New Approach to Ru(II) Pincer Ligand Chemistry. Bis(*tert*-butylaminomethyl)pyridine Coordinated to Ruthenium(II)

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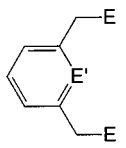
Reaction of 2,6-bis-(^{t}BuNHCH$_2$)$_2$NC$_5$H$_3$ ("N$_2$py") with RuCl$_2$(PPh$_3$)$_3$ gives two isomers of Ru(N$_2$py)Cl$_2$(PPh$_3$), **5**, while reaction with RuCl$_2$(DMSO)$_4$ (DMSO = Me$_2$SO) gives isomerically pure Ru(N$_2$py)Cl$_2$(DMSO), whose structure is reported. The PPh$_3$ of **5** can be replaced by CO, P(OPh)$_3$, or pyridine. The chlorides in Ru(N$_2$py)Cl$_2$(CO) can both be replaced by F$_3$CSO$_3^-$. Isomer structure preferences are discussed, and the reaction of Ru(N$_2$py)Cl$_2$(pyridine) with O$_2$ gives apparent oxidation of N$_2$py to give the diimine.

Introduction

In many catalytic reactions, coordinatively unsaturated complexes appear as reactive intermediates at some stage. Such species initiate catalytic processes (catalyst precursor) and, of course, are part of catalytic cycles themselves. Thus, investigations of the factors controlling and affecting the reactivity and stability of unsaturated compounds are very important not only for intrinsic reasons but for the understanding of virtually all homogeneously catalyzed processes. In the case of many 16-electron ruthenium complexes, one of the stabilizing factors is the presence of π-stabilizing ligands such as alkoxides, thiolates, and even halides.[1−3]

Recently, the pincer ligand class (**1**) has experienced a



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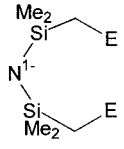

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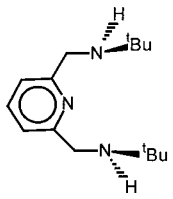
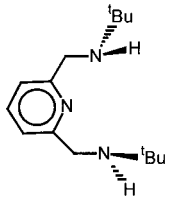
renaissance[4] from its earliest incarnations in monometal coordination chemistry. Here, E is a nitrogen or phosphorus donor and E′ can be either a pyridine nitrogen or a ring sp^2 carbon. This ligand is most often found as a meridional ligand (i.e., E′ and the two E will be approximately coplanar in the metal coordination sphere).

The Fryzuk ligand class (**2**) has some similar characteristics but seems more flexible in that it can occasionally occupy three facial sites on a metal.[5−8] Ligands of class **1** have been very productive, when bound to Rh and Ir, in supporting C−H and Si−H reaction chemistry, including catalyzed dehydrogenation of alkanes.[9−16] Class **2** ligands support similar reactivity.

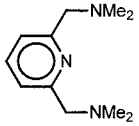
It is our purpose here to report progress on a related goal: pincer ligand chemistry of Ru with a secondary amine donor at sites E. We are interested in exploring systematically the comparison of nitrogen and phosphorus donors beyond their classical distinctions of nitrogen as a hard and pure σ-donor and phosphorus soft and a potential π-acid. Moreover, we have decided to make the donors E secondary (i.e., NH^{t}Bu) rather than tertiary amines for the specific purpose of having a reactive hydrogen accompanied by a bulky but 3-fold symmetric substituent. This substitution pattern (ligand abbreviation N$_2$py when E′ = N) will give rise to both mirror and C_2 symmetric isomers **3**, which are not anticipated to interconvert on the



3(m)



3(C$_2$)



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synthetic time scale when the nitrogens are coordinated. Isomer **3**(m) clearly has a crowded ("up") and an uncrowded ("down")

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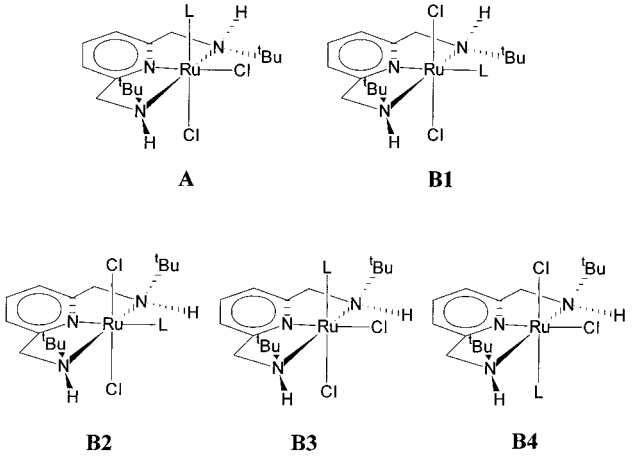
Chart 1

