Transition-Metal Complexes with Sulfur Ligands. 112.[1] Synthesis and Characterization of Ruthenium Complexes with $[RuPS_2N_2]$ Cores. Substitution, Redox, and Acid−Base Reactions of $[Ru^{II}(L)(PR_3)('S_2N_2H_2')]$ (L = CO, PPr_3, R = Pr or Cy) and Five-Coordinate $[Ru^{IV}(PCy_3)('S_2N_2')]$[†]

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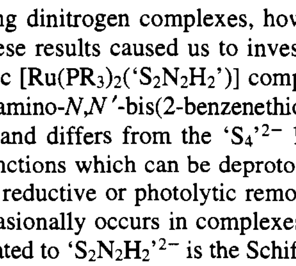
In order to find new ruthenium complexes with $[RuPS_2N_2]$ frameworks, $[Ru(PPr_3)_2('S_2N_2H_2')]$ (**2**), ($'S_2N_2H_2'^{2-}$ = 1,2-ethanediamine-*N,N′*-bis(2-benzenethiolate)(2−)), $[Ru(CO)(PPr_3)('S_2N_2H_2')]$ (**7**), $[Ru(CO)(PCy_3)('S_2N_2H_2')]$ (**4**), $[Ru(PCy_3)('S_2N_2')]$ (**5**), ($'S_2N_2'^{4-}$ = 1,2-ethanediamide-*N,N′*-bis(2-benzenethiolate)(4−)), $[Ru(Br)(PPh_3)('Et_2S_2N_2H_2')]Br$ (**8**), ($'Et_2S_2N_2H_2'$ = 1,10-diethyl-2,3,8,9-dibenzo-1,10-dithia-4,7-diazadecane), and $[Ru(Br)(PPh_3)('(PhCH_2)_2S_2N_2H_2')]Br$ (**9**) ($'(PhCH_2)_2S_2N_2H_2'$ = 1,10-dibenzyl-2,3,8,9-dibenzo-1,10-dithia-4,7-diazadecane) were synthesized. The molecular structures of **2, 5** and **9** were elucidated by X-ray structure determination. (**2**: triclinic space group $P\bar{1}$; a = 11.103(3) Å, b = 11.720(2) Å, c = 13.813(3) Å; α = 79.43(2)°, β = 85.73(2)°, γ = 82.91(2)°; Z = 2; R/R_w = 5.1/4.6%. **5**: monoclinic space group $P2_1/n$; a = 12.019(4) Å, b = 15.132(6) Å, c = 33.566(11) Å; β = 90.56(3)°; Z = 8; R/R_w = 5.0/4.7%. **9**: monoclinic space group Cc; a = 17.839(9) Å, b = 15.846(8) Å, C = 15.706(10) Å; β = 109.18(5)°; Z = 4; R/R_w = 6.0/6.0%.) **2** and **9** exhibit pseudooctahedral six-coordinate Ru(II) centers. The five-coordinate Ru(IV) center contained in **5** has a distorted coordination polyhedron, which can be described as trigonal bipyramid or tetragonal pyramid. The Ru(IV) oxidation state of **5** is stabilized by strong π donation of the thiolato and the amido groups. The reversible conversion of the Ru(IV) complex **5** into the Ru(II) complex $[Ru(CO)(PCy_3)('S_2N_2H_2')]$ (**4**) requires the simultaneous transfer of electrons, protons and CO and can be achieved by reaction with formic acid. In protic solvents, **2** yields the Schiff base complex $[Ru(PPr_3)_2(gma)]$ (**10**) (gma^{2-} = 1,2-diiminoethane-*N,N′*-bis(2-benzenethiolate)(2−)) upon reaction with CO which functions as proton and electron acceptor. The analogous $[Ru(PMe_3)_2(gma)]$ (**11**) is formed by the reaction of the Ru(IV) complex **5** with PMe_3. Mechanisms for the conversions of **2** into **10** and **5** into **11** are discussed.

Introduction

Transition metals in coordination spheres of oxygen, sulfur, or nitrogen form the active sites of numerous oxidoreductases.[2] Complexes which model structural *and* functional features of these active sites are of interest for biochemical, spectroscopic and technical reasons.[3] In quest of model complexes for the active centers of nitrogenases, we recently observed unexpected ligand effects in $[Fe(L_1)(PR_3)('S_4')]$ complexes ($'S_4'^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethane(2−)). Only if the phosphine ligand PR_3 was PPr_3 or PBu_3, but not if it was PMe_3 or PCy_3, did the reaction according to eq 1 yield diazene complexes of the general formula $[\mu\text{-}N_2H_2\{Fe(PR_3)('S_4')\}_2]$[4] in a very convenient way and in high yield.

$$Fe^{2+} + 'S_4'^{2-} + 2\ PR_3 \xrightarrow[THF\ /\ 20\ °C]{+\ exc.\ N_2H_4\ +\ O_2}$$



(1)

The desired corresponding dinitrogen complexes, however, could not be obtained. These results caused us to investigate reactions of the isoelectronic $[Ru(PR_3)_2('S_2N_2H_2')]$ complexes ($'S_2N_2H_2'^{2-}$ = 1,2-ethanediamino-*N,N′*-bis(2-benzenethiolate)-(2−)). The $'S_2N_2H_2'^{2-}$ ligand differs from the $'S_4'^{2-}$ ligand (Chart 1) by its two NH functions which can be deprotonated, and it is more inert toward reductive or photolytic removal of the C_2H_4 bridge which occasionally occurs in complexes with $[M'S_4']$ cores.[5] Closely related to $'S_2N_2H_2'^{2-}$ is the Schiff base ligand gma^{2-} which results from $'S_2N_2H_2'^{2-}$ by dehydrogenation of the $[NH-CH_2]$ entities or upon condensation of *o*-mercaptoaniline with glyoxal. Previous investigations, had shown that

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[†] Ligand abbreviations: $'S_2N_2H_2'^{2-}$ = 1,2-ethanediamine-*N,N′*-bis(2-benzenethiolate)(2−); $'S_2N_2'^{4-}$ = 1,2-ethanediamide-*N,N′*-bis(2-benzenethiolate)(4−).

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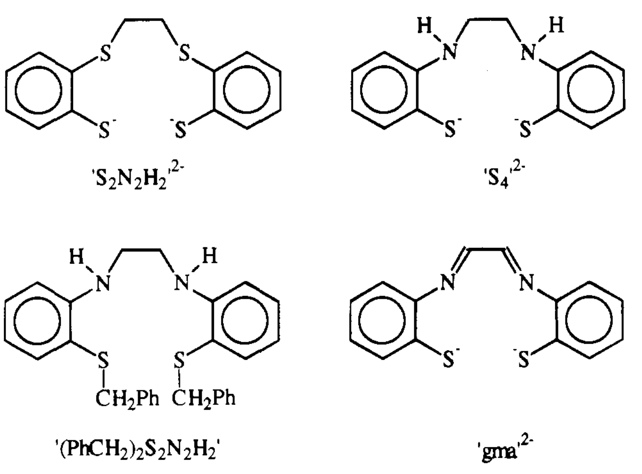
Chart 1



[Ru(PR$_3$)$_2$('S$_2$N$_2$H$_2$')] complexes with R = Me or Ph are inert toward substitution of PR$_3$ in neutral media.[6,7] On account of this, we tried to synthesize the analogous PPr$_3$ and PCy$_3$ derivatives in order to obtain complexes which are more labile toward substitution of PR$_3$ but sufficiently inert to allow coordination not only of N$_2$H$_4$ or N$_2$H$_2$ but also of N$_2$.

In this paper, we describe our attempts to obtain the target precursor complexes [Ru(PR$_3$)$_2$('S$_2$N$_2$H$_2$')] (R = Pr, Cy). These investigations showed that complexes with isoelectronic [Ru('S$_2$N$_2$H$_2$')] and [Ru('S$_4$')] fragments exhibit completely different reactivities leading, for instance, to the formation of the remarkable Ru(IV) species [Ru(PCy$_3$)('S$_2$N$_2$')] containing the fully deprotonated 'S$_2$N$_2$'$^{4-}$ ligand or to the formation of Schiff base complexes of the type [Ru(PR$_3$)$_2$(gma)], (gma^{2-} = glyoxal bis(2-mercaptoanil)(2−)). (According to IUPAC nomenclature, gma^{2-} is more correctly named 1,2-diiminoethane-*N,N'*-bis(2-benzenethiolate)(2−).)

Experimental Section

General Methods. Unless noted otherwise, all reactions were carried out under an atmosphere of dinitrogen at room temperature in dried N$_2$-saturated solvents by using standard Schlenk techniques. IR spectra of solutions were recorded in CaF$_2$ cuvettes with compensation of the solvent bands; solids were measured as KBr pellets. Physical measurements were carried out with the following instruments: IR spectra, Perkin-Elmer IR 983 and Perkin-Elmer 1600 FT IR; NMR spectra, Jeol FT-NMR JNM-GX 270 and EX 270; mass spectra, Varian MAT 212; magnetism (solid samples, 295 K), magnetic susceptibility balance, Johnson Matthey Chemicals Limited; cyclic voltammetry, EG&G Potentiostat (Model PAR 264A) equipped with Rotel A (glassy carbon working electrode, Ag/AgCl reference, and Pt counter electrode; conducting salt, 0.1 m NBu$_4$PF$_6$. Redox potentials were referred to NHE via ferrocene as internal reference); UV-radiation source, 150 W high pressure burner of Original Quarzlampen GmbH, Hanau, Germany.

H$_2$'S$_2$N$_2$H$_2$',[8] [RuCl$_2$(PPh$_3$)$_3$],[9] H$_2$-gma,[10] [Ru(NO)(PMe$_3$)('S$_2$N$_2$H')],[11] [RuCl$_2$(DMSO)$_4$],[12] and [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')][6] were prepared as described in the literature.

X-ray Structure Analyses of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (2), [Ru(PCy$_3$)('S$_2$N$_2$')] (5), and [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (9).

Table 1. Crystallographic Data for [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**), [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**), and [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (**9**)

	2	**5**	**9**
formula	C$_{32}$H$_{56}$N$_2$P$_2$RuS$_2$	C$_{32}$H$_{45}$N$_2$PRuS$_2$	C$_{46}$H$_{43}$Br$_2$N$_2$PRuS$_2$
fw	695.9	653.9	979.8
cryst dimens (mm^3)	0.50 × 0.40 × 0.40	0.80 × 0.50 × 0.50	0.80 × 0.70 × 0.60
space group	$P\bar{1}$	$P2_1/n$	Cc
cryst syst	triclinic	monoclinic	monoclinic
a (Å)	11.103(3)	12.019(4)	17.839(9)
b (Å)	11.720(2)	15.132(6)	15.846(8)
c (Å)	13.813(3)	33.566(11)	15.706(10)
α (deg)	79.43(2)	90.00(0)	90.00(0)
β (deg)	85.73(2)	90.56(3)	109.18(5)
γ (deg)	82.91(2)	90.00(0)	90.00(0)
Z	2	8	4
cell vol (Å^3)	1750(1)	6104(4)	4193(4)
d_{calc} (g/cm^{-3})	1.32	1.42	1.55
F(000)	736	2736	1976
μ (cm^{-1})	6.81	7.27	24.52
meas temp (K)	200	200	293
no. of meas refls	11360	16769	9304
no. of indep refls	7545	12849	8981
no. of obsd refls	5514	7529	6290
refined params	352	685	485
R; R_w (%)[a]	5.1; 4.6	5.0; 4.7	6.0; 6.0

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

Single crystals were grown as follows: Yellow blocks of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**) from a saturated CH$_2$Cl$_2$ solution which was layered with hexane, black [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**) from a saturated THF solution which was layered with MeOH at −30 °C , and yellow [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (**9**) from a saturated CH$_2$Cl$_2$ solution which slowly evaporated in the course of 2 d, in the presence of air.

