Fluxionality and Phosphane Arm-off Reactions of Octahedral Ruthenium(II) Complexes with the Tripodal Polyphosphane $MeC(CH_2PPh_2)_3$

Claudia Landgrafe, William S. Sheldrick*, and Marc Südfeld

Lehrstuhl für Analytische Chemie der Ruhr-Universität Bochum,
D-44780 Bochum, Germany

Received November 14, 1997

Keywords: Ruthenium / Phosphorus / Triphos complexes / Fluxionality / Arm-off dissociation

Structural fluxionality is apparent in the ^{1}H- and ^{31}P-NMR spectra of compounds of the type [Ru(L)(MeCN)(triphos)](CF_3SO_3), **2**−**5**, at 25°C, where L represents a diorganyldithiocarbamate or a heterocyclic κ^2N,S coordinating thioamide. In contrast, complexes [Ru(Et_2NCS_2)(Y)(triphos)]$^{n+}$ (**6**, n = 1, Y = CO; **7**, n = 0, Y = CN^-; **8**, n = 0, Y = H^-) are stereochemically rigid in solution at this temperature, indicating that MeCN dissociation must occur for the crowded octahedral coordination spheres of **2**−**5**. Reaction of [Ru$(MeCN)_3$(triphos)]$(CF_3SO_3)_2$, **1**, with Na(Et_2NCS_2) at a 1:2 molar ratio yields [Ru$(Et_2NCS_2$-$\kappa^2S)(Et_2NCS_2$-$\kappa S)$(triphos)], **9**, which slowly converts to [Ru$(Et_2NCS_2$-$\kappa^2S)_2$(triphosO-κ^2P)], **10**, on recrystallization from ethanol/acetone under air [triphosO is O=P$(Ph)_2CH_2C(CH_3)(CH_2PPh_2)_2$]. A similar $\kappa^3P\rightarrow\kappa^2P$ arm-off dissociation leads to the formation of [Ru(mpy-$\kappa^2N,S)_2$(triphosO-κ^2P)] (**13**) and [Ru(mmim-$\kappa^2N,S)_2$(triphosO-κ^2P)] (**14**) (Hmpy = 2-mercaptopyridine, Hmmim = 2-mercapto-1-methylimidazole). Crystal structures are reported for [Ru(mbt-κ^2N,S)(MeCN)(triphos-κ^3P)](CF_3SO_3) (**4**) (Hmbt = 2-mercaptobenzothiazole), [Ru(mpym-κ^2N,S)(mpym-κS)(triphos-κ^3P)] (**11**) (Hmpym = 2-mercaptopyrimidine) and **14**, the latter of which is present as the OC-6-13 isomer.

The employment of transition metal complexes of tripodal polyphosphanes such as $CH_3C(CH_2PPh_2)_3$ (triphos) in homogeneous catalysis has attracted considerable interest[1][2][3][4].Although triphos is often regarded as a typical innocent ligand, whose neopentyl skeleton $CH_3C(CH_2)_3$ allows a relatively unstrained occupation of three facial sites in a square-pyramidal, trigonal-bipyramidal or octahedral coordination sphere[5], dissociation of a phosphane arm to provide the more flexible κ^2P binding mode has been implicated for a number of five-coordinate Rh^I and Ir^I complexes[6][7][8][9][10][11][12][13]. The kinetic lability of M^I-P bonds (M = Rh, Ir) can also lead to structural fluxionality at higher temperatures. For instance dissociation of a triphosphane arm in [IrCl(CO)(triphos)] at room temperature enables exchange between the two phosphorus environments and the ^{31}P-NMR spectrum consists solely of a singlet at $\delta = -16.1$[14]. An explanation for this behavior has been sought in the marked reduction in ring strain that may be achieved on going from the facial κ^3P geometry in an $18e^-$ trigonal-bipyramidal complex to the open κ^2P geometry of a square planar $16e^-$ species[11][15].