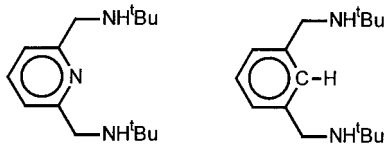


sides, while in **3**(C_2) these are equivalent. The Ru(II)/Cl^-, NCMe, PPh_3 chemistry of the related (but C_{2v} symmetric) ligand **4** was recently reported, showing (a) a tendency for PPh_3 to occupy the coordination position in the plane of ligand **4** in six-coordinate species and (b) PPh_3 in the axial site of the square-pyramidal cations (**4**)$Ru(PPh_3)X^+$ (X = Cl or CF_3SO_3) and (c) that in the absence of PPh_3, the metal will avoid unsaturation by binding N_2 to form (**4**)$Cl_2Ru(\mu\text{-}N_2)RuCl_2$(**4**).[17,18]

Results

Synthesis of $Ru(N_2py)Cl_2(PPh_3)$ (5). Reaction of $RuCl_2(PPh_3)_3$ with 1 equiv of N_2py in refluxing benzene for 5 h gives compound **5** in a yield of 70% as orange microcrystals crystallizing directly from the benzene solution. **5** is only soluble in CH_2Cl_2, but not in benzene, toluene, THF, acetone, or nitromethane. The red benzene filtrate contains neither of the starting compounds nor the product, and also doubling the amount of N_2py has no effect on the yield. The ^1H NMR spectrum of **5** reveals two distinct isomers in a ratio of 1:4. The major isomer shows three distinct chemical shifts for the pyridine protons, four chemical shifts the benzylic CH_2 protons, two NH resonances (it should be noted that the NH proton shows detectable coupling to the benzylic hydrogen in most of the compounds reported here), and two separate singlets for the ^{t}Bu groups. That is, there is no molecular symmetry element. A structure without any symmetry element (major isomer) is only consistent with the ^{t}Bu groups on each nitrogen being trans (anti) to each other and the PPh_3 ligand being in an axial position (**A**, Chart 1). In contrast, the minor isomer shows only half of the resonances, thus two chemical shifts for the pyridine protons, two chemical shifts for the CH_2 groups, only one singlet for the ^{t}Bu groups, and also only one NH resonance. Thus, we conclude that the structure of the second isomer contains either a mirror plane or a C_2 axis and that four different structures are possible: either the ^{t}Bu being trans (anti) and the PPh_3 ligand in an equatorial position (**B1**) or the ^{t}Bu being cis (syn) and the PPh_3 ligand being in either position (the two axial positions are now not equivalent, thus three different structures are possible, i.e., **B2**, **B3**, and **B4** in Chart 1). Attempted isomerization of **5** by heating to reflux in THF leads only to decomposition of the complex. The instability of compound **5** in CD_2Cl_2 also prevented the recording of a ^{13}C spectrum; within 5 h all peaks in the ^1H spectrum disappear with a comparable rate for both isomers.

Interestingly, the same reaction as for the preparation of **5**, that is, heating $RuCl_2(PPh_3)_3$ to reflux in benzene or toluene for 12 h in the presence of 1,3-(bis-*tert*-butylaminomethyl)-benzene (N_2bzH) does not give the expected C−H attack product $RuH(N_2bz)$ complex, but rather almost pure starting materials were recovered.



This suggests that an important step in the reaction of $RuCl_2(PPh_3)_3$ with N_2py is coordination of the pyridine nitrogen atom followed by loss of PPh_3 ligands and coordination of the secondary aliphatic nitrogens. Perhaps this means that the secondary amine nitrogens are incompetent Lewis bases to $RuCl_2(PPh_3)_3$ unless the pyridine nitrogen can initiate binding to Ru. These observations are consistent with other reports where phenyl-based Ru(II) pincer ligand complexes cannot be made by C−H oxidative addition;[19,20] the aryllithium salt of the ligand has to be used as the starting material rather than the free ligand itself.[21−23]