Suitable single crystals were sealed in glass capillaries and mounted on a Siemens P4 diffractometer. Data were collected with Mo Kα radiation (0.710 73 Å) in a 2θ range from 3.0 to 54.0°. Structures were solved by direct methods (SHELXTL-PLUS); non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen positions were taken from the difference Fourier synthesis and fixed on their positions with a common isotropic thermal parameter.

Tables 1−4 contain selected crystallographic data, fractional atomic coordinates, and equivalent isotropic thermal parameters of **2**, **5**, and **9**.[13]

Preparation of Compounds. [RuCl$_2$(PPr$_3$)$_3$] (1). PPr$_3$ (5.6 mL, 28 mmol) was added to a suspension of [RuCl$_2$(PPh$_3$)$_3$] (3.84 g, 4 mmol) in 100 mL of hexane and stirred for 3 d. The resultant green solution was filtered and evaporated to dryness. The viscous residue was dissolved in 30 mL of CH$_2$Cl$_2$ and filtered over 10 g of SiO$_2$. The SiO$_2$ was rinsed with CH$_2$Cl$_2$ until the washing CH$_2$Cl$_2$ became nearly colorless, the absorbed product was subsequently eluted with 40 mL of MeOH. The dark yellow solution was evaporated to dryness, and the orange residue was recrystallized from 30 mL of hexane (+20 → −78 °C). **1** precipitated as yellow microcrystals which were collected and dried in vacuo. Yield: 1.14 g (43%). Anal. Calcd for C$_{27}$H$_{63}$RuP$_3$Cl$_2$ (M_r = 652.68): C, 49.69; H, 9.73. Found: C, 50.20; H, 9.28. IR (KBr): ν(CH) = 2956, 2867 cm^{-1}; δ(PC) = 1076 cm^{-1}.

[Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (2). (a) From [RuCl$_2$(PPr$_3$)$_3$] (1). H$_2$'S$_2$N$_2$H$_2$' (155 mg, 0.51 mmol) and LiOMe (45 mg, 1.18 mmol) were added to a yellow solution of [RuCl$_2$(PPr$_3$)$_3$] (335 mg, 0.51 mmol) in 50 mL of MeOH and stirred for 1 d in the course of which yellow microcrystals of **2** precipitated. They were collected, washed with 30 mL of MeOH, and dried in vacuo. Yield: 250 mg (70%).

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Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^{-1}$ pm^2) of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	2263(1)	1189(1)	3092(1)	21(1)
S(1)	570(1)	2152(1)	3930(1)	28(1)
S(2)	4057(1)	42(1)	2629(1)	26(1)
N(1)	3226(4)	1440(4)	4351(3)	25(1)
N(2)	1943(4)	−413(4)	4134(3)	26(1)
C(15)	2631(5)	2379(4)	4854(3)	27(2)
C(14)	3310(5)	2877(5)	5436(4)	32(2)
C(13)	2749(6)	3746(5)	5925(4)	39(2)
C(12)	1523(6)	4094(5)	5838(4)	37(2)
C(11)	844(5)	3590(5)	5264(4)	32(2)
C(10)	1404(5)	2716(4)	4742(3)	28(2)
C(25)	2660(5)	−1464(4)	3864(3)	24(2)
C(24)	2350(5)	−2570(5)	4308(4)	33(2)
C(23)	3014(6)	−3553(5)	4067(4)	41(2)
C(22)	4023(6)	−3447(5)	3406(4)	40(2)
C(21)	4339(5)	−2351(5)	2971(4)	31(2)
C(20)	3673(5)	−1345(4)	3195(3)	25(2)
C(16)	3410(5)	310(5)	5032(4)	28(2)
C(26)	2232(5)	−236(5)	5136(3)	30(2)
P(1)	2819(1)	2867(1)	2134(1)	27(1)
C(31)	4063(5)	3491(5)	2603(4)	34(2)
C(32)	5316(5)	2792(5)	2613(4)	39(2)
C(33)	6213(6)	3263(6)	3167(5)	54(3)
C(34)	1660(6)	4130(5)	1887(5)	49(2)
C(35)	1597(10)	5114(10)	2311(11)	142(7)
C(36)	706(9)	6135(7)	2033(7)	90(4)
C(37)	3431(5)	2766(5)	871(4)	34(2)
C(38)	3937(7)	3817(6)	239(4)	56(3)
C(39)	4129(8)	3704(6)	−831(5)	65(3)
P(2)	1141(1)	686(1)	1936(1)	26(1)
C(41)	−44(5)	−226(5)	2519(4)	32(2)
C(42)	−912(5)	−606(6)	1854(4)	39(2)
C(43)	−2018(7)	−1069(7)	2409(5)	65(3)
C(44)	1880(6)	−316(6)	1109(5)	46(2)
C(45)	2814(7)	120(6)	332(5)	51(2)
C(46)	3424(7)	−861(7)	−202(6)	63(3)
C(47)	249(5)	1807(5)	1092(4)	34(2)
C(48)	−845(6)	2450(6)	1557(5)	44(2)
C(49)	−1453(7)	3458(7)	873(6)	66(3)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensors.

(b) From [RuCl$_2$(PPh$_3$)$_3$]. PPr$_3$ (4 mL, 20 mmol) was added to a red-brown suspension of [RuCl$_2$(PPh$_3$)$_3$] (3.39 g, 3.54 mmol) in 50 mL of hexane and stirred for 12 h. The resultant green solution was filtered and evaporated to dryness, and the green residue was suspended in 50 mL of MeOH. H$_2$'S$_2$N$_2$H$_2$' (980 mg, 3.54 mmol) and LiOMe (270 mg, 7.1 mmol) were added, and the reaction mixture was stirred for 24 h. The color of the suspension turned from green to yellow, and microcrystalline **2** formed. It was separated, washed with 30 mL of MeOH, and dried in vacuo. Yield: 2 g (81%). Anal Calcd for $C_{32}H_{56}RuN_2P_2S_2$ ($M_r = 695.95$): C, 55.23; H, 8.11; N, 4.02; S, 9.21. Found: C, 55.42; H, 8.25; N, 4.03; S, 9.17. IR (KBr): ν(NH) = 3297, 3272 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 7.4−6.8 (m, 8 H, C$_6$H$_4$), 4.8 (s, 2 H, NH), 3.45−2.65 (m, 4 H, C$_2$H$_4$), 1.65−0.95 (m, 42 H, P(C$_3$H$_7$)). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 67.94 MHz): 156, 148, 131, 127, 125, 120 (C$_6$H$_4$), 56 (C$_2$H$_4$), 31, 18, 16 (P(C$_3$H$_7$)). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 109.38 MHz): 27.5 (s, P(C$_3$H$_7$)).

[RuCl(H)(CO)(PCy$_3$)$_2$] (3). PCy$_3$ (6.1 g, 21.8 mmol) was added to a dark-red solution of RuCl$_3$·3H$_2$O (955 mg, 3.66 mmol) in 50 mL of MeOH. The resultant red brown suspension was heated under reflux for 2 h in the course of which it became dark yellow. After this cooled to room temperature, a yellow powder of **3** was collected, washed with 10 mL of MeOH and 10 mL of Et$_2$O, and dried in vacuo. Yield: 2 g (80%). Anal. Calcd for $C_{37}H_{67}RuOP_2Cl$ ($M_r = 726{,}4$): C, 61.18; H, 9.3. Found: C, 60.64; H, 9.7. IR (KBr): ν(RuH) = 2103 cm^{-1}; ν(CO) = 1905 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ [ppm], 270 MHz): 2.5−1.0 (m, 66 H, P(C$_6$H$_{11}$)), −24.1 (t, $^2J(^1H^{31}P) = 18$ Hz, 1 H, RuH).

[Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')] (4). (a) From [Ru(Cl)(H)(CO)(PCy$_3$)$_2$] (3). [Ru(Cl)(H)(CO)(PCy$_3$)$_2$] (450 mg, 0.62 mmol) was added to a

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^{-1}$ pm^2) of [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	3154(1)	9022(1)	1477(1)	29(1)
P(1)	3643(1)	10336(1)	1186(1)	26(1)
S(1)	3359(2)	8405(1)	850(1)	34(1)
S(2)	4833(2)	8855(1)	1776(1)	35(1)
N(1)	1581(4)	8659(4)	1397(2)	33(2)
N(2)	2686(5)	9197(3)	2031(2)	33(2)
C(15)	1241(6)	8225(4)	1070(2)	37(2)
C(14)	131(6)	7919(5)	1014(2)	47(3)
C(13)	−173(7)	7534(6)	665(3)	55(3)
C(12)	575(7)	7418(5)	356(2)	50(3)
C(11)	1651(7)	7702(5)	404(2)	41(3)
C(10)	1976(6)	8090(4)	763(2)	34(2)
C(25)	3346(6)	9191(4)	2349(2)	34(2)
C(24)	3061(7)	9326(5)	2759(2)	47(3)
C(23)	3797(9)	9275(5)	3055(2)	55(3)
C(22)	4937(8)	9088(6)	2969(2)	57(3)
C(21)	5251(7)	8973(5)	2581(2)	44(2)
C(20)	4491(6)	9027(4)	2272(2)	38(2)
C(16)	924(6)	8760(5)	1750(2)	42(2)
C(26)	1463(6)	9292(5)	2066(2)	42(3)
C(50)	4836(6)	10297(4)	828(2)	30(2)
C(51)	5237(6)	11210(4)	703(2)	38(2)
C(52)	6116(7)	11119(5)	380(2)	42(3)
C(53)	7067(6)	10544(5)	518(2)	41(2)
C(54)	6668(6)	9631(5)	629(2)	40(2)
C(55)	5790(6)	9704(4)	954(2)	34(2)
C(60)	2476(6)	10845(4)	885(2)	30(2)
C(61)	2454(6)	10636(5)	446(2)	43(3)
C(62)	1519(7)	11122(5)	228(2)	46(3)
C(63)	390(6)	10933(6)	405(2)	47(3)
C(64)	428(6)	11144(5)	845(2)	45(3)
C(65)	1328(6)	10627(5)	1059(2)	38(2)
C(70)	3971(6)	11261(4)	1530(2)	30(2)
C(71)	5048(6)	11143(4)	1770(2)	36(2)
C(72)	5318(7)	11967(5)	2013(2)	46(3)
C(73)	4360(8)	12178(5)	2292(2)	50(3)
C(74)	3294(7)	12281(5)	2065(2)	42(3)
C(75)	3033(6)	11473(4)	1813(2)	33(2)
Ru(2)	4716(1)	15041(1)	1627(1)	32(1)
P(2)	6142(2)	15452(1)	1213(1)	30(1)
S(3)	4250(2)	13862(1)	1233(1)	39(1)
S(4)	5878(2)	14437(1)	2100(1)	40(1)
N(3)	3323(5)	15550(4)	1404(2)	35(2)
N(4)	4495(5)	15944(4)	2035(2)	34(2)
C(35)	2719(6)	15143(5)	1122(2)	39(2)
C(34)	1764(7)	15509(5)	936(3)	49(3)
C(33)	1202(7)	15015(7)	651(3)	58(3)
C(32)	1541(7)	14169(7)	550(3)	65(4)
C(31)	2468(7)	13799(5)	724(3)	50(3)
C(30)	3043(6)	14272(4)	1012(2)	38(2)
C(45)	5031(6)	15949(5)	2395(2)	37(2)
C(44)	4910(7)	16590(5)	2695(2)	44(3)
C(43)	5525(8)	16540(6)	3043(2)	56(3)
C(42)	6242(8)	15857(7)	3104(2)	62(3)
C(41)	6383(7)	15200(5)	2823(2)	49(3)
C(40)	5787(6)	15239(5)	2460(2)	41(2)
C(36)	3052(7)	16409(5)	1566(2)	43(3)
C(46)	3572(7)	16564(5)	1961(2)	47(3)
C(80)	5570(6)	16141(4)	790(2)	33(2)
C(81)	4897(6)	15575(5)	503(2)	35(2)
C(82)	4247(6)	16155(5)	216(2)	45(3)
C(83)	5048(8)	16719(5)	−26(2)	50(3)
C(84)	5749(7)	17285(5)	252(2)	46(3)
C(85)	6377(6)	16734(5)	563(2)	42(3)
C(90)	6917(6)	14517(4)	975(2)	35(2)
C(91)	7952(6)	14780(5)	741(2)	43(3)
C(92)	8400(6)	13972(5)	515(2)	47(3)
C(93)	8648(7)	13215(5)	796(2)	50(3)
C(94)	7620(7)	12971(5)	1030(2)	48(3)
C(95)	7179(6)	13752(4)	1258(2)	38(2)
C(100)	7199(6)	16204(4)	1434(2)	36(2)
C(101)	7974(7)	15816(5)	1740(2)	48(3)
C(102)	8831(7)	16495(5)	1882(2)	50(3)
C(103)	8259(7)	17315(5)	2031(3)	55(3)
C(104)	7500(6)	17713(5)	1727(2)	47(3)
C(105)	6638(6)	17047(5)	1593(2)	39(2)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensors.