The idealized P−M−P angles in octahedral Rh^{III} or Ir^{III} complexes provide a relatively unstrained κ^3P geometry for a tripodal polyphosphane, so that the energetic advantage of an open κ^2P coordination mode should be less pronounced than for five-coordinated M^I complexes. However an arm-off dissociation has been implicated for the reaction of the octahedral Rh^{III} complexes [RhL_3(triphos)] (L = Me, H) with CO and H_2[7][15] and ^{1}H- and ^{31}P-NMR evidence have been presented for a $\kappa^3P\rightleftharpoons\kappa^2P$ equilibrium of the triphosphane ligand in solutions of [$RhMe_2$(MeCN)(triphos)]$^+$ at room temperature[11]. We ourselves have recently reported[16][17] the stereochemical non-rigidity of the complex cations [RhL(MeCN)(triphos)]$^{2+}$ in which L represents the bidentate diorganyldithiocarbamates $R_2NCS_2^-$ (R = Et, Bz) or the heterocyclic thioamide $mpym^-$ (Hmpym = 2-mercaptopyrimidine). Both CH_3CN and phosphane arm-off dissociation processes can be proposed to explain the fluxional behavior of such species. κ^2P coordinated complexes of the type [RhL_2(triphos-κ^2P)]$^+$ (L = $Et_2NCS_2^-$, $Me_2NCS_2^-$ $mpym^-$) may be obtained on treating the starting compound [Rh$(MeCN)_3$(triphos)]$^{3+}$ with two equivalents of the potentially chelating ligands L.

These results prompted the present comparative study of fluxionality and phosphane arm-off reactions for analogous isoelectronic octahedral Ru^{II} complexes. Our continuing choice of diorganyldithiocarbamates and heterocyclic thioamides as ligands L was motivated by their ability to coordinate in both a mono- or bidentate fashion[18][19], by the pronounced *trans* effect of their sulfur donor atoms and by their relatively restricted steric demands owing to a small chelating angle of bite. The ambidentate thioamides $mpym^-$, mpy^- (Hmpy = 2-mercaptopyridine), and $mmim^-$(Hmmim = 2-mercapto-1-methylimidazole) were employed for a mechanistic study of isomer formation for complex cations of the type [RuL_2(triphos-κ^2P)]$^+$ and [RuL_2(triphosO-κ^2P)]$^+$ [triphosO is O=P$(Ph)_2CH_2$-$C(CH_3)(CH_2PPh_2)_2$].

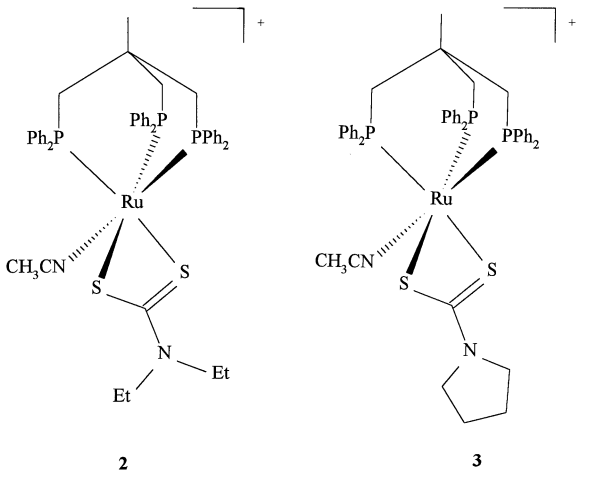
Results

Treatment of [Ru$(MeCN)_3$(triphos)]$(CF_3SO_3)_2$ (**1**) with selected anionic ligands L affords the octahedral complexes [Ru(Et_2NCS_2)(MeCN)(triphos)](CF_3SO_3) (**2**), [Ru(pyrdtc)(MeCN)(triphos)](CF_3SO_3) (**3**) (pyrdtc$^-$ = pyrrolidindithi-