Synthesis of $Ru(N_2py)Cl_2(DMSO)$ (6). Reacting $RuCl_2(DMSO)_4$ with N_2py in refluxing benzene for 15 h yields an orange precipitate with the empirical formula $Ru(N_2py)Cl_2(DMSO)$. The ^1H NMR spectrum of this compound in CD_2Cl_2 shows an unsymmetrical surrounding of the metal (isomer **A**); that is, the DMSO ligand is placed in an axial position and the two ^{t}Bu groups are mutually trans. The two methyl groups of the DMSO ligand appear as two singlets at 3.60 and 2.85 ppm, respectively. Suitable crystals of **6** could be obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **6**. The solid-state structure determination (Figure 1 and Table 2) confirms the meridional coordination of the N_2py ligand, the cis stereochemistry of the chlorides, the inequivalence of the sulfoxide methyls, and the trans (anti) relationship of the ^{t}Bu groups. It also shows that the DMSO is sulfur-bound. The two fused five-membered rings each has an envelope conformation, and the bulk of the ^{t}Bu groups is accommodated by the occupying equatorial ring positions. Because of this, our supposition (see Introduction) that one conformation of the ^{t}Bu groups crowds the cis axial coordination sites is proven to be false. This makes the amine hydrogens axial, which orients them so that intramolecular hydrogen bonding is possible. In fact, H15 on N17 hydrogen-bonds to the DMSO oxygen O5. The N−O distance is 2.79 Å, and the angle N17−H15−O5 is 141.4°. H7 on N8 is 2.46 Å from Cl2, but the angle at H7 is not so favorable for hydrogen bonding. The unit cell incorporates CH_2Cl_2; H35 on its C26 is 2.60 Å from Cl2, and the angle C26−H35−Cl2 is 158.4°. However, the two chemically inequivalent Ru−Cl distances are essentially identical. The Ru−N(py) distance is over 0.2 Å shorter than those to the secondary amines. While the angles within the octahedron are 90 ± 12°, the constraints of the N_2-

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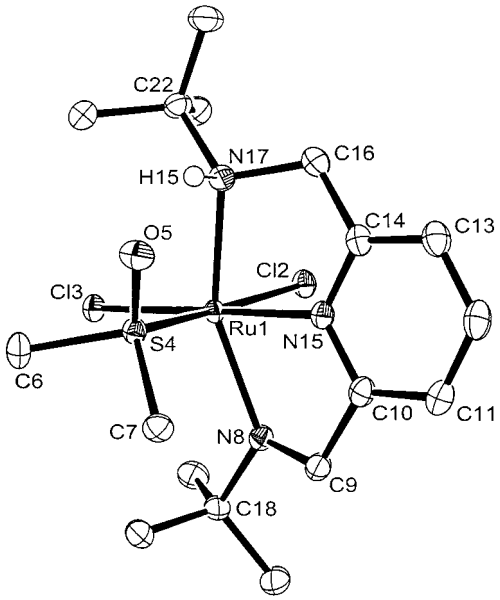


Figure 1. ORTEP drawing of $Ru(N_2py)Cl_2(DMSO)$, showing intramolecular NH···O hydrogen bonding.

Table 1. Crystallographic Data for $RuCl_2(DMSO)(N_2py)CH_2Cl_2$

formula	$C_{18}H_{35}Cl_4N_3ORuS$	space group	$P2_1/c$
a, Å	13.353(2)	T, °C	−163
b, Å	11.228(1)	λ, Å	0.710 69
c, Å	17.536(2(5)	ρ_{calc}, g/cm^{-3}	1.565
β, deg	109.30(1)	μ(Mo Kα), cm^{-1}	11.61
V, Å^3	2481.3(9)	R [a]	0.0290
Z	4	R_w [b]	0.0319
fw	584.44		

[a] $R = ||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/[\sigma^2(|F_o|)]$.

py ligand are evident. The five-membered rings pull the two aliphatic amine nitrogens away from Cl3 (and make N8−Ru−N17 only 156.7°), and the envelope ring conformation pulls N8 and N17 as much as 12° away from octahedral sites. The constraints of the five-membered rings, which increase the cis N−Ru−Cl3 angle, also serve to create additional room for the ^{t}Bu groups. The two ^{t}Bu groups have the same conformation arround the C−N(ring) bond, and this conformation maximizes the distance between Cl3 and the ^{t}Bu methyl group.

Other common Ru(II) starting materials, such as $[Ru(\eta^6\text{-cymene})Cl_2]_2$, $Ru(NH_3)_6Cl_2$, and $RuCl_2(COD)$, gave in all cases complex mixtures of compounds on reaction with N_2py, as judged by the complexity of their NMR spectra.

$Ru(N_2py)Cl_2(L)$. Reaction of **5** with ligands L (L = CO or two moles of $P(OPh)_3$ or pyridine) leads to the substitution products $Ru(N_2py)Cl_2(L)$ (**7**−**9**). The reactions of **5** with CO and $P(OPh)_3$ take place at room temperature within a few minutes, whereas the reaction with pyridine needs heating to reflux in acetone for 2 h. In all cases free PPh_3 could be detected by ^{31}P NMR. The ^{1}H NMR in CD_2Cl_2 shows that $Ru(N_2py)Cl_2(CO)$ (**9**) and $Ru(N_2py)Cl_2$(pyridine) (**8**) both give only one isomer, which possesses an element of symmetry (structure **B**). In contrast, $Ru(N_2py)Cl_2(P(OPh)_3)$ (**7**) shows two isomers in the same ratio as the starting complex **5**. However, heating this mixture in acetone to reflux for 2 h leads to clean isomerization of the minor isomer (**A**, no symmetry) into the major isomer (**B**, 2-fold symmetry).