Table 4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^{-1}$ pm^2) of [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (**9**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	0	1425(1)	0	31(1)
Br(1)	811(1)	1457(1)	1639(1)	50(1)
Br(2)	−526(1)	−1151(1)	1600(1)	54(1)
S(1)	1209(2)	1220(2)	−199(2)	38(1)
S(2)	−1144(2)	1659(2)	318(2)	37(1)
N(1)	47(6)	78(6)	154(6)	39(3)
N(2)	−775(5)	1077(6)	−1306(6)	35(3)
C(15)	789(8)	−334(8)	205(9)	48(5)
C(14)	919(11)	−1153(10)	448(12)	71(8)
C(13)	1631(10)	−1536(11)	493(12)	75(8)
C(12)	2186(10)	−1056(12)	278(12)	76(8)
C(11)	2078(9)	−231(10)	61(11)	67(7)
C(10)	1355(7)	137(8)	−1(8)	42(4)
C(25)	−1607(6)	1231(8)	−1428(8)	39(4)
C(24)	−2153(8)	1120(9)	−2272(9)	55(5)
C(23)	−2949(9)	1254(12)	−2390(10)	64(6)
C(22)	−3190(8)	1488(12)	−1702(10)	70(6)
C(21)	−2672(7)	1599(10)	−867(10)	55(5)
C(20)	−1866(7)	1451(8)	−717(8)	42(4)
C(16)	−618(8)	−278(8)	−582(9)	47(5)
C(26)	−644(8)	168(8)	−1427(8)	46(5)
C(1)	1228(8)	1357(10)	−1328(9)	56(5)
C(35)	2663(10)	1663(12)	−841(13)	76(8)
C(34)	3404(14)	1564(19)	−901(20)	129(14)
C(33)	3496(22)	1072(27)	−1497(28)	174(27)
C(32)	2924(26)	629(20)	−2118(22)	154(24)
C(31)	2138(15)	715(12)	−2048(14)	101(12)
C(30)	2021(11)	1222(10)	−1423(12)	61(7)
C(2)	−1330(8)	883(9)	1077(9)	53(5)
C(45)	−1946(12)	1749(11)	1968(12)	79(8)
C(44)	−2609(19)	1929(16)	2231(16)	112(13)
C(43)	−3266(16)	1524(18)	1910(19)	105(13)
C(42)	−3309(12)	904(17)	1378(16)	100(11)
C(41)	−2704(11)	670(11)	1075(12)	75(8)
C(40)	−2005(8)	1107(8)	1374(8)	40(4)
P(1)	−18(2)	2834(2)	−264(2)	34(1)
C(55)	1568(7)	3108(8)	304(9)	49(5)
C(54)	2284(8)	3432(11)	289(11)	65(6)
C(53)	2288(12)	3949(12)	−403(14)	83(9)
C(52)	1599(12)	4178(11)	−1061(12)	77(8)
C(51)	909(9)	3849(10)	−1020(9)	63(6)
C(50)	885(7)	3298(8)	−375(8)	39(4)
C(65)	−328(9)	4437(9)	259(10)	61(6)
C(64)	−461(10)	5008(9)	836(12)	70(7)
C(63)	−454(9)	4772(10)	1668(12)	66(6)
C(62)	−294(9)	3998(14)	1905(10)	72(7)
C(61)	−185(8)	3377(9)	1358(9)	50(5)
C(60)	−209(6)	3610(8)	502(7)	42(4)
C(75)	−1517(8)	3378(9)	−1282(9)	51(5)
C(74)	−2127(9)	3500(10)	−2087(13)	66(7)
C(73)	−1990(11)	3362(10)	−2870(11)	71(7)
C(72)	−1301(9)	3096(8)	−2923(9)	53(5)
C(71)	−685(7)	2955(7)	−2121(8)	41(4)
C(70)	−780(7)	3108(7)	−1302(8)	38(4)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensors.

pale yellow suspension of H$_2$'S$_2$N$_2$H$_2$' (170 mg, 0.61 mmol) and NaN(SiMe$_3$)$_2$ (140 mg, 0.76 mmol) in 40 mL of THF. Under evolution of gas, a dark-blue solution containing a few undissolved particles resulted. The solution was filtered and evaporated to dryness. The resultant light-blue residue was stirred for 2 d in 40 mL of hexane, collected, dried in vacuo, and identified as a mixture of [Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')] and [Ru(PCy$_3$)('S$_2$N$_2$')] by ^{1}H NMR spectroscopy. Yield: 300 mg (71%).

(b) From [Ru(CO)$_2$('S$_2$N$_2$H$_2$')] (6). A solution of [Ru(CO)$_2$('S$_2$N$_2$H$_2$')] (1.8 g, 4.17 mmol) and PCy$_3$ (1.4 g, 5.0 mmol) in 200 mL of THF was UV-irradiated for 11 h at 30 °C, in the course of which the color of the solution changed from yellow to green. The solution was evaporated to dryness, and the resultant residue was rinsed with Et$_2$O and dried in vacuo. Recrystallization from CH$_2$Cl$_2$ at −78 °C yielded pale yellow [Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')]·0.5CH$_2$Cl$_2$. Yield: 1 g (36%). Anal. Calcd for C$_{33.5}$H$_{48}$RuN$_2$OPS$_2$Cl (M_r = 726.4 = [Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')]·0.5CH$_2$Cl$_2$): C, 55.4; H, 6.7; N, 3.9; S, 8.83. Found: C, 55.9; H, 6.7; N, 4.1; S, 9.24. IR (KBr): ν(NH) = 3125 cm^{-1}; ν(CO) = 1927 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 7.5−6.8 (m, 8 H, C$_6$H$_4$), 5.35 (s, 1 H, NH), 5.1 (s, 1 H, NH,), 3.7-2.65 (m, 4 H, C$_2$H$_4$), 2.0−1.0 (m, 33 H, P(C$_6$H$_{11}$)). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 67.94 MHz): 205 (CO), 151−122 (C$_6$H$_4$), 55 (C$_2$H$_4$), 37, 30, 28, 27 (P(C$_6$H$_{11}$)). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 109.38 MHz): 46 (s, P(C$_6$H$_{11}$)).

[Ru(PCy$_3$)('S$_2$N$_2$')] (5). (a) From [RuCl$_2$(DMSO)$_4$]. H$_2$'S$_2$N$_2$H$_2$' (550 mg, 2 mmol), LiOMe (160 mg, 4 mmol) and PCy$_3$ (2.4 g, 8.6 mmol) were added to [RuCl$_2$(DMSO)$_4$] (1 g, 2 mmol) in 50 mL of MeOH. The resultant green suspension was heated under reflux for 12 h and subsequently stirred for 2 d at room temperature. The resultant gray-blue precipitate was collected, washed with 50 mL of MeOH and 50 mL of hexane, and dried in vacuo. Yield: 500 mg (38%).

(b) From RuCl$_3$·3H$_2$O. A yellow suspension of H$_2$'S$_2$N$_2$H$_2$' (2.1 g, 7.6 mmol) and LiOMe (580 mg, 15.2 mmol) in 125 mL of MeOH was combined with RuCl$_3$·3H$_2$O (2 g, 7.6 mmol) and PCy$_3$ (10 g, 35.7 mmol) and heated under reflux for 5 h in the course of which the color of the suspension changed to gray and finally to dark-blue. After this was cooled to room temperature, the precipitated dark blue **5** was collected, washed with 50 mL of MeOH and 100 mL of hexane, and dried in vacuo. Yield: 3.4 g (75%). Anal. Calcd for C$_{32}$H$_{45}$RuN$_2$PS$_2$ (M_r = 653.9): C, 58.79; H, 6.94; N, 4.28. Found: C, 59.18; H, 6.98; N, 4.37. ^{1}H NMR (CDCl$_3$, δ [ppm], 270 MHz): 8.0−6.9 (m, 8 H, C$_6$H$_4$), 5.9 (m, 2 H, C$_2$H$_4$), 5.1 (m, 2 H, C$_2$H$_4$), 2.0−0.6 (m, 33 H, P(C$_6$H$_{11}$)). ^{13}C{^{1}H} NMR (CDCl$_3$, δ [ppm], 67.94 MHz): 162, 161, 130, 124, 118, 114 (C$_6$H$_4$), 63 (C$_2$H$_4$), 41, 29, 27, 26 (P(C$_6$H$_{11}$)). ^{31}P{^{1}H} NMR (CDCl$_3$, δ [ppm], 109.38 MHz): 68 (s, P(C$_6$H$_{11}$)).

[Ru(CO)$_2$('S$_2$N$_2$H$_2$')] (6). CO was bubbled through a dark-red solution of RuCl$_3$·3H$_2$O (3.5 g, 13.3 mmol) in 50 mL of 2-methoxyethanol at 125 °C, until the color of the solution had changed to pale-yellow. The solvent was evaporated in vacuo, the resultant viscous residue was dissolved in 50 mL of MeOH, and H$_2$'S$_2$N$_2$H$_2$' (3.7 g, 13.3 mmol) and LiOMe (1 g, 26 mmol) were added. **6** slowly precipitated as a pale-yellow powder from the resultant yellow solution and was collected after 1 d, washed with 30 mL of MeOH and 30 mL of hexane, dried in vacuo, and identified by IR spectroscopy. Yield: 4.3 g (75%). IR (KBr): ν(CO) = 2050, 1979 cm^{-1}.