  1434−1948/98/0303−0407 $ 17.50+.50/0

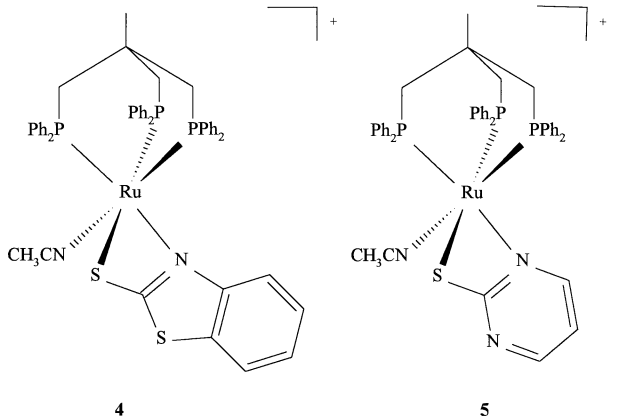
ocarbamate), [Ru(mbt)(MeCN)(triphos)](CF_3SO_3) (**4**) (Hmbt = 2-mercaptobenzothiazole), and [Ru(mpym)(MeCN)(triphos)](CF_3SO_3) (**5**) (schemes 1 and 2). Mononuclear structures for the complex cations of **2**−**5** are confirmed by their highest FAB mass peaks, which each correspond to [M − MeCN − CF_3SO_3]$^+$. In contrast, the reduced steric demands of the facially coordinated cyclic thioether 1,4,7-trithiacyclononane ([9]aneS_3) allow the adoption of tridentate μ-1κ*S*:2κ^2*S*,*S*′ and μ-1κ*S*:2κ^2*N*,*S* bridging modes by respectively $Me_2NCS_2^-$ and mbt$^-$ in the dinuclear complexes [{Ru(μ-Me_2NCS_2)([9]aneS_3)}$_2$](CF_3SO_3)$_2$[20] and [{Ru(μ-mbt)([9]aneS_3)}$_2$](CF_3SO_3)$_2$[21]. The latter coordination pattern has also been reported for the organometallic half-sandwich complex [{Ru(μ-mtz)(C_6H_6)}$_2$Cl]Cl[18] (Hmtz = 2-mercapto-2-thiazoline).

Scheme 1. [Ru(Et_2NCS_2)(MeCN)(triphos)]$^+$ cation of **2** and [Ru(pyrdtc)(MeCN)(triphos)]$^+$ cation of **3**



2 **3**

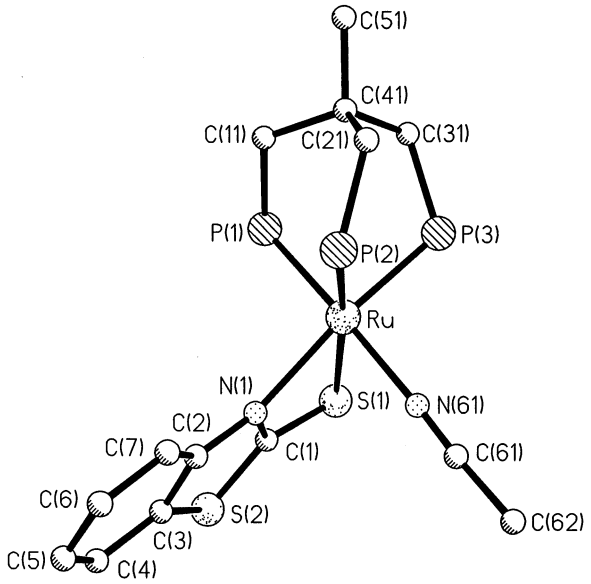
Scheme 2. [Ru(mbt)(MeCN)(triphos)]$^+$ cation of **4** and [Ru(mpym)(MeCN)(triphos)]$^+$ cation of **5**