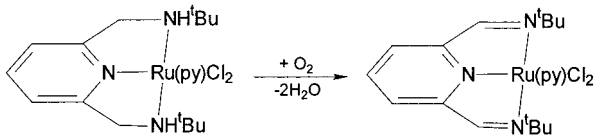
Reaction with O_2. Reaction of **8** with 1 equiv of O_2 in CD_2Cl_2 gives a deep-purple solution. In the ^{1}H NMR spectrum all resonances of the CH_2 groups and the NH protons have disappeared and instead a new singlet with an integral area assignable to two protons is detectable. This leads us to the suggestion of a coordinated imine formed by an oxidation of the benzylic CH_2 and the NH groups (Scheme 1). Such β-oxidation reactions are known to happen on coordinated amines upon reaction with O_2.[24−27]

Table 2. Selected Bond Distances(Å) and Angles (deg) for $RuCl_2(DMSO)(N_2py)$

Distance			
Ru(1)−Cl(2)	2.4521(6)	S(4)−C(6)	1.7843(27)
Ru(1)−Cl(3)	2.4574(6)	S(4)−C(7)	1.7969(26)
Ru(1)−S(4)	2.2090(6)	N(8)−C(9)	1.490(3)
Ru(1)−N(8)	2.2204(20)	N(8)−C(18)	1.526(3)
Ru(1)−N(15)	1.9855(20)	N(17)−C(16)	1.492(3)
Ru(1)−N(17)	2.1970(21)	N(17)−C(22)	1.524(3)
S(4)−O(5)	1.4980(18)		

Angle			
Cl(2)−Ru(1)−Cl(3)	91.973(22)	O(5)−S(4)−C(6)	104.45(12)
Cl(2)−Ru(1)−S(4)	174.431(22)	O(5)−S(4)−C(7)	102.80(11)
Cl(2)−Ru(1)−N(8)	79.82(6)	C(6)−S(4)−C(7)	97.84(12)
Cl(2)−Ru(1)−N(15)	85.20(6)	Ru(1)−N(8)−C(9)	106.80(14)
Cl(2)−Ru(1)−N(17)	90.72(6)	Ru(1)−N(8)−C(18)	130.33(15)
Cl(3)−Ru(1)−S(4)	92.563(23)	C(9)−N(8)−C(18)	112.80(19)
Cl(3)−Ru(1)−N(8)	99.96(6)	Ru(1)−N(15)−C(10)	119.85(17)
Cl(3)−Ru(1)−N(15)	176.98(6)	Ru(1)−N(15)−C(14)	118.94(17)
Cl(3)−Ru(1)−N(17)	101.60(6)	C(10)−N(15)−C(14)	121.19(21)
S(4)−Ru(1)−N(8)	102.55(6)	Ru(1)−N(17)−C(16)	105.23(15)
S(4)−Ru(1)−N(15)	90.32(6)	Ru(1)−N(17)−C(22)	126.60(15)
S(4)−Ru(1)−N(17)	85.20(6)	C(16)−N(17)−C(22)	113.16(19)
N(8)−Ru(1)−N(15)	78.51(8)	N(8)−C(9)−C(10)	111.21(20)
N(8)−Ru(1)−N(17)	156.72(8)	N(15)−C(10)−C(9)	115.60(22)
N(15)−Ru(1)−N(17)	79.54(8)	N(15)−C(10)−C(11)	120.41(23)
Ru(1)−S(4)−O(5)	113.99(7)	N(15)−C(14)−C(13)	120.53(24)
Ru(1)−S(4)−C(6)	117.89(9)	N(15)−C(14)−C(16)	114.49(21)
Ru(1)−S(4)−C(7)	117.47(9)	Cl(27)−C(26)−Cl(28)	111.58(16)
Ru(1)−N(8)−H(7)	100.45(14)		
C(9)−N(8)−H(7)	100.51(19)		
C(18)−N(8)−H(7)	100.55(18)		
Ru(1)−N(17)−H(15)	103.06(15)		
C(16)−N(17)−H(15)	102.88(19)		
C(22)−N(17)−H(15)	102.93(19)		

Scheme 1



$Ru(N_2py)(CF_3SO_3)_2(CO)$ (10). Replacement of the chlorides in **9** by $CF_3SO_3^-$ can be achieved by reaction with two moles of $AgCF_3SO_3$ in CH_2Cl_2 within 30 min at 25 °C. The ^{1}H NMR data are consistent with a single product having a symmetric structure **B**. However, the ^{19}F spectrum shows two quartets (J = 3.1 Hz) separated by 0.23 ppm. This lack of symmetry in the ^{19}F spectrum, however, rules out structure **B1** ($CF_3SO_3^-$ trans, ^{t}Bu trans) because only one ^{19}F signal should be observed. The relatively large F−F coupling between the two CF_3 groups (^8J = 3.1 Hz) can be due to a trans coordination of the $CF_3SO_3^-$ ligands. Thus, the NMR features of this compound are consistent with a structure with cis ^{t}Bu groups and trans $CF_3SO_3^-$ ligands (**B2**). This F−F coupling excludes an ionic formulation $[Ru(N_2py)(CF_3SO_3)(CO)]^+(CF_3SO_3)^-$.