[Ru(CO)(PPr$_3$)('S$_2$N$_2$H$_2$')] (7). A solution of [Ru(CO)$_2$('S$_2$N$_2$H$_2$')] (570 mg, 1.32 mmol) and PPr$_3$ (0.27 mL, 1.32 mmol) in 75 mL of THF was UV-irradiated for 11 h at 30 °C , after which time the IR spectrum of the solution showed two weak ν(CO) bands of unreacted [Ru(CO)$_2$('S$_2$N$_2$H$_2$')] and an intensive ν(CO) band at 1930 cm^{-1} with a shoulder at 1945 cm^{-1}. The solution was filtered and evaporated to dryness, and the resultant residue was redissolved in 10 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was layered with 30 mL of hexane and cooled to −78 °C. A brown oil separated, which was collected after 2 d and dried in vacuo, in the course of which it solidified to give lustrous golden-brown microcrystals of [Ru(CO)(PPr$_3$)('S$_2$N$_2$H$_2$')]. It still contained minor amounts of [Ru(CO)$_2$('S$_2$N$_2$H$_2$')], identified by IR spectroscopy. Yield: 150 mg (21%). Anal. Calcd for C$_{24}$H$_{35}$RuN$_2$OPS$_2$ (M_r = 563.73): C, 51.13; H, 6.26; N, 4.97. Found: C, 50.57; H, 6.54; N, 4.68. IR (KBr): ν(CO) = 1934 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 7.5−6.8 (m, 8 H, C$_6$H$_4$), 5.5 (s, 1 H, NH); 4.8 (s, 1 H, NH), 3.5 (m, 2 H, C$_2$H$_4$), 2.8 (m, 2 H, C$_2$H$_4$), 1.8−0.9 (m, 21 H, P(C$_3$H$_7$)). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 109.38 MHz): 31 (s, P(C$_3$H$_7$)).

[Ru(Br)(PPh$_3$)('Et$_2$S$_2$N$_2$H$_2$')]Br (8). A yellow-green suspension of [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] (2015 mg, 2.24 mmol) and C$_2$H$_5$Br (20 mL, 268 mmol) in 20 mL of THF was heated under reflux for 16 h, during which time a yellow solution formed, and pale yellow **8** slowly precipitated. **8** was collected at room temperature, washed with 20 mL of hexane, and dried in vacuo. Yield: 1240 mg (65%). Anal. Calcd for C$_{36}$H$_{39}$RuS$_2$N$_2$PBr$_2$ (M_r = 855.7): C, 50.53; H, 4.59; N, 3,27. Found: C, 51.05; H, 4.57; N, 2.69. IR (KBr): ν(NH) = 3160 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 8.0−7.0 (m, 23 H, C$_6$H$_4$ and P(C$_6$H$_5$)), 6.6 (s, 1 H, NH), 5.95 (s, 1 H, NH), 4.8−2.7 (m, 8 H, CH$_2$ and C$_2$H$_4$), 1.85 (t, 3 H, CH$_3$), 1.1 (t, 3 H, CH$_3$).

[Ru(Br)(PPh$_3$)(‘(PhCH$_2$)$_2$S$_2$N$_2$H$_2$’)]Br (9). A yellow-green suspension of [Ru(PPh$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (540 mg, 0.6 mmol) and benzyl bromide, PhCH$_2$Br, (2 mL, 16.7 mmol) in 20 mL of THF was heated under reflux for 5 h, during which time the color of the suspension changed from yellow-green to yellow. The yellow solid was separated at room temperature, washed with 10 mL of THF and 10 mL of MeOH, and dried in vacuo. Yield: 550 mg (96%). Anal. Calcd for $C_{46}H_{43}Br_2N_2PRuS_2$ (M_r = 980.12): C, 56.39; H, 4.42; N, 2.87. Found: C, 56.57; H, 4.76; N, 2.49. IR (KBr): ν(NH) = 3250 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 8.0−6.8 (m, 32 H, C$_6$H$_4$ and P(C$_6$H$_5$)), 6.6 (s, 1 H, NH), 6.25 (d, 1 H, C$_6$H$_5$), 6.1 (s, 1 H, NH), 5.2−5.05 (m, 2 H, CH$_2$), 4.45 (d, 1 H, CH$_2$), 3.7−2.7 (m, 5 H, CH$_2$ and C$_2$H$_4$).

Reaction of [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (4) with *n*-BuLi and Air. A 1 mL aliquot of a 1.6 M solution of *n*-BuLi in hexane (1.6 mmol) was added to a suspension of [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (340 mg, 0.5 mmol) in 50 mL of THF at −78 °C, whereupon the color turned from yellow to brown. When the suspension was warmed up to room temperature, a red violet solution formed whose IR spectrum showed two ν(CO) bands at 1913 and 1769 cm^{-1}. When air was bubbled through the solution, the color instantaneously turned to dark-blue due to formation of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] **5**. Also the formation of minor amounts of [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] **4** (ν(CO): 1928 cm^{-1}) could be detected IR spectroscopically.

Reaction of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (5) with HCOOH and CO. A 0.12 mL aliquot of a 98% solution of HCOOH in H$_2$O (3 mmol) was added to the blue solution of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (500 mg, 0.76 mmol) in a mixture of 50 mL of THF and 10 mL of MeOH. The resultant solution was saturated with CO and stirred for 17 h under CO atmosphere. A yellow-brown solution formed, which was filtered and evaporated to dryness. The resultant residue was washed with 40 mL of MeOH and 20 mL of Et$_2$O, dried in vacuo, and identified as a mixture of [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (**4**) and [Ru(CO)$_2$(‘S$_2$N$_2$H$_2$’)] (**6**) by IR spectroscopy.

[Ru(PPr$_3$)$_2$(gma)] (10). (a) From [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (2) and CO. CO was bubbled through a solution of [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] **2** (380 mg, 0.55 mmol) in 50 mL of a mixture of MeOH/THF (1:1) for 1 h at 0 °C and for additional 2 h at room temperature. The color of the solution turned from yellow-green to green, but IR spectroscopically no ν(CO) could be detected. When the solution was subsequently stirred under an atmosphere of CO, red microcrystalline **10** slowly precipitated. It was separated after 12 h, washed with 20 mL of MeOH and 20 mL of hexane, and dried in vacuo. Yield: 210 mg (55%).

(b) From [RuCl$_2$(PPr$_3$)$_3$] (1) and Li$_2$gma. A green suspension of [RuCl$_2$(PPr$_3$)$_3$] (600 mg, 0.88 mmol) in 50 mL of MeOH was combined with H$_2$-gma (240 mg, 0.9 mmol) and LiOMe (70 mg, 1.8 mmol) and stirred for 1 d to give a red solution which was filtered. In the course of 1 d red plates of **10** crystallized from the filtrate, which were separated. Crystallization of **10** was completed by reducing the mother liquor in volume to 25 mL and cooling to 0 °C. The combined crystals were washed with 10 mL of hexane and dried in vacuo. Yield: 400 mg (66%). Anal. Calcd for $C_{32}H_{52}RuN_2P_2S_2$ (M_r = 691.9): C, 55.55; H, 7.57; N, 4.05; S, 9.27. Found: C, 55.94; H, 7.72; N, 3.98; S, 8.80. ^{1}H NMR (CD$_2$Cl$_2$, δ [ppm], 270 MHz): 7.35 (s, 2 H, C$_2$H$_2$), 7.25−6.6 (m, 8 H, C$_6$H$_4$), 2.0−0.7 (m, 42 H, P(C$_3$H$_7$)). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ [ppm], 109.38 MHz): 14 (s, P(C$_3$H$_7$)).

Reaction of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (5) with PMe$_3$. (a) In THF/MeOH. When PMe$_3$ (0.036 mL, 0.35 mmol) was added to a blue solution of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (**5**) (230 mg, 0.35 mmol) in 50 mL of THF/MeOH (1:1), the color instantaneously turned to red and a red-brown precipitate formed. It was separated after 3 h, washed with 10 mL of hexane, dried in vacuo, and identified as a mixture (1:1) of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (**5**) and [Ru(PMe$_3$)$_2$(gma)] (**11**) by NMR spectroscopy. Yield: 170 mg.

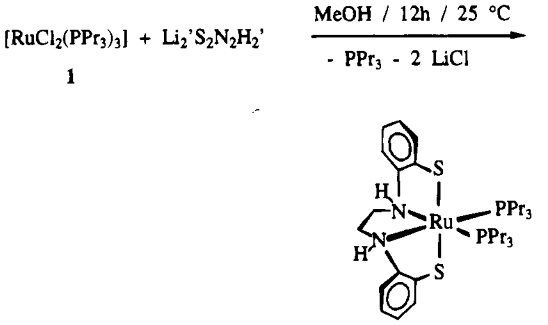
(b) In THF. PMe$_3$ (0.036 mL, 0.35 mmol) was added to the blue solution of [Ru(PCy$_3$)(‘S$_2$N$_2$’)] **5** (230 mg, 0.35 mmol) in THF. In this case, due to the good solubility of **5** in THF, no color change could be detected and the solution stayed deep-blue. However, when the solution was evaporated to dryness after 3 h, a red-violet residue resulted, which was washed with 20 mL of hexane, dried in vacuo, and identified as 1:1 mixture of **5** and **11** by NMR spectroscopy.

[Ru(PMe$_3$)$_2$(gma)] (11) from [Ru(NO)(PMe$_3$)(‘S$_2$N$_2$H’)]. A solution of [Ru(NO)(PMe$_3$)(‘S$_2$N$_2$H’)] (600 mg, 1.25 mmol) and PMe$_3$ (ca. 1 mmol) in 35 mL of THF was layered with 30 mL of MeOH, and cooled to −30 °C. After 3 d, greenish-golden crystals had separated, which were collected, washed with 10 mL of MeOH and 5 mL of Et$_2$O, and dried in vacuo. Yield: 190 mg (29%). Anal. Calcd for $C_{20}H_{30}RuN_2S_2P_2$ (M_r = 525.6): C, 45.70; H, 5.75; N, 5.33. Found: C, 45.77; H, 5.66; N, 4.83. MS (FD): *m/z* = 527 (M$^+$). IR (KBr): δ(PC) = 942 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ [ppm], 270 MHz): 7.0 (b, 2 H, C$_2$H$_2$), 7.2−6.5 (m, 8 H, C$_6$H$_4$), 1.4 (t, 18 H, P(CH$_3$)). ^{31}P{^{1}H} NMR (DMSO-d_6, δ [ppm], 109.38 MHz): 2 (s, P(CH$_3$)).

