–1827.
(17) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.* **2002**, *658*, 62–70.
(18) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *29*, 10166–10167.
(19) Appukuttan, V.; Zhang, L.; Ha, J. Y.; Chandran, D.; Bahuleyan, B. K.; Ha, C.-S.; Kim, I. *J. Mol. Catal. A* **2010**, *325*, 84–90.
(20) Dey, S.; Sarkar, S.; Paul, H.; Zangrando, E.; Chattopadhyay, P. *Polyhedron* **2010**, *6*, 1583–1587.
(21) Singh, A.; Chetia, B.; Mobin, S. M.; Das, G.; Iyer, P. K.; Mondal, B. *Polyhedron* **2008**, *8*, 1983–1988.
(22) Cho, H. Y.; Tarte, N. H.; Cui, L.; Hong, D. S.; Woo, S. I.; Gong, Y.-D. *Macromol. Chem. Phys.* **2006**, *21*, 1965–1971.
(23) Zhang, W.; Sun, W.-H.; Zhang, S.; Hou, J.; Wedeking, K.; Schultz, S.; Froehlich, R.; Song, H. *Organometallics* **2006**, *8*, 1961–1969.
(24) Lytwak, L. A.; Stanley, J. M.; Mejia, M. L.; Holliday, B. J. *Dalton Trans.* **2010**, *33*, 7692–7699.
(25) Zhao, B.; Shu, H.-M.; Hu, H.-M.; Qin, T.; Chen, X.-L. *J. Coord. Chem.* **2009**, *6*, 1025–1034.
(26) Coronado, E.; Dias, J. C.; Gimenez-Lopez, M. C.; Gimenez-Saiz, C.; Gomez-Garcia, C. J. *J. Mol. Struct.* **2008**, *890*, 215–220.
(27) Zabel, D.; Schubert, A.; Wolmershaeuser, G.; Jones, R. L., Jr.; Thiel, W. R. *Eur. J. Inorg. Chem.* **2008**, *23*, 3648–3654.
(28) Halcrow, M. A. *Coord. Chem. Rev.* **2005**, *24*, 2880–2908and references therein.
(29) Lu, X.-Y.; Xu, H.-J.; Chen, X.-T. *Inorg. Chem. Commun.* **2009**, *9*, 887–889.
(30) Doğan, F.; Dayan, O.; Yürekli, M.; Çetinkaya, B. *J. Therm. Anal. Calorim.* **2008**, *3*, 943–949.
(31) Öter, O.; Ertekin, K.; Dayan, O.; Çetinkaya, B. *J. Fluoresc.* **2008**, *2*, 269–276.
(32) Dayan, O.; Çetinkaya, B. *J. Mol. Catal. A* **2007**, *271*, 134–141.
(33) Özdemir, N.; Dinçer, M.; Dayan, O.; Çetinkaya, B. *Acta Crystallogr., Sect. C* **2007**, *63*, m407–m409.
(34) Özdemir, N.; Dinçer, M.; Dayan, O.; Çetinkaya, B. *Acta Crystallogr., Sect. C* **2007**, *63*, m264–m266.
(35) Yoo, H.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2006**, *18*, 6038–6039.
(36) Jiang, Y.-F.; Xi, C.-J.; Liu, Y.-Z.; Niclos-Gutierrez, J.; Choquesillo-Lazarte, D. *Eur. J. Inorg. Chem.* **2005**, *8*, 1585–1588.
(37) Britovsek, G. J. P.; England, J.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2005**, *5*, 945–955.
(38) Seçkin, T.; Köytepe, S.; Çetinkaya, E. *J. Polym. Res.* **2004**, *2*, 119–125.
(39) Shiotsuki, M.; Suzuki, T.; Iida, K.; Ura, Y.; Wada, K.; Kondo, T.; Mitsudo, T. *Organometallics* **2003**, *6*, 1332–1339.
(40) Dias, E. L.; Brookhart, M.; White, P. S. *Organometallics* **2000**, *24*, 4995–5004.
(41) Bianchini, C.; Lee, H. M. *Organometallics* **2000**, *10*, 1833–1840.
(42) Çetinkaya, B.; Çetinkaya, E.; Brookhart, M.; White, P. S. *J. Mol. Catal. A* **1999**, *2*, 101–112.
(43) Bhaumik, C.; Das, S.; Saha, D.; Dutta, S.; Baitalik, S. *Inorg. Chem.* **2010**, *11*, 5049–5062.
(44) Concepcion, J. J.; Jurss, J. W.; Hoertz, P. G.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2009**, *50*, 9473–9476.
(45) Singh, A.; Pramanik, A.; Das, G.; Mondal, B. *Organometallics* **2008**, *24*, 6403–6404.
(46) Singh, A.; Chetia, B.; Mobin, S. M.; Das, G.; Iyer, P. K.; Mondal, B. *Polyhedron* **2008**, *8*, 1983–1988.
(47) Vaidyanathan, V. G.; Nair, B. U. *Dalton Trans.* **2005**, *17*, 2842–2848.
(48) Zadykowicz, J.; Potvin, P. G. *Inorg. Chem.* **1999**, *10*, 2434–2441.