All attempts to abstract the weakly coordinating $CF_3SO_3^-$ ligand with reagents such as $NaBPh_4$ or $NaB(Ar')_4$ (Ar′ = 3,5-

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bistrifluoromethylphenyl) failed and lead only to decomposition of the complex, as judged by ^{1}H NMR. Because the expected product is +2 charged and contains acidic protons on the amine ligand, the same reactions were repeated in the presence of an acid trap (Na_2CO_3), in the hope of getting a single product, but no clean reaction could be observed.

Dehydrohalogenation Reactions. In attempts to dehydrohalogenate the HNRuCl unit in **9** to give Ru(N_2py−2H)(CO), compound **9** was reacted with a variety of bases, namely, 2,6-lutidine, lithium 2,2,6,6-tetramethylpiperidide, MeLi, and BuLi. All of these attempts failed in that they led only to intractable materials. In a typical experiment, a slurry of Ru(N_2py)Cl_2(CO) (**9**) in Et_2O was cooled to −78 °C and reacted with 2 mol of BuLi in Et_2O to give an orange solution. However, warming this solution led to a color change to dark-brown at room temperature, and in ^{1}H NMR no peaks assignable to N_2py were detectable. The orange solution obtained by reaction of **9** with BuLi was also reacted with Cl_2 at −78 °C, giving immediately a yellow precipitate that was identified as the starting complex **9**.

Discussion

Because several isomers of Ru(N_2py)Cl_2L are observed, the question of thermodynamic preference must be considered. The situation with L = P(OPh)$_3$ is most clear because isomer **A** transforms on heating to one symmetric isomer **B**. Conversion from **A** to **B3** involves only one inversion at the nitrogen. All others require a change of the metal coordination sphere as well.

It is noteworthy that there is obviously considerable stereochemical rigidity at the coordinated secondary amine. If there were not, the **A** to **B3** conversion would be fast. Moreover, the degenerate rearrangement of **A** into its enantiomers (i.e., inversion at both of its nitrogens) could produce a time-averaged mirror plane for isomer **A**. Therefore, the isomerization of Ru(N_2py)Cl_2(PPh_3) was carried out in the presence of a base, i.e., 1.5 equiv of 2,6-lutidine in CD_2Cl_2 solution, but no considerable rate enhancement was observed.

Because only the DMSO complex clearly favors isomer **A**, it may be that the intramolecular hydrogen bonding is the cause. Moreover, given that putting both ^{t}Bu in equatorial positions is clearly sterically favorable, it may be that only the anti ^{t}Bu stereochemistry is favored. The syn relationship puts the two fused five-membered rings in conflict at their phenyl fusion. If so, then structures **A** and **B1** will be generally favored.

Experimental Section

General. All manipulations were carried out with standard Schlenk and glovebox techniques under purified argon. Benzene, toluene, Et_2O, CH_2Cl_2, and pentane were dried using appropriate agents, distilled, and stored in gastight solvent bulbs. Benzene-d_6, CD_2Cl_2, and toluene-d_8 were dried by appropriate methods and vacuum-distilled prior to use. Pyridine and P(OPh)$_3$ were purchased from Aldrich and used without further purification. Gaseous reagents were purchased from Air Products and used as received. $RuCl_2(PPh_3)_3$[28] and $RuCl_2(DMSO)_4$[29] were synthesized according to literature. ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer (^{1}H, 300 MHz; ^{31}P, 122 MHz; ^{19}F, 282 MHz; ^{13}C, 75 MHz) or on a Varian INOVA 400 spectrometer (^{1}H, 400 MHz; ^{31}P, 161 MHz; ^{19}F, 376 MHz; ^{13}C, 100 MHz). ^{1}H NMR chemical shifts are reported in ppm downfield of tetramethylsilane with use of residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are relative to an external 85% H_3PO_4. ^{19}F NMR chemical shifts are externally referenced to CF_3COOH in benzene. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer.

2,6-Pyridinedicarboxylic Acid Dimethyl Ester ($C_9H_9NO_4$). 2,6-Pyridinedicarboxylic acid (26.0 g, 155.7 mmol) and $H_2SO_{4(concentrated)}$ (0.2 mL) in methanol (200 mL) were heated to reflux for 100 h. After evaporation of the solvent, the residue was redissolved in CH_2Cl_2 (200 mL) extracted twice with saturated aqueous solution of $NaHCO_3$ (100 mL), followed by H_2O (100 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent removed. The white product was dried in vacuo. Yield: 25.0 g (82%). ^{1}H NMR (25 °C, $CDCl_3$): 8.33 (d, 2H, J = 7.8 Hz), 8.02 (t, 1H, J = 7.8 Hz), 4.02 (s, 6H).