Results

Syntheses. Primary target compounds were [Ru(PR$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] complexes with R = Pr and Cy. [RuCl$_2$(PPr$_3$)$_3$] (**1**) as precursor for [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (**2**) formed in 40% yield according to eq 2. In a second step, **1** was converted into yellow-red [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (**2**) according to eq 3. **2** could be obtained in yields of ca. 80% referred to [RuCl$_2$(PPh$_3$)$_3$] by evaporating the reaction mixture formed according to eq 2 and combining the resultant residue directly with Li$_2$‘S$_2$N$_2$H$_2$’ in MeOH. **2** dissolves in THF and CH$_2$Cl$_2$, and is insoluble in hexane or MeOH.

$$[RuCl_2(PPh_3)_3] + 7PPr_3 \xrightarrow{\text{hexane/25 °C/12 h}} \underset{\mathbf{1}}{[RuCl_2(PPr_3)_3]} + \text{other products} \quad (2)$$



2 (3)

It was not possible to obtain the PCy$_3$ derivative [RuCl$_2$(PCy$_3$)$_3$] by an analogous synthesis. A reaction between PCy$_3$ and [RuCl$_2$(PPh$_3$)$_3$] could only be observed when MeOH was used as solvent. The resultant major product, however, was [Ru(Cl)(H)(CO)(PCy$_3$)$_2$] (**3**), which formed according to eq 4.

$$[RuCl_2(PPh_3)_3] + 7PCy_3 \xrightarrow{\text{MeOH/1 h/64 °C}} \underset{\mathbf{3}}{[Ru(Cl)(H)(CO)(PCy_3)_2]} + \text{other products} \quad (4)$$

The resultant **3** precipitated from the reaction mixture as an orange solid and was heavily contaminated by other products. **3**, which had previously been described,[14] could now be obtained in high yield (80%) and purity according to eq 5.

$$RuCl_3{\cdot}3H_2O + 6PCy_3 \xrightarrow[\text{64 °C/2 h}]{\text{MeOH}} \underset{\mathbf{3}}{[Ru(Cl)(H)(CO)(PCy_3)_2]} \quad (5)$$

According to eq 6, the reaction of **3** with H$_2$‘S$_2$N$_2$H$_2$’ in presence of one equivalent of NaN(SiMe$_3$)$_2$ yielded [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (**4**) as major product and, in addition, the

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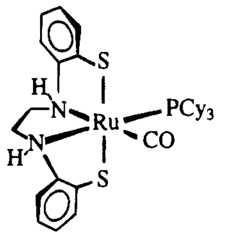
(14) Moers, F. G.; Langhout, J. P. *Rec. Trav. Chim. Pays-Bas.* **1971**, *91*, 591.

ruthenium(IV) complex [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**) in ca. 10% yield. The formation of **5** could be observed visually by the

[Ru(Cl)(H)(CO)(PCy$_3$)$_2$] + H$_2$'S$_2$N$_2$H$_2$' + NaN(SiMe$_3$)$_2$

3

$\xrightarrow{\text{THF / 12h / 25 °C}}$



(6)

4

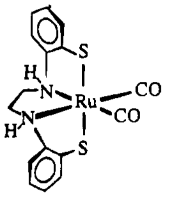
+ [Ru(PCy$_3$)('S$_2$N$_2$')] **5**

+ other products

colorchange from yellow to blue, when [Ru(Cl)(H)(CO)(PCy$_3$)$_2$] (**3**) was added to the suspension of H$_2$'S$_2$N$_2$H$_2$' and NaN(SiMe$_3$)$_2$ in THF. The isolated mixture of **4** and **5** was a light blue powder, the components of which could not be separated.

Synthesis of pure **4** succeeded photochemically from [Ru(CO)$_2$('S$_2$N$_2$H$_2$')] (**6**) and PCy$_3$. The required **6** was obtained as pale-yellow powder in ca. 75% yield by a one-pot reaction[15] and gave **4** according to eqs 7 and 8. IR spectroscopy allowed

RuCl$_3$ · 3 H$_2$O + CO + Li$_2$'S$_2$N$_2$H$_2$' $\xrightarrow[\text{7h / 125 °C}]{\text{2-methoxyethanol}}$



6 (7)

$$[\mathrm{Ru(CO)_2('S_2N_2H_2')}] + \mathrm{PCy_3} \xrightarrow[\text{15 h/30 °C}]{\mathrm{THF}/h\nu}$$

6

[Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')] + other products (8)

4

monitoring of the photolysis and showed the decrease of **6** (ν(CO): 2037, 1972 cm^{-1}) and simultaneous formation of **4** (1927 cm^{-1}). The isolated crude product exhibited an additional ν(CO) band at 1954 cm^{-1} which disappeared when **4** was recrystallized.

[Ru(CO)(PCy$_3$)('S$_2$N$_2$H$_2$')] (**4**) proved extremely stable. Neither extended heating nor prolonged UV irradiation in solution led to the removal of CO, PCy$_3$ or to decomposition. Even in the presence of excessive PCy$_3$, no substitution of the remaining CO ligand and formation of [Ru(PCy$_3$)$_2$('S$_2$N$_2$H$_2$')] took place.

The analogous PPr$_3$ complex [Ru(CO)(PPr$_3$)('S$_2$N$_2$H$_2$')] (**7**) was also obtained photochemically according to eq 9 and isolated as golden-brown microcrystals. Because none of the

$$[\mathrm{Ru(CO)_2('S_2N_2H_2')}] + \mathrm{PPr_3} \xrightarrow[\text{30 °C/11 h}]{\mathrm{THF}/h\nu/-\mathrm{CO}}$$

6

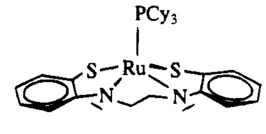
[Ru(CO)(PPr$_3$)('S$_2$N$_2$H$_2$')] (9)

7

described attempts yielded the target complex [Ru(PCy$_3$)$_2$('S$_2$N$_2$H$_2$')], we finally tried to obtain it by a direct synthesis according to eq 10.

RuCl$_3$ · 3 H$_2$O + 5 PCy$_3$ + Li$_2$'S$_2$N$_2$H$_2$' $\xrightarrow[\text{64 °C / 5h}]{\text{MeOH}}$

(10)



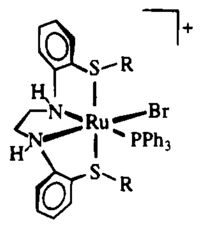
5

+ other products

Contrary to our expectations, however, this reaction gave the ruthenium(IV) complex [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**) in yields of about 70%. **5** was isolated as dark-blue crystals and formed also when the ruthenium(II) complex [RuCl$_2$(DMSO)$_4$] was used as starting complex instead of RuCl$_3$·3H$_2$O. **5** contains the 'S$_2$N$_2$'$^{4-}$ ligand having amide donor functions resultant from 4-fold deprotonation of H$_2$'S$_2$N$_2$H$_2$'. **5** is diamagnetic, well soluble in CH$_2$Cl$_2$ and THF, moderately soluble in Et$_2$O and hexane, and insoluble in MeOH and H$_2$O.

In further experiments we tested whether alkylation of the thiolato S atoms of [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')][6] would labilize the PPh$_3$ ligands which are inert toward substitution in neutral media. According to eq 11, [Ru(Br)(PPh$_3$)('Et$_2$S$_2$N$_2$H$_2$')]Br (**8**) and [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (**9**) formed and precipitated from the reaction mixtures as pale-yellow powders. **8** and **9** were characterized by elemental analyses and spectroscopy, **8** also by X-ray structure analysis, but they proved almost as inert as [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] toward substitution.

[Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] $\xrightarrow[\text{THF / 12h}]{\text{+ exc. RBr / }\Delta\text{T}}$



Br$^-$ (11)

R = Et **8**, PhCH$_2$ **9**

X-ray Structure Analyses of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (2), [Ru(PCy$_3$)('S$_2$N$_2$')] (5) and [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]Br (9). The molecular structure of **2** is shown in Figure 1, selected distances and angles are listed in Table 5. The ruthenium center in [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**) is pseudooctahedrally surrounded by two sulfur, two nitrogen, and two phosphorus atoms. As in the analogous complex [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')],[6] amino N and phosphorus donors occupy cis positions, and thiolato S donors occupy trans positions. The average Ru$-$S (239.0 pm) and Ru$-$N (219.2 pm) distances are similar to those in [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] ($\bar{d}$(Ru$-$S) = 237.3 pm, $\bar{d}$(Ru$-$N) = 216.5 pm) and indicate single bond character of the respective bonds. Average Ru$-$P distances and the (P$-$Ru$-$P) angles are slightly smaller in **2** ($\bar{d}$(Ru$-$P) = 229.0 pm, angle (P$-$Ru$-$P) = 96°) than in [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] ($\bar{d}$(Ru$-$P) = 232.6 pm, angle (P$-$Ru$-$P) = 103.5°) presumably because PPr$_3$ is smaller than PPh$_3$ with respect to size and cone angles. N$-$Ru$-$N angles in **2** (79.8°) and in [Ru(PPh$_3$)$_2$('S$_2$N$_2$H$_2$')] (79.5°) are almost identical.

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[15] Cf. Lindner, E.; Bader, A.; Mayer, H. A. *Z. Anorg. Allg. Chem.* **1991**, *598/599*, 235.

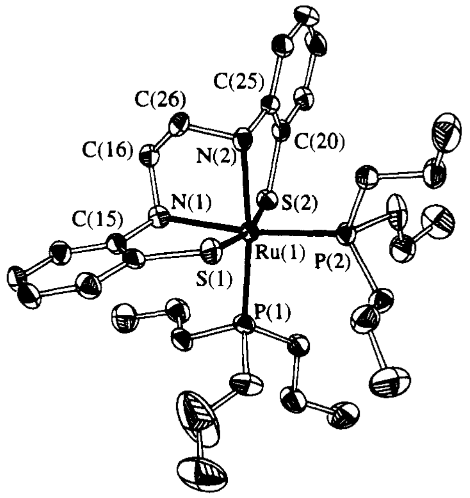

Figure 1. Molecular structure of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**) (H atoms omitted).

Table 5. Selected Distances (pm) and Angles (deg) of [Ru(PPr$_3$)$_2$('S$_2$N$_2$H$_2$')] (**2**)

Ru(1)−S(1)	240.4(2)	S(1)−Ru(1)−P(2)	95.7(1)
Ru(1)−S(2)	237.7(1)	N(1)−Ru(1)−P(2)	171.1(1)
Ru(1)−N(1)	218.9(5)	P(1)−Ru(1)−P(2)	96.0(1)
Ru(1)−N(2)	219.5(4)	Ru(1)−N(1)−C(16)	108.5(3)
Ru(1)−P(1)	228.5(2)	Ru(1)−N(2)−C(25)	113.0(3)
Ru(1)−P(2)	229.6(2)	C(25)−N(2)−C(26)	111.1(4)
S(1)−C(10)	177.0(6)	S(1)−Ru(1)−N(1)	82.5(1)
N(1)−C(15)	147.1(7)	S(1)−Ru(1)−N(2)	87.1(1)
N(1)−C(16)	147.9(6)	N(1)−Ru(1)−N(2)	79.8(2)
S(2)−C(20)	175.8(5)	S(2)−Ru(1)−P(1)	93.3(1)
N(2)−C(26)	150.0(7)	N(2)−Ru(1)−P(1)	172.1(1)
N(2)−C(25)	147.4(6)	N(2)−Ru(1)−P(2)	91.5(1)
C(16)−C(26)	151.1(8)	Ru(1)−N(1)−C(15)	113.9(3)
C(25)−C(20)	140.6(7)	C(15)−N(1)−C(16)	112.1(4)
C(15)−C(10)	138.2(8)	Ru(1)−N(2)−C(26)	107.3(3)

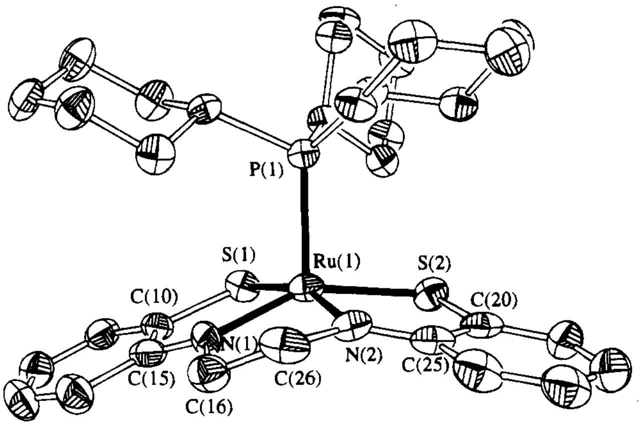

Figure 2. Molecular structure of [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**) (H atoms omitted).

Figure 2 shows the molecular structure of [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**). Table 6 lists selected distances and angles. (Because the two independent molecules in the asymmetric unit in **5** differ marginally in distances and angles, only one molecule is listed).