4 **5**

Figure 1 depicts the molecular structure of the monocation of **4**. As a result of the very small angle of bite [S(1)−Ru−N(1) = 66.1(2)°] of the coordinating heterocyclic thioamide mbt$^-$, an acetonitrile ligand can occupy the vacant sixth position of a coordination octahedron. However, the narrow S(1)−Ru−N(1) angle causes pronounced distortions in the geometry of the chelating polyphosphane cage. Whereas P(1)−Ru−P(2) [90.6(1)°] remains close to the idealised octahedral angle, both P(1)−Ru−P(3) and P(2)−Ru−P(3) narrow markedly [84.7(1), 86.4(1)°]. A marked *trans* influence of the thioamide sulfur atom is not apparent, indeed Ru−P(2) [2.302(2) Å] is slightly shorter than Ru−P(1) or Ru−P(3) [2.314(2), 2.307(2) Å]. It is instructive to contrast the formation of octahedral monocations in **2**−**5** with the recently reported five-coordinated product [Rh(bdt)(triphos)]$^+$ of the reaction of [$RhCl_3$(triphos)] with Na_2(bdt) [bdt = *o*-benzenedithiolate(2−)][22]. The angle of bite of the κ^2*S* coordinated *o*-benzenedithiolate ligand is no less than 20.3° wider than that of the κ^2*N*,*S* chelating 2-mercaptobenzothiazolate ligand in **4**. This finding suggests that the large Tolman cone angle of at least 220° for the tripodal polyphosphane ligand[23] will prevent the occupation of the potential sixth coordination site in [Rh(bdt)(triphos)]$^+$.

Figure 1. Molecular structure of the cation of **4**. Phenyl rings are omitted for clarity[a]

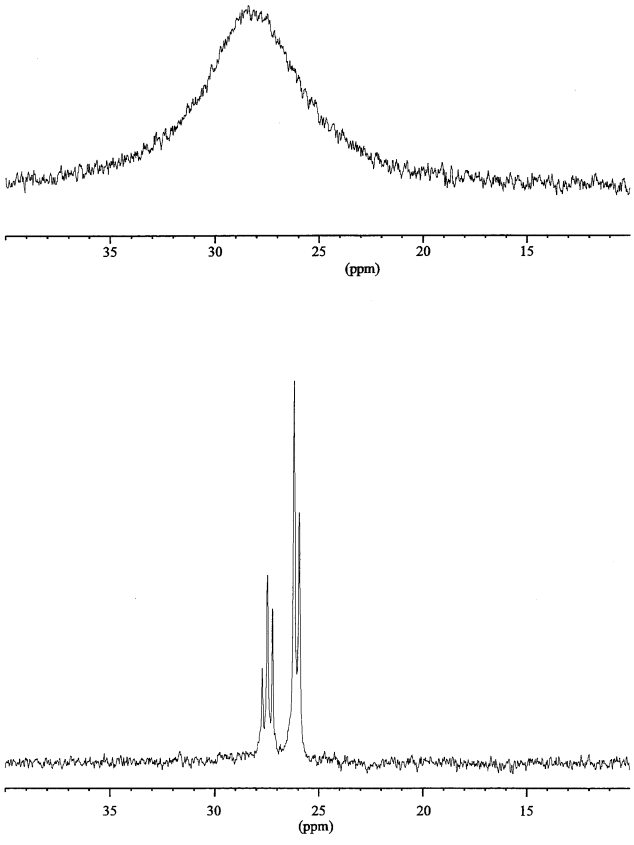


[a] Selected bond lengths [Å] and angles [°]: Ru−P(1) 2.314(2), Ru−P(2) 2.302(2), Ru−P(3) 2.307(2), Ru−S(1) 2.503(2), Ru−N(1) 2.242(6), Ru−N (61) 2.095(5), S(1)−C(1) 2.242(6), Ru−N(61) 2.095(5), S(1)−C(1) 1.714(8), S(2)−C(1) 1.723(8), S(2)−C(3) 1.735(9), S(1)−Ru−P(2) 168.9(1), N(1)−Ru−P(3) 169.9(2), N(61)−Ru−P(1) 178.2(2), P(1)−Ru−P(2) 90.6(1), P(1)−Ru−P(3) 84.7(1), P(2)−Ru−P(3) 86.4(1), S(1)−Ru−N(1) 66.1(2).