(49) Ye, W; Zhao, M.; Du, W.; Jiang, Q.; Wu, K.; Wu, P.; Yu, Z. *Chem. Eur. J.* **2011**, 4737–4741.
(50) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30* (2), 97–102.
(51) Yamada, I.; Noyori, R. *Org. Lett.* **2000**, *22*, 3425–3427.
(52) Seidel, S. W.; Deming, T. J. *Macromolecules* **2003**, *4*, 969–972.
(53) Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M. *J. Am. Chem. Soc.* **2005**, *20*, 7318–7319.
(54) Canivet, J.; Labat, G.; Stoeckli-Evans, H.; Suss-Fink, G. *Eur. J. Inorg. Chem.* **2005**, *22*, 4493–4500.
(55) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *27*, 8724–8725.
(56) Ohkuma, T.; Tsutsumi, K.; Utsumi, N.; Arai, N.; Noyori, R.; Murata, K. *Org. Lett.* **2007**, *2*, 255–257.
(57) Martins, J. E. D.; Morris, D. J.; Tripathi, B.; Wills, M. *J. Organomet. Chem.* **2008**, *23*, 3527–3532.
(58) Martins, J. E. D.; Clarkson, G. J.; Wills, M. *Org. Lett.* **2009**, *4*, 847–850.
(59) Letko, C. S.; Heiden, Z. M.; Rauchfuss, T. B. *Eur. J. Inorg. Chem.* **2009**, *33*, 4927–4930.
(60) Cheung, F. K.; Clarke, A. J.; Clarkson, G. J.; Fox, D. J.; Graham, M. A.; Lin, C.; Criville, A. L.; Wills, M. *Dalton Trans.* **2010**, *5*, 1395–1402.
(61) Wu, X.; Li, X.; King, F.; Xiao, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3407–3411.
(62) Zhang, B.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2009**, *11*, 4712–4715.
(63) Wang, C.; Li, C.; Wu, X.; Pettman, A.; Xiao, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6524–6528.
(64) Gutierrez, L.; Alzuet, G.; Borras, J.; Gozalez, M. L.; Sanz, F.; Castineiras, A. *Polyhedron* **2001**, *20*, 703–709.
(65) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borras, J.; Castineiras, A. *Inorg. Chem.* **2000**, *39*, 3608–3614.
(66) Kilpin, K. J; Henderson, W.; Nicholson, B. K. *Dalton Trans.* **2008**, 3899–3906.
(67) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1998**, *39*, 3493–3496.
(68) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 63–66.
(69) Otter, C. A.; Couchman, S. M .; Jeffery, J. C .; Mann, K. L. V.; Psillakis, E.; Ward, M. D. *Inorg. Chim. Acta* **1998**, *278*, 178–184.
(70) Soltani, O.; Ariger, M. A.; Vazquez-Villa, H.; Carreira, E. M. *Org. Lett.* **2010**, *12* (13), 2893–2895.
(71) Baratta, W; Rigo, P. *Eur. J. Inorg. Chem.* **2008**, *26*, 4041–4053.
(72) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74–76.
(73) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204–209.
(74) Miller, K. J.; Kitagawa, T. T.; Abu-Omar, M. M. *Organometallics* **2001**, *20*, 4403–4412.
(75) Addison, A. W.; Burke, P. J. *J. Heterocycl. Chem.* **1981**, *18*, 803–805.
(76) Pleier, A. K.; Glas, H.; Grosche, M.; Sirsch, P.; Thiel, W. R. *Synthesis* **2001**, 55.
(77) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borras, J.; Castineiras, A. *Eur. J. Inorg. Chem.* **2002**, 2094–2102.
(78) Sheldrick, G. M. *SHELXS-97; Program for the Solution of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.
(79) Sheldrick, G. M. *SHELXL-97; Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997.
(80) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *30*, 837–838.
(81) *X-AREA Version 1.18* and *X-RED32 Version 1.04*; Stoe & Cie, Darmstadt, Germany, 2002.
(82) Spek, A. L. *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.
(83) Keene, F. R. *Coord. Chem. Rev.* **1999**, *187*, 121–148.
(84) Gomez, J.; Herbosa, G. G.; Cuevas, J. V.; Arnaiz, A.; Carbayo, A.; Munoz, A.; Falvello, L.; Fanwick, F. E. *Inorg. Chem.* **2006**, *45*, 2483–2493.
(85) Huang, W.; Qian, H. *J. Mol. Struct.* **2008**, *874*, 64–76.
(86) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(87) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
(88) Eliopoulos, E.; Sheldrick, B.; Hamodrakas, S. *Acta Crystallogr., Sect. C* **1983**, *39*, 1693–1695.
(89) Basak, A. K.; Chaudhuri, S.; Mazumdar, S. K. *Acta Crystallogr., Sect. C* **1984**, *40*, 1848–1851.
(90) Bar, I.; Bernstein, J. *J. Pharm. Sci.* **1985**, *74*, 255–263.
(91) Bernstein, J. *Acta Crystallogr., Sect. C* **1988**, *44*, 900–902.
(92) Cabaleiro, S.; Castro, J.; Vázquez-López, E.; García-Vázquez, J. A.; Romero, J.; Sousa, A. *Polyhedron* **1999**, *18*, 1669–1674.
(93) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555–1573.