Table 6. Selected Distances (pm) and Angles (deg) of [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**)

Ru(1)−S(1)	231.8(2)	N(1)−Ru(1)−P(1)	115.4(2)
Ru(1)−S(2)	226.0(2)	Ru(1)−N(1)−C(16)	112.9(4)
Ru(1)−N(1)	198.4(5)	Ru(1)−N(2)−C(25)	126.0(5)
Ru(1)−N(2)	196.4(5)	C(15)−N(1)−C(16)	124.1(6)
Ru(1)−P(1)	229.6(2)	S(1)−Ru(1)−N(1)	82.8(2)
S(1)−C(10)	175.1(7)	S(1)−Ru(1)−N(2)	161.3(2)
N(1)−C(16)	143.7(9)	N(1)−Ru(1)−N(2)	83.4(2)
N(1)−C(15)	134.0(9)	S(2)−Ru(1)−P(1)	93.2(1)
S(2)−C(20)	173.8(7)	N(2)−Ru(1)−P(1)	111.3(2)
N(2)−C(26)	148.2(9)	Ru(1)−N(1)−C(15)	122.0(5)
N(2)−C(25)	132.5(9)	Ru(1)−N(2)−C(26)	112.5(4)
C(15)−C(10)	137.7(10)	C(25)−N(2)−C(26)	121.4(6)

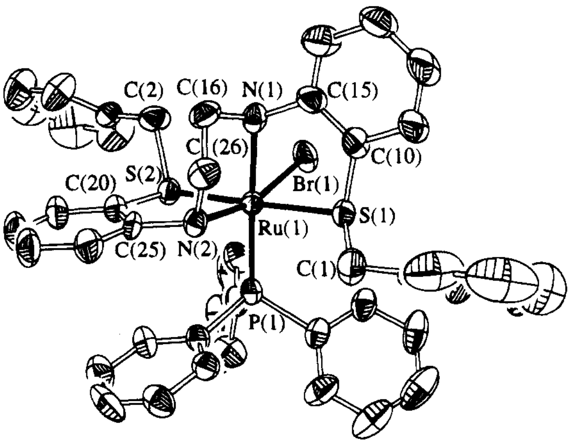

Figure 3. Molecular structure of [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]-Br (**9**) (H atoms omitted).

The ruthenium center in [Ru(PCy$_3$)('S$_2$N$_2$')] (**5**) is surrounded by one phosphorus, two sulfur, and two nitrogen donors. The N(1) donor is located 34 pm below the plane defined by the S(1), S(2), and N(2) atoms. Thus the coordination polyhedron can be described either as a distorted trigonal bipyramid or as a tetragonal pyramid. In the latter case, thiolate S and amido N atoms form the base of the pyramid above which at a distance of ca. 40 pm the ruthenium center is located. In crystalline state, **5** possesses only C_1 symmetry; in solution, however, NMR spectra show that the aromatic rings of the 'S$_2$N$_2$'$^{4-}$ ligand are magnetically equivalent indicating unhindered rotation of the PCy$_3$ ligand around the Ru−P axis and C_s symmetry of **5**. **5** exhibits distinctly shorter average Ru−S and Ru−N distances ($\bar{d}$(Ru−S) = 229.0 pm, $\bar{d}$(Ru−N) = 197.4 pm) than the Ru(II) complex **2** ($\bar{d}$(Ru−S) = 239.0 pm, $\bar{d}$(Ru−N) = 219.2 pm). This indicates a significant double bond character of the respective bonds in **5** and is compatible with the π donor capacity of amide and thiolate ligands.[16]

Of particular importance are the angle sums around the nitrogen atoms. They amount to 359°, prove the planar coordination of the N atoms by (only) ruthenium and two carbon atoms, and corroborate the amide character of the N donors. The amide character of the N donors in the 'S$_2$N$_2$'$^{4-}$ ligand, in contrast to the N donors of the closely related Schiff base gma^{2-} = glyoxal bis(2-mercaptoanil)(2−), is further corroborated by the N−C distances of the N−C$_2$H$_4$−N bridge. The respective N−C distances in **5** (143.7(9), 148.2(9) pm) are only slightly shorter than those in **2** (147.1(7), 150.0(7) pm), but distinctly longer than those in [Fe(gma)].[17] In conjunction with the spectroscopic data, these results confirm the amide−thiolate character of the 'S$_2$N$_2$'$^{4-}$ ligand.

Figure 3 shows the molecular structure of **9**, and selected distances and angles are listed in Table 7.

The ruthenium center in [Ru(Br)(PPh$_3$)('(PhCH$_2$)$_2$S$_2$N$_2$H$_2$')]-Br (**9**) is pseudooctahedrally surrounded by one Br, one P, two S, and two N atoms. The thioether donors occupy trans positions, while the amine donors as well as the phosphine and the bromide donors occupy cis positions. The average Ru−N

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(16) (a) Wilkinson, G., *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, 1987; Vol. 2, p 176. (b) Sellmann, D.; Geck, M.; Knoch, F.; Ritter, G.; Dengler, J. *J. Am. Soc.* **1991**, *113*, 3819.

(17) Sellmann, D.; Hannakam, M.; Knoch, F.; Moll, M. *Z. Naturforsch.* **1992**, *47B*, 1545.

Table 7. Selected Distances (pm) and Angles (deg) of $[Ru(Br)(PPh_3)('(PhCH_2)_2S_2N_2H_2')]Br$ (**9**)

Ru(1)−S(1)	230.1(4)	Br(1)−Ru(1)−S(2)	91.6(1)
Ru(1)−S(2)	228.4(4)	S(1)−Ru(1)−S(2)	175.3(1)
Ru(1)−N(1)	214.6(10)	Br(1)−Ru(1)−N(1)	85.2(2)
Ru(1)−N(2)	213.5(8)	S(1)−Ru(1)−N(1)	82.6(3)
Ru(1)−P(1)	227.0(4)	S(2)−Ru(1)−N(1)	98.1(3)
Ru(1)−Br(1)	250.5(2)	Br(1)−Ru(1)−S(1)	83.8(1)
S(1)−C(1)	179.7(15)	S(1)−Ru(1)−N(2)	99.9(3)
S(2)−C(2)	181.7(16)	S(2)−Ru(1)−N(2)	84.8(3)
N(1)−C(16)	146.9(14)	N(1)−Ru(1)−N(2)	80.8(3)
N(2)−C(26)	148.1(16)	N(2)−Ru(1)−P(1)	96.5(3)
C(16)−C(26)	149.1(19)	N(1)−C(16)−C(26)	107.4(10)

distances of **9** (214.0 pm) are slightly shorter than those in $[Ru(PPr_3)_2('S_2N_2H_2')]$ (**2**) (219.2 pm), but clearly longer than those in $[Ru(PCy_3)('S_2N_2')]$ (**5**) (197.4 pm). The average Ru−S distances of **9** (229.3 pm) show no anomalies and lie in the same range as found in other ruthenium(II) thioether complexes, e.g., $[Ru(I)(PPh_3)('Me_2\text{-}S_4')]I$ (231.5 pm) ('Me_2-S_4' = 1,10-dimethyl-2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane),[18] $[Ru(Cl)_2$(1,4,8,11-tetrathiacyclotetradecane)] (229.7 pm),[19] [Ru(1,4,7-trithiacyclononane)$_2$]$(BPh_4)_2$ (233.1 pm),[20] [Ru(1,5,9-trithiacyclododecane)$_2$]$(BF_4)_2$ (237.2 pm),[21] or [Ru(bzo$_2$-18S6)]$(PF_6)_2$ (235.0 pm) (bzo$_2$-18S6 = 2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane).[22] However, it is remarkable that the average Ru−S(thioether) distances in **9** (229.3 pm) and the average Ru−S(thiolate) distances in **5** (229.0 pm) are nearly identical. As we could recently demonstrate for related iron complexes, similar or even identical M−S distances, which appear to be independent of the thiolate or the thioether nature of the sulfur donors, often can be traced back to a varying degree of π character of these M−S bonds, resultant from either sulfur π donor or sulfur π acceptor bonds.[23]

Reactions of $[Ru(CO)(PCy_3)('S_2N_2H_2')]$ (4) and $[Ru(PCy_3)('S_2N_2')]$ (5). $[Ru(CO)(PCy_3)('S_2N_2H_2')]$ (**4**) and $[Ru(PCy_3)('S_2N_2')]$ (**5**) differ in oxidation states, coordination numbers, and ligands, but they both possess $[RuPS_2N_2]$ frameworks so closely related that the question arose as to how **4** and **5** could be interconverted. Successive deprotonation and oxidation of **4** to give **5** was possible according to eq 12. Upon

$$\underset{\mathbf{4}}{[Ru(CO)(PCy_3)('S_2N_2H_2')]} \xrightarrow[\text{THF}]{+3BuLi/+O_2} \underset{\mathbf{5}}{[Ru(PCy_3)('S_2N_2')]} + \text{other products} \quad (12)$$

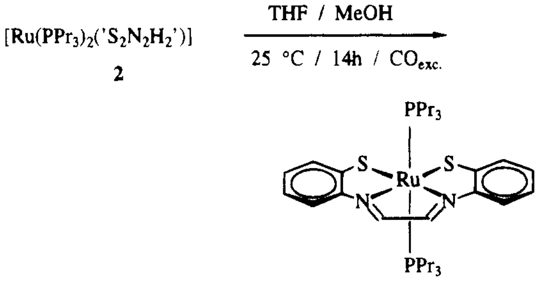
addition of an excess of *n*-BuLi in order to deprotonate the NH functions of **4**, the initially yellow suspension became a red-violet solution, whose color instantaneously turned to deep-blue when air was bubbled through indicating the formation of **5**. Monitoring the reaction by IR spectroscopy showed that in the second step minor amounts of **4** were regenerated what probably was due to moisture dragged in with the air.

Conversely, the Ru(II) complex **4** could be generated from the Ru(IV) complex **5** according to eq 13. Formic acid served

$$\underset{\mathbf{5}}{[Ru(PCy_3)('S_2N_2')]} + 4HCOOH \xrightarrow[\text{CO/25 °C/24 h}]{\text{THF/MeOH}} \underset{\mathbf{4}}{[Ru(CO)(PCy_3)('S_2N_2H_2')]} + \underset{\mathbf{6}}{[Ru(CO)_2('S_2N_2H_2')]} + \text{other products} \quad (13)$$

as Brönsted acid, reducing reagent, and CO source. As a byproduct of **4**, the dicarbonyl complex $[Ru(CO)_2('S_2N_2H_2')]$ (**6**) also formed. Its formation could be traced back to the substitution of PCy_3 in **4** by CO resulting from excessive formic acid.