Stereochemical non-rigidity is observed for each of the monocations of **2**−**5** at room temperature. Whereas a doublet and triplet at an integral ratio of 2:1 would be expected for the magnetically inequivalent phosphorus atoms of the diorganyldithiocarbamate complexes **2** and **3**, their ^{31}P-NMR spectra in various solvents ($CDCl_3$, MeOD, [D_6]acetone) consist of a single broad uncontoured resonance (in $CDCl_3$ **2** δ = 22−36, **3** δ = 22−32) at ambient temperature [see Figure 2(a)]. As illustrated for **2** in Figure 2(b), cooling to −30°C provides the predicted spin pattern with resolved doublets (**2** δ = 26.10, **3** δ = 25.70) for the P atoms *trans* to the diorganyldithiocarbamate S atoms and a triplet (**2** δ = 27.44, **3** δ = 28.56) for the single P atom *trans* to acetonitrile. Each of the phosphorus atoms in the thioamide-con-

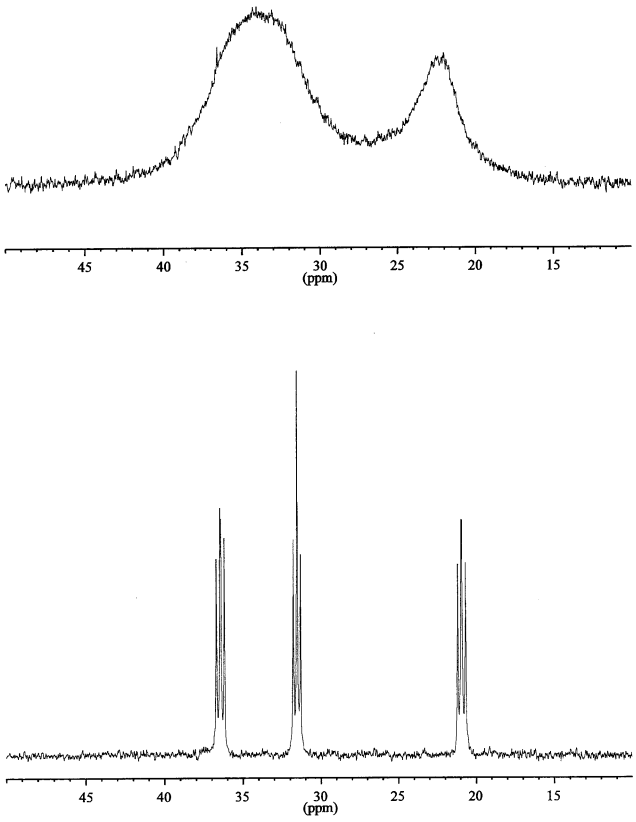
taining cations of **4** and **5** should generate its own separate ^{31}P-NMR resonance. In fact, the fluxional behavior of **4** in $CDCl_3$ solution leads to the observation of only two broad resonances at room temperature [Figure 3(a)]. Although three signals can be identified for **5** at this temperature, they are likewise broad and without fine structure. As may be seen for **4** in Figure 3(b), cooling to −30°C once again provides stereochemical rigidity and three individual triplets (**4** δ = 20.92, 31.52, 36.53; **5** δ = 19.89, 28.05, 37.59) appear in the ^{31}P-NMR spectrum at this temperature. The ^1H-NMR spectra of **2**−**5** are also in accordance with cation fluxionality at room temperature. For instance, whereas only a single broad resonance at δ = 2.43 can be observed for the triphos CH_2 protons of **2** at 25°C, three multiplets can be identified in $CDCl_3$ solution at −30°C: δ = 2.19, 2.30, 2.68). Restricted rotation about the diorganyldithiocarbamate C−N bond also leads to the observation of two signals for the ethyl CH_2 protons of this cation at −30°C (δ = 3.64, 3.84), which then coalesce to a single resonance (δ = 3.82) at ambient temperature.