2,6-Pyridinedimethanol ($C_7H_9NO_2$). To 2,6-pyridinedicarboxylic acid dimethylester (20.9 g, 107.1 mmol) in MeOH (200 mL) was slowly added $NaBH_4$ (6.08 g, 160.7 mmol), whereupon the exothermic reaction warmed the reaction mixture to reflux. The solution was then stirred at room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in saturated aqueous $NaHCO_3$ solution (200 mL) and extracted with $CHCl_3$ (300 mL) by continuous liquid−liquid extraction for 15 h. After evaporation of the solvent, the product was washed with Et_2O and dried in vacuo. Yield: 10.7 g (72%). ^{1}H NMR (25 °C, $CDCl_3$/DMSO-d_6): δ 7.35 (t, 1H, J = 7.8 Hz), 6.94 (d, 2H, J = 7.8 Hz), 4.34 (s, 4H), 3.64 (bs, 2H).

2,6-Bis(toluenesulfonylmethyl)pyridine ($C_{21}H_{21}NO_6S_2$). A solution of 2,6-pyridinedimethanol (2.24 g, 16.1 mmol) and KOH (2.58 g, 46.0 mmol) in 50 mL of THF was cooled in an ice bath. and toluenesulfonyl chloride (7.0 g, 36.7 mmol) in 150 mL of THF was added dropwise. The temperature was not allowed to rise over 0 °C. The mixture was stirred for 5 h at 0 °C and then for another 12 h at room temperature. The white residue (KOH, KCl) was filtered off and washed twice with THF (30 mL). The THF fractions were combined, and after evaporation of the solvent, the product was dried in vacuo. Yield: 5.32 g (74%). ^{1}H NMR (25 °C, $CDCl_3$): δ 7.80 (m, 4H), 7.69 (m, 1H), 7.33 (m, 6H), 5.04 (s, 4H), 2.44 (s, 6H).

2,6-Bis(*tert*-butylaminomethyl)pyridine ($C_{15}H_{27}N_3$). 2,6-Bis(toluenesulfonylmethyl)pyridine (5.19 g, 11.6 mmol) and *tert*-butylamine (36 mL, 350 mmol) were dissolved in benzene and heated to reflux for 15 h. After evaporation of the solvent, the residue was redissolved in CH_2Cl_2, extracted twice with saturated aqueous $NaHCO_3$ (100 mL) and H_2O (100 mL), and dried over Na_2SO_4. The solvent was removed and the product dried in vacuo. Yield: 2.66 g (92%). ^{1}H NMR (25 °C, $CDCl_3$): δ 7.52 (t, 1H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 3.83 (s, 4H), 1.75 (bs, 2H), 1.34 (s, 18H).

Ru(N_2py)Cl_2(PPh_3) (5; $C_{33}H_{42}Cl_2N_3PRu$). A solution of $RuCl_2(PPh_3)_3$ (1.14 g, 1.20 mmol) and 2,6-bis(*tert*-butylaminomethyl)pyridine (0.3 g, 1.20 mmol) in benzene (50 mL) was heated to reflux for 5 h. After the reaction mixture was cooled, the orange crystals formed were collected on a glass frit, washed with Et_2O several times, and dried in vacuo. Yield: 0.56 g (68%). Anal. Calcd. for ($C_{33}H_{42}Cl_2N_3PRu$): C, 57.98; H, 6.19; N, 6.15. Found: C, 57.67; H, 6.34; N, 6.44. ^{1}H NMR (25 °C, CD_2Cl_2). For isomer I, δ 7.70 (m, 6H, PPh_3), 7.44 (t, 1H, J = 8.1 Hz, N_2py), 7.32 (m, 9H, PPh_3), 6.85 (2H, d, J = 8.1 Hz, N_2py), 4.23 (dd, 2H, J_1 = 15.9 Hz, J_2 = 6.6 Hz, NH), 3.22 (dd, 2H, J_1 = 15.9 Hz, J_2 = 6.6 Hz, CH_2), 2.80 (dd, J_1 = J_2 = 6.6 Hz, CH_2), 1.121 (s, 18H, ^{t}Bu). For isomer II, δ 7.83 (dd, 1H, J_1 = J_2 = 8.1 Hz, N_2py), 7.71 (m, 6H, PPh_3), 7.31 (m, 9H, PPh_3), 7.10 (d, 1H, J = 8.1 Hz, N_2py), 6.79 (d, 1H, J = 8.1 Hz, N_2py), 6.02 (dd, 1H, J_1 = 12.7 Hz, J_2 = 5.0 Hz, NH), 4.02 (dd, 1H, J_1 = 15.9 Hz, J_2 = 5.0 Hz), 3.30 (m, 2H), 2.53 (dd, J_1 = J_2 = 5.0 Hz), 1.99 (dd, 1H, J_1 = 12.7 Hz, J_2 = 15.9 Hz), 1.16 (s, 9H), 1.09 (s, 9H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) for isomer II: δ 56.0.