$[Ru(PPr_3)_2('S_2N_2H_2')]$ (**2**) had been synthesized in order to obtain a complex, with labile phosphine ligands which could easily be exchanged for small molecules such as CO or N_2H_4. Such reactions, however, could not be observed. When **2** was treated with CO according to eq 14, no ν(CO) band was



10 (14)

observed in the IR spectrum of the reaction solution indicating no substitution of PPr_3 by CO and formation of **7**. Rather and completely unexpected, red microcrystals precipitated which were identified as the Schiff base complex $[Ru(PPr_3)_2(gma)]$ (**10**) resulting from dehydrogenation of the '$S_2N_2H_2$'$^{2-}$ ligand leading to the gma^{2-} ligand. **10** is well soluble in THF, but only sparingly soluble in MeOH and insoluble in Et_2O and hexane. Its identity could be further substantiated by direct synthesis according to eq 15.

$$\underset{\mathbf{1}}{[RuCl_2(PPr_3)_3]} + Li_2gma \xrightarrow[-PPr_3,\ -2LiCl]{\text{MeOH/25 °C/12 h}} \underset{\mathbf{10}}{[Ru(PPr_3)_2(gma)]} \quad (15)$$

In order to gain better insight into the unexpected reaction according to eq 14, we carried out a series of control experiments which yielded the following results. (a) **10** formed according to eq 14 also when extreme care was taken to exclude air strictly. (b) The solvents appear to affect the reaction. If **2** was treated with CO in THF, a small ν(CO) band at 1930 cm^{-1} could be observed in the IR spectrum indicating the formation of $[Ru(CO)(PPr_3)('S_2N_2H_2')]$ (**7**). Its intensity, however, did not increase upon further stirring under an atmosphere of CO, and the color of the reaction mixture immediately turned from yellow to red when MeOH was added. Subsequently, **10** began to precipitate. The same effect was observed when H_2O was added. (c) **10** also formed when a THF/MeOH solution of **2** was treated with air in the absence of CO, but in this case the resultant **10** was contaminated by impurities which were not further characterized.

These observations indicate that **2** is dehydrogenated by CO if protons are present in solution such that CO functions as hydrogen acceptor.

This conclusion is supported by results which we had previously obtained with $[Ru(NO)('S_2N_2H_X')]$ complexes.[24] Attempts to recrystallize $[Ru(NO)(PMe_3)('S_2N_2H')]$ from THF/MeOH in the presence of an excess of PMe_3 yielded [Ru-

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$(PMe_3)_2(gma)]$ (**11**), according to eq 16. **11** is an analogue of

$$[Ru(NO)(PMe_3)(`S_2N_2H')] \xrightarrow[+PMe_3]{THF/MeOH} \underset{\mathbf{11}}{[Ru(PMe_3)_2(gma)]} \quad (16)$$

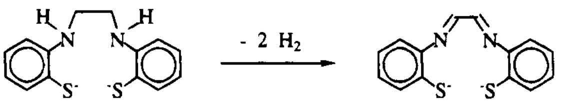
10, and in this case, NO can reasonably be assumed to function as hydrogen acceptor.

Finally the formation of **11** was also observed in the reaction according to eq 17, when we tried to coordinate the sterically

$$\underset{\mathbf{5}}{[Ru(PCy_3)(`S_2N_2')]} + 2PMe_3 \xrightarrow[25\ °C/3\ h]{THF} \underset{\mathbf{11}}{[Ru(PMe_3)_2(gma)]} + \text{other products} \quad (17)$$

undemanding PMe_3 to coordinatively unsaturated **5** in order to obtain $[Ru(PCy_3)(PMe_3)(`S_2N_2')]$. In this case dehydrogenation of the $`S_2N_2'^{4-}$ ligand is accompanied by reduction of the metal center from Ru(IV) to Ru(II).

Thus the reactions according to eqs 14, 16, and 17 demonstrate a high tendency of the $`S_2N_2H_2'^{2-}$ ligand to dehydrogenate in order to give the gma^{2-} ligand (eq 18) under very diverse conditions.



(18)

Spectroscopic Results. The complexes with $[Ru(`S_2N_2H_2')]$ frameworks show two characteristic and relatively intensive $\nu$(NH) bands between 3300 und 3100 $cm^{-1}$ in the KBr IR spectra. They appear in $[Ru(PPr_3)_2(`S_2N_2H_2')]$ (**2**) at 3297 and 3272 cm^{-1}, in $[Ru(CO)(PCy_3)(`S_2N_2H_2')]$ (**4**) at 3300 and 3125 $cm^{-1}$, and in $[Ru(CO)(PPr_3)(`S_2N_2H_2')]$ (**7**) at 3291 and 3138 cm^{-1}. The ν(CO) bands of the carbonyl complexes **4** (1927 cm^{-1}) and **7** (1934 cm^{-1}) lie in the same range as those of $[Ru(CO)(PPh_3)(`S_2N_2H_2')]$ (1935 $cm^{-1}$) and $[Ru(CO)(PMe_3)(`S_2N_2H_2')]$ (1930 cm^{-1}).[6] The alkylated derivatives $[Ru(Br)(PPh_3)(`R_2S_2N_2H_2')]Br$ (R = Et (**8**), $PhCH_2$ (**9**)) show only broad and little characteristic bands in the ν(NH)-range.

The ^1H NMR spectra of **2**, **4**, and **7** exhibit, in addition to multiplets of the aromatic protons (7.5−6.7 ppm) and C_2H_4 protons (3.7−2.6 ppm), NH signals at about 5 ppm. The carbonyl complexes **4** (5.35, 5.1 ppm) and **7** (5.5, 4.8 ppm) show two NH signals, but $[Ru(PPr_3)_2(`S_2N_2H_2')]$ (**2**), however, shows only one signal, indicating C_1 symmetry of **4** and **7** and C_2 symmetry of **2**. This is supported by $^{13}C\{^1H\}$ NMR spectra of **4** and **2**, which exhibit 12 ^{13}C signals for the aromatic protons in case of **4**, but only six signals in the case of **2**. As expected, the ^1H NMR spectra of the thioether complexes $[Ru(Br)(PPh_3)(`Et_2S_2N_2H_2')]Br$ (**8**) (6.6, 6.0 ppm) and $[Ru(Br)(PPh_3)(`(PhCH_2)_2S_2N_2H_2')]Br$ (**9**) (6.6, 6.1 ppm) each show two NH signals, which are low field shifted due to the cationic character of these complexes.

The Schiff base complexes $[Ru(PPr_3)_2(gma)]$ (**10**) and $[Ru(PMe_3)_2(gma)]$ (**11**) possess spectroscopic properties which clearly differ from those of $[Ru(`S_2N_2H_2')]$ complexes. Neither their IR spectra nor their NMR spectra exhibit ν(NH) bands or NH resonances. Rather, the ^1H NMR spectra of **10** and **11** exhibit broad but characteristic C_2H_2 singletts for the gma ligand which are low field shifted into the aromatic region at 7.35 (**10**) and 7.0 ppm (**11**).

IR and NMR spectra were important also for the unambiguous characterization of the ruthenium(IV) complex $[Ru(PCy_3)(`S_2N_2')]$ (**5**). They showed no NH bands or NH signals proving the absence of NH groups. Furthermore, the $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra of **5** indicated that **5** assumes $C_s$ symmetry in solution, because, for example, the 12 aromatic C atoms of the $`S_2N_2'^{4-}$ ligand give rise to only six ^{13}C signals. Also characteristic are the low field shifted C_2H_4 signals at 5.1 and 5.9 ppm, whose A_2B_2 splitting pattern and intensities prove the intactness of the C_2H_4 bridge.

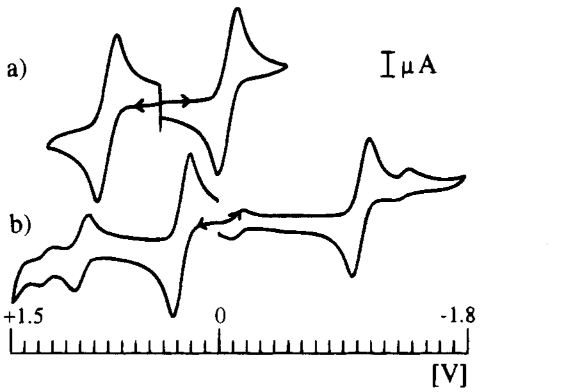


Figure 4. Cyclic voltammograms of (a) **2** and (b) **5** (CH_2Cl_2, potentials vs NHE, 0.1 mol/L NBu_4PF_6, 100 mV/s).

Table 8. Redox Potentials $E^{\circ\prime}$ of $[Ru(PPr_3)_2(`S_2N_2H_2')]$ (**2**) and $[Ru(PCy_3)(`S_2N_2')]$ (**5**)[a]

redox process	$E_{p,c}$ (V)	$E_{p,a}$ (V)	$E^{\circ\prime}$ (V)
$[2]^+/[2]^0$ (Ru(III)/Ru(II))	−0.18 (r)	−0.06 (r)	−0.12
$[2]^+/[2]^{2+}$ (Ru(III)/Ru(IV))	+0.67 (r)	+0.79 (r)	+0.73
$[5]^{2-}/[5]^{3-}$ (Ru(II)/Ru(I))	−1.44 (ir)		
$[5]^-/[5]^{2-}$ (Ru(III)/Ru(II))	−1.19 (r)	−1.07 (r)	−1.13
$[5]^-/[5]^0$ (Ru(III)/Ru(IV))	+0.17 (r)	+0.29 (r)	+0.23
$[5]^0/[5]^+$ (Ru(IV)/Ru(V))	+0.90 (r)	+1.02 (r)	+0.96
$[5]^+/[5]^{2+}$ (Ru(V)/Ru(VI))	+1.16 (r)	+1.26 (r)	+1.20

[a] In CH_2Cl_2; potentials vs NHE, 0.1 mol/L NBu_4PF_6; v = 100 mV/s; (r) = reversible and (ir) = irreversible; $E_{p,c}$ = cathodic peak potential, $E_{p,a}$ = anodic peak potential, and $E^{\circ\prime}$ = formal redox potential.

Cyclovoltammetric Results. Figure 4 shows the cyclic voltammograms of $[Ru(PPr_3)_2(`S_2N_2H_2')]$ (**2**) and $[Ru(PCy_3)(`S_2N_2')]$ (**5**). The cyclic voltammogram of **2** exhibits two quasireversible redox waves at +0.73 and −0.12 V. We assign them to the redox pairs $[2]^+/[2]^{2+}$ and $[2]^+/[2]$, assuming that at a potential of 0 V the $[2]^+$ cation is present in the solution. Otherwise, at a potential of only −0.12 V, **2** would have to be reduced to the $[2]^-$ anion, which is a 19-electron Ru(I) complex. Such a complex, however, can be expected to be unstable and not to give rise to a reversible redox wave.

The cyclic voltammogram of **5** is also dominated by two intensive redox waves. They appear at +0.23 and −1.13 V, and for similar reasons as mentioned above, they can be assigned to the redox pairs $[5]^-/[5]$ (Ru(III)/Ru(IV)) and $[5]^-/[5]^{2-}$ (Ru(III)/Ru(II)), assuming that at 0 V the $[5]^-$ anion is present. This allows one to correlate the redox waves of **2** and **5** demonstrating that the respective Ru(II)/Ru(III) and Ru(III)/Ru(IV) steps of **2** (+0.73, −0.12 V) and **5** (+0.23, −1.13 V) are shifted to lower potentials when amine σ donors are replaced by amide $\sigma-\pi$ donors. In other words, the Ru(III) center of $[5]^-$ is more easily oxidized because amide π donors better than amine σ donors stabilize high-valent metal centers. The further redox waves in the cyclic voltammogram of **5** are tentatively assigned to the redox pairs indicated in Table 8 which summarizes the electrochemical data.

Summary and Discussion. $[Ru(PR_3)_2(`S_2N_2H_2')]$ complexes with R = Pr or Cy, had been target compounds in order to obtain labile complexes allowing the exchange of PR_3 ligands for small molecules such as CO, N$_2$H$_4$, or even N$_2$. [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (**2**) formed in good yields from [RuCl$_2$(PPr$_3$)$_3$] (**1**) and ‘S$_2$N$_2$H$_2$’$^{2-}$ but is practically as inert as the analogous PPh$_3$ or PMe$_3$ complexes which had previously been investigated. **2** reacts with CO yielding [Ru(CO)(PPr$_3$)(‘S$_2$N$_2$H$_2$’)] (**7**), but the reaction is slow, incomplete, and can only be observed in aprotic solvents like THF, such that, on a preparative scale, **7** had to be synthesized photolytically from [Ru(CO)$_2$(‘S$_2$N$_2$H$_2$’)] (**6**) and PPr$_3$.