Figure 2. ^{31}P-NMR spectrum of **2** in $CDCl_3$: (a) at room temperature, (b) at −30°C.



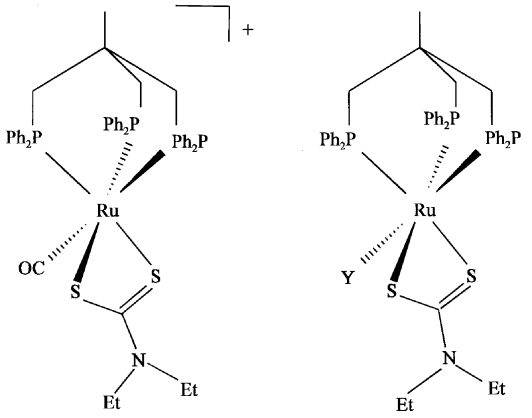
Both CH_3CN and phosphane arm-off dissociation can be discussed as possible mechanisms to explain the stereochemical non-rigidity of the cations $[Ru(L)(MeCN)(triphos)]^+$ of **2**−**5** in solution at 25°C. The position and width of the sharp MeCN singlets in the ^1H-NMR spectra of these complexes in $CDCl_3$ (−30°C: **2** δ = 1.80, **3** δ = 1.87, **4** δ = 1.87, **5** δ = 1.61) remain effectively unchanged on raising the solution temperature from −30°C to 25°C and, therefore, provide no evidence for a rapid acetonitrile exchange process. This finding prompted us to investigate whether fluxionality is also a general phenomenon for other sterically crowded Ru^{II} complexes of the type $[Ru(Et_2NCS_2)(Y)(triphos)]^{n+}$ (**6**, n = 1, Y = CO; **7**, n = 0, Y = CN^- **8**, n = 0, Y = H^-) depicted in Scheme 3. However, ^1H and ^{31}P NMR spectra for **6**−**8** in $[D_6]DMSO$ or $CDCl_3$ at both 25°C or 60°C indicate that these non-acetonitrile complexes are, in fact, all stereochemically rigid in solution. Pronounced highfield shifts are apparent for the P atom in *trans* position to the monodentate ligand Y in both **6** (**6**, L = CO, δ = 3.54) and the hydride complex **8** (δ = 5.29).

Figure 3. ^{31}P-NMR spectrum of **4** in $CDCl_3$: (a) at room temperature, (b) at −30°C.



The implicated lack of triphos arm-off dissociation for Ru^{II} complexes of the type $[Ru(L)(Y)(triphos)]^{n+}$ in solution led us to investigate whether κ^2P coordinated triphos complexes with a dangling phosphone arm can be stabilized by the presence of an excess of a small bite chelating ligand such as $Et_2NCS_2^-$, $mpym^-$, mpy^-, or $mmim^-$. A facial replacement of one binding P atom is observed when $[Rh(MeCN)_3(triphos)]^{3+}$ is treated with two equivalents of bidentate ligands L, thereby yielding[16][17] κ^2P coordinated complexes such as $[Rh(R_2NCS_2\text{-}\kappa^2S)_2(triphos\text{-}\kappa^2P)][CF_3SO_3]$ (R = Et, Me) or $[Rh(mpym\text{-}\kappa^2N,S)_2(triphos\text{-}\kappa^2P)][CF_3SO_3]$. In contrast, retention of a κ^3S facial coordination mode has been reported for the cyclic thioether [9]$aneS_3$ in [Rh(mpym-κ^2N,S)(mpym-

Scheme 3. $[Ru(Et_2dtc)(CO)(triphos)]^+$ cation of **6** and molecules $[Ru(Et_2dtc)(L)(triphos)]^+$ [(L = CN (**7**), H (**8**)]