Ru(N_2py)Cl_2(DMSO) (6; $C_{17}H_{33}Cl_2N_3OSRu$). A solution of $RuCl_2(DMSO)_4$ (226 mg, 0.466 mmol) and 2,6-bis(*tert*-butylaminomethyl)-pyridine (120 mg, 0.481 mmol) in benzene (5 mL) was heated to reflux for 15 h. After evaporation of the solvent, the precipitate was collected on a glass frit, washed several times with small portions of Et_2O, and dried in vacuo. Yield: 189 mg (81%). Anal. Calcd for ($C_{17}H_{33}Cl_2N_3OSRu$): C, 40.88; H, 6.66; N, 8.41. Found: C, 40.94; H, 6.70; N, 8.55. ^{1}H NMR (25 °C, CD_2Cl_2): δ 7.55 (dd, 1H, J_1 = J_2 = 8.0 Hz), 7.20 (d, 1H, J = 8.0 Hz), 7.17 (d, 1H, J = 8.0 Hz), 5.25 (d, 1H, J = 8.4 Hz), 4.91 (d, 1H, 9.9 Hz), 4.40 (dd, 1H, J_1 = 15.9 Hz, J_2 = 12.3 Hz), 4.07

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(dd, 1H, $J_1 = 15.9$ Hz, $J_2 = 3.6$ Hz), 3.85 (m, 2H), 3.60 (s, 3H, DMSO), 2.85 (s, 3H, DMSO), 1.15 (s, 9H, ^{t}Bu), 1.10 (s, 9H, ^{t}Bu).

Structure Determination of Ru(N_2py)Cl_2(DMSO)·CH_2Cl_2. An irregular triangular prism was attached to a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −163 °C for characterization and data collection. A preliminary search for peaks and analysis using the programs DIRAX and TRACER revealed a primitive monoclinic unit cell. Unit cell dimensions were obtained by an unrestrained least-squares fit of the setting angles for 65 carefully centered reflections having 2θ values between 19° and 21°. The upper limit for the data collection was extended to 55° because of the strong diffraction observed. Following the completed data collection, the systematic extinction of $0k0$ for $k = 2n + 1$ and of $h0l$ for $l = 2n + 1$ uniquely identified the space group as $P2_1/c$. Four standards measured every 300 reflections showed no significant trends. The limits for h, k, and l were −17 to 17, 0 to −14, and −22 to 20, respectively. An analytical absorption correction was carried out over the 0.685−0.810 transmission factor range. The structure was solved using DIRDIF-96. The major part of the main molecule as well as the solvent molecule was located in the initial run of the program. The remaining atoms were located in the usual manner using least-squares refinement followed by a difference Fourier calculation. Hydrogen atoms were introduced in fixed, calculated positions with isotropic thermal parameters equal to 1.0 plus the isotropic equivalent of the parent atom. The final full matrix least-squares refinement was carried out using anisotropic thermal parameters on all nonhydrogen atoms. The total number of parameters, including the scale factor and an overall isotropic extinction parameter, was 254. The final difference map was featureless. The largest peak was 0.31 e/Å^3 located 1.2 Å from O(5), and the deepest hole was −0.19 e/Å^3.

Ru(N_2py)Cl_2(P(OPh)$_3$) (7; $C_{33}H_{42}Cl_2N_3O_3PRu$). A solution of **5** (101.3 mg, 0.148 mmol) and triphenyl phosphite (91.9 mg, 0.296 mmol) in THF (5 mL) was heated to reflux for 15 h. After evaporation of the solvent, the precipitate was collected on a glass frit, washed several times with small portions of Et_2O, and dried in vacuo. Yield: 88.2 mg (81%). ^{1}H NMR (25 °C, CD_2Cl_2). For isomer I: δ 7.64 (dd, 1H, $J_1 = J_2 = 7.2$ Hz, N_2py), 7.6−6.8 (m, 17H, N_2py, P(OPh)$_3$), 5.95 (d, 2H, $J = 13$ Hz, NH), 4.17 (dd, 2H, $J_1 = 15.6$ Hz, $J_2 = 3.6$ Hz, CH_2), 3.85 (dd, 2H, $J_1 = 13$ Hz, $J_2 = 15.6$ Hz, CH_2), 1.33 (s, 18H). For isomer II: δ 7.61 (dd, 1H, $J_1 = J_2 = 7.2$ Hz), 7.25 (d, 1H, $J = 7.2$ Hz), 7.05 (m, 16H), 5.0 (d, 1H, $J = 11.2$ Hz, NH), 4.53 (m, 2H), 4.08 (dd, 1H, $J_1 = 14.8$ Hz, $J_2 = 3.6$ Hz, CH_2), 3.37 (m, 2H, CH_2), 1.48 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu). ^{31}P{^{1}H) NMR (CD_2Cl_2, 25 °C). For isomer I: δ 124.3. For isomer II: δ 122.9.