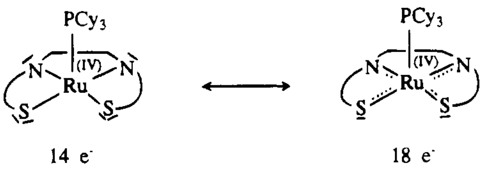
In protic media such as THF/MeOH or THF/H$_2$O mixtures, the reaction of **2** with CO took a completely different course. Dehydrogenation of the ‘S$_2$N$_2$H$_2$’$^{2-}$ ligand of **2** led to the Schiff base complex [Ru(PPr$_3$)$_2$(gma)] (**10**). Control experiments indicated that in this case CO functions as hydrogen acceptor.

Formation of the Schiff base ligand gma^{2-} from the ‘S$_2$N$_2$H$_2$’$^{2-}$ ligand or its further deprotonated ‘S$_2$N$_2$H’$^{3-}$ and ‘S$_2$N$_2$’$^{4-}$ derivatives was also observed when the Ru(II) complex [Ru(NO)(PMe$_3$)(‘S$_2$N$_2$H’)] or the Ru(IV) complex [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (**5**) were treated with PMe$_3$. In both cases [Ru(PMe$_3$)$_2$(gma)] (**11**) formed which is analogous to [Ru(PPr$_3$)$_2$(gma)] (**10**).

This shows that the gma^{2-} ligand can form from ‘S$_2$N$_2$H$_x$’$^{n-}$ precursors regardless of the oxidation state of the Ru center and it further indicates different reaction mechanisms. These mechanisms probably also differ from those which are discussed for the oxidation of Ru(II) amine complexes such as [Ru(en)$_3$]Cl$_2$ (en = 1,2-ethanediamine),[25] [Ru(phen)$_2$(en)]I$_2$ (phen = 1,10-phenanthroline),[26] or [Ru(bpy)$_2$(ampy)](ClO$_4$)$_2$ (bpy = 2,2′-bipyridine; ampy = 2-(aminomethyl)pyridine)[27] by I$_2$, AgCl, or Ce(SO$_4$)$_2$, yielding Ru(II) imine or Ru(II) Schiff base complexes. In these cases, the primary formation of Ru(III) complexes was proposed which is followed by disproportionation, acid−base, and intramolecular redox reactions.[28]

The target complex [Ru(PCy$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] was not accessible, indicating that the [Ru(‘S$_2$N$_2$H$_2$’)] core can not accomodate two of the sterically very demanding PCy$_3$ ligands. Complexes with [Ru(PCy$_3$)(‘S$_2$N$_2$’)] cores formed only as six-coordinate carbonyl Ru(II) species [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (**4**) or five-coordinate Ru(IV) species [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (**5**). **5** is very unusual due to its oxidation state, coordination number and ligand sphere. **5** shows a high tendency of formation and results from reactions of either [RuCl$_2$(DMSO)$_4$] or RuCl$_3$·3H$_2$O with H$_2$‘S$_2$N$_2$H$_2$’ as well as by oxidation of [Ru(CO)(PCy$_3$)(‘S$_2$N$_2$H$_2$’)] (**4**) in the presence of bases. Usually, Ru(IV) complexes have six-coordinate ruthenium centers and oxo, nitrido, or imido ligands.[29] To our knowledge, **5** is the only five-coordinate Ru(IV) complex carrying thiolate and amide donors, and so far, five-coordinate Ru(IV) complexes had been obtained only with bulky thiolate ligands such as 2,3,5,6-tetramethylthiophenolate(1−) = SC$_6$H$_{13}$$^-$, e.g., [Ru(SC$_{10}H_{13}$)$_4$(CH$_3$CN)],[30] [Ru(SC$_{10}H_{13}$)$_4$(CO)],[31] and [Ru(SC$_{10}H_{13}$)$_3$(CH$_3$CN)$_2$](PF$_6$).[32]

The stability of **5** can be traced back to the π donor properties of the tetraanionic ‘S$_2$N$_2$’$^{4-}$ ligand. The π donor bonds from the amide and/or thiolate donors to empty π acceptor ruthenium orbitals[33] reduce the electron deficiency of the ruthenium center such that **5** can be regarded not only as a 14 electron complex, but also as an 18 electron complex.



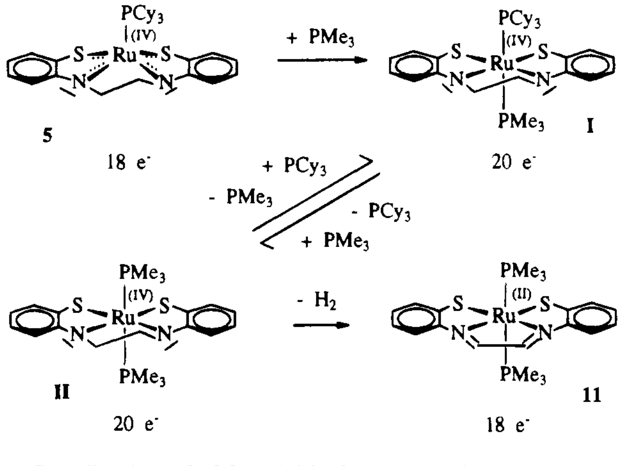
The π donor bonds, partial double bond character of Ru−S and Ru−N bonds, and the resultant stabilization of the Ru(IV) center in **5** can be inferred from the comparison of distances and redox potentials of **5** and [Ru(PPr$_3$)$_2$(‘S$_2$N$_2$H$_2$’)] (**2**) or the amide complex [Ru(L)(PPh$_3$)(py)] (L = 1,2-bis(3,5-dichloro-2-hydroxybenzeneamido)ethane).[34]

The potential 18 electron configuration of **5** may also explain why the reductive carbonylation of **5** according to eq 19 requires the simultaneous transfer of protons. The protons are necessary in order to convert the σ donor π donor amide into σ donor amine functions.

$$\underset{\mathbf{4}}{[\mathrm{Ru(CO)(PCy_3)('S_2N_2H_2')}]} \underset{+2e^-,\ +CO,\ +2H^+}{\overset{-2e^-,\ -CO,\ -2H^+}{\rightleftharpoons}} \underset{\mathbf{5}}{[\mathrm{Ru(PCy_3)('S_2N_2')}]} \quad (19)$$

Coordinatively unsaturated Ru(IV) complexes like **5** could also play a key role when a common denominator is sought for the mechanisms of the various reactions leading to [Ru(PR$_3$)(gma)] complexes. Because [Ru(PCy$_3$)(‘S$_2$N$_2$’)] (**5**), due to its S=Ru and N=Ru π donor bonds, can be considered as 18 electron complex, we suggest Scheme 1 for the reaction of **5** with PMe$_3$ yielding the Schiff base complex **11**.

Scheme 1



Coordination of PMe$_3$ yields the six-coordinate 20 electron species **I** which can be expected to have two antibonding electrons.[35] The antibonding electrons not only facilitate PCy$_3$/PMe$_3$ exchange processes yielding **II** but also activate the CH bonds of the N−CH$_2$−CH$_2$−N bridge. Spontaneous loss of H$_2$

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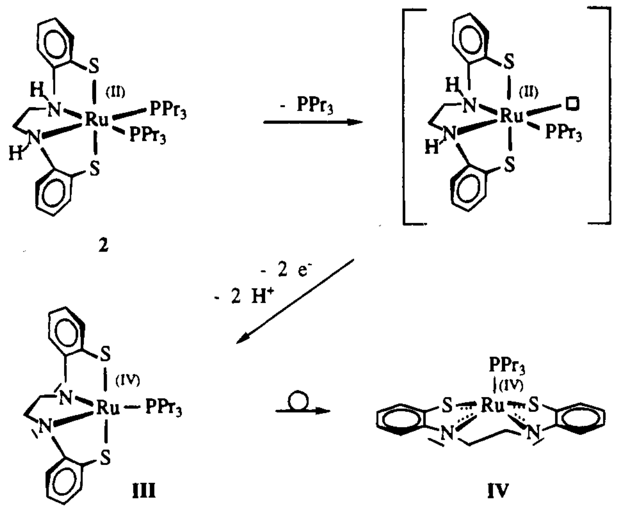
Scheme 2



accompanied by intramolecular reduction of the Ru(IV) center is the consequence leading to the 18 electron species **11**. A precedent for the last step is the spontaneous dehydrogenation of $[Os(en)(en\text{-}H)_2]^{2+}$ (en = 1,2-ethanediamine; en-H = 1,2-ethanediaminate(1−)) which gives the Schiff base complex $[Os(en)_2(\text{ethanediimine})]^{2+}$.[36]

Intermediate occurrence of $[Ru(IV)(PPr_3)(\text{'}S_2N_2\text{'})]$ (**III**), which is analogous to **5**, plausibly explains also the formation of $[Ru(PPr_3)_2(gma)]$ (**10**) from $[Ru(PPr_3)_2(\text{'}S_2N_2H_2\text{'})]$ (**2**) and CO in the presence of MeOH or H_2O (Scheme 2).

The formation of **III** could be initiated by reversible dissoziation of PPr_3 from **2**. In this case, however, an acceptor for electrons and protons is necessary in order to oxidize and to deprotonate the resultant Ru(II) species. The experimental results indicate that this acceptor is CO, which is possibly reduced to give formaldehyde needing MeOH or H_2O for its stabilization as formaldehyde acetal or hydrate. **III** could subsequently rearrange to give **IV**, which again coordinates PPr_3 that had dissociated before. The resultant $[Ru(IV)(PPr_3)_2(\text{'}S_2N_2\text{'})]$ finally dehydrogenates analogously to complex **II** of Scheme 1.

Finally, also the reaction of $[Ru(NO)(PMe_3)(\text{'}S_2N_2H\text{'})]$ with PMe_3 to give **11** can be explained in the same way. $[Ru(NO)(PMe_3)(\text{'}S_2N_2H\text{'})]$ contains labile NO and the tris-anionic $\text{'}S_2N_2H\text{'}^{3-}$ ligand. Dissociation of NO, oxidation and deprotonation of the resultant $[Ru(PMe_3)(\text{'}S_2N_2H\text{'})]$ fragment by the liberated NO could yield the ruthenium(IV) complex $[Ru(PMe_3)(\text{'}S_2N_2\text{'})]$, which in the end gives **11** upon reaction with PMe_3, according to Scheme 1.

Results and discussion indicate that ruthenium (IV) species of the type $[Ru(PR_3)(\text{'}S_2N_2\text{'})]$ may be important intermediates in reactions of $[Ru(PR_3)(\text{'}S_2N_2H_2\text{'})]$ complexes. The size of the PR_3 ligand appears to determine whether these species are isolable or not, but Brönsted acid−base and π donor properties of the ligand pair $\text{'}S_2N_2H_2\text{'}^{2-}/\text{'}S_2N_2\text{'}^{4-}$ favor the redox activity of the corresponding Ru complexes and are finally responsible for their versatile reactions.

Acknowledgment. We gratefully acknowledge financial support of this work by Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie.

Supporting Information Available: Tables of hydrogen atom fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (15 pages). Ordering information is given on any current masthead page.

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