Ru(N_2py)Cl_2(pyridine) (8; $C_{20}H_{32}Cl_2N_4Ru$). A solution of **5** (61.7 mg, 0.0903 mmol) and pyridine (14.3 mg, 0.181 mmol) in acetone (5 mL) was heated to reflux for 2 h. After evaporation of the solvent, the precipitate was collected on a glass frit, washed several times with small portions of Et_2O, and dried in vacuo. Yield: 25.8 mg (57%). ^{1}H NMR (25 °C, CD_2Cl_2): δ 10.37 (dd, 2H, $J_1 = 6.9$ Hz, $J_2 = 1.2$ Hz, pyridine), 7.71 (t, 1H, $J = 6.9$ Hz), 7.52 (t, 1H, $J = 8.1$ Hz), 7.34 (m, 5H), 4.20 (m, 6H), 0.91 (s, 18H, ^{t}Bu).

Ru(N_2py)Cl_2(CO) (9; $C_{16}H_{27}Cl_2N_3$ORu). **5** (230 mg, 0.336 mmol) in acetone (5 mL) was purged with CO for 2 min and stirred at room temperature for 2 h. After evaporation of the solvent, the precipitate was collected on a glass frit, washed with small portions of Et_2O, and dried in vacuo. Yield: 125 mg (83%). Anal. Calcd for ($C_{16}H_{27}Cl_2N_3$ORu): C, 42.76; H, 6.06; N, 9.35. Found: C, 42.53; H, 6.19; N, 9.62. ^{1}H NMR (25 °C, CD_2Cl_2): δ 7.74 (t, 1H, $J_1 = 8.1$ Hz, N_2py), 7.32 (d, 2H, $J = 8.1$ Hz, N_2py), 4.57 (dd, 2H, $J_1 = 15.9$ Hz, $J_2 = 5.4$ Hz, CH_2), 4.25 (m, 2H, NH), 4.05 (dd, 2H, $J_1 = 15.9$ Hz, $J_2 = 8.1$ Hz, CH_2), 1.37 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 205.5 (CO), 161.4 (N_2py), 137.4 (N_2py), 119.5 (N_2py), 59.6 (^{t}Bu−C), 57.3 (CH_2), 28.1 (^{t}Bu−CH_3). IR (CH_2Cl_2, 25 °C): 1935 cm^{-1} (ν_{CO}).

Ru(N_2py)(CO)(CF_3SO_3)$_2$ (10; $C_{18}H_{27}F_6N_3S_2O_7Ru$). A solution of **9** (49.8 mg, 0.111 mmol) and $AgCF_3SO_3$ (56.9 mg, 0.221 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 30 min. The AgCl formed was filtered off, the solvent was removed, and the residue was collected on a glass frit, washed with small portions of Et_2O, and dried in vacuo. Yield: 42 mg (84%). ^{1}H NMR (25 °C, CD_2Cl_2): δ 7.90 (t, 1H, $J_1 = 7.8$ Hz, N_2py), 7.43 (d, 2H, $J = 7.8$ Hz, N_2py), 5.22 (m, 2H, NH), 4.67 (dd, 2H, $J_1 = 16.4$ Hz, $J_2 = 6$ Hz, CH_2), 4.25 (dd, 2H, $J_1 = 16.4$ Hz, $J_2 = 6$ Hz, CH_2), 1.37 (s, 18H, ^{t}Bu). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2): δ −80.54 (q, $J = 3.1$ Hz), −80.77 (q, $J = 3.1$ Hz). IR (CH_2Cl_2, 25 °C): 1960 cm^{-1} (ν_{CO}).

Ru(py(CHN^{t}Bu)$_2$)Cl_2(pyridine) (11; $C_{20}H_{28}Cl_2N_4Ru$). **8** (50 mg, 0.12 mmol) was dissolved in CD_2Cl_2, and O_2 (0.13 mmol) was added. When the solution was stirred at room temperature, the color turned from light-orange to deep-purple within 1 h. After 2 h, a ^{1}H NMR spectrum was recorded. ^{1}H NMR (25 °C, CD_2Cl_2): δ 10.44 (d, 2H, $J = 5.1$ Hz, pyridine), 8.32 (s, 2H, CH=N), 7.92 (m, 1H), 7.75 (d, 2H, $J = 8.1$ Hz), 7.56 (m, 3H), 1.21 (s, 18H, ^{t}Bu).

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

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