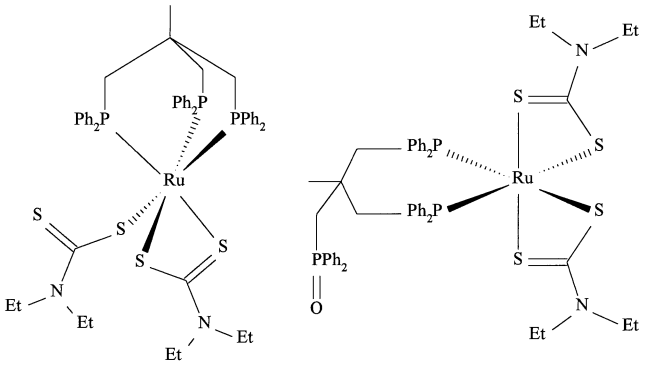


6 **7** (Y = CN^-), **8** (Y = H^-)

κS)([9]aneS$_3$-$\kappa^3 S$)][CF_3SO_3][19] and [Ru(mbt-$\kappa^2 N,S$)(mbt-κS)([9]aneS$_3$-$\kappa^3 S$)][21]. The presence of both mono- and bidentate dimethyldithiocarbamate ligands has been confirmed for the organometallic half-sandwich complex [Rh(η^5-C_5Me_5)(Me_2NCS_2-$\kappa^2 S$)(Me_2NCS_2-κS)][24].

Treatment of **1** with Na(Et_2NCS_2) at a 1:2 or 1:3 ratio affords the $\kappa^3 P$-triphos coordinated complex [Ru(Et_2NCS_2-$\kappa^2 S$)(Et_2NCS_2-κS)(triphos-$\kappa^3 P$)] (**9**), whose structure (Scheme 4) was established by elemental analysis, FAB mass spectrometry, and NMR spectroscopy. **9** exhibits a doublet at δ = 19.06 for the P atoms *trans* to the $\kappa^2 S$ coordinated chelating ligand and a triplet at δ = 32.37 for the remaining P atom *trans* to the monodentate $Et_2NCS_2^-$ ligand. The presence of a singlet at δ = ca. −25 to −30 would be characteristic for the P atom of a free dangling phosphane arm in a $\kappa^2 P$ coordinated complex[16][17]. Both the ^{1}H- and ^{31}P-NMR spectra are in accordance with stereochemical rigidity of **9** in $CDCl_3$ solution at 25°C. However attempts to recrystallize **9** from an ethanol/acetone solution under air led to formation of the $\kappa^2 P$ coordinated complex [Ru($EtNCS_2$-$\kappa^2 S$)$_2$(triphosO-$\kappa^2 P$)] (**10**) over a period of 14 d in relatively good yield (50%). The oxidation of the uncoordinated P atom is confirmed by the observation of a FAB MS basis peak *m*/*z* for $[M]^+$ at 1038, by a characteristic IR absorption band for $\tilde{\nu}$(PO) at 547 cm^{-1}, and by the presence of a typical ^{31}P-NMR resonance at δ = 26.86, a value very similar to that of 27.18 found for the analogous Rh^{III} complex [Rh(Et_2NCS_2-$\kappa^2 S$)$_2$(triphosO-$\kappa^2 P$)]Cl[16]. It is possible to follow the required $\kappa^3 P \rightarrow \kappa^2 P$ arm-off reaction of the initially $\kappa^3 P$ coordinated triphos in **9** by ^{31}P NMR spectroscopy. After 2d, respective singlets at δ = −26.00 and 26.86 for the dangling phosphorus atom in $\kappa^2 P$ coordinated triphos and its oxidation product triphosO in the final product **10** can be identified. These resonances also appear in the ^{31}P-NMR spectrum of the mixture of [Ru(Et_2NCS_2)$_2$(triphos-$\kappa^2 P$)] and [Ru(Et_2NCS_2)$_2$(triphos-O-$\kappa^2 P$)] present after 7 d in a $CDCl_3$ solution of **9** exposed to air. Whereas overlapping signals for the coordinated P atoms of these complexes may be located in the range δ = 38−40, the phosphorus resonances of **9** (δ = 19.06, 32.37) are now completely absent. It may be assumed that the driving force for the $\kappa^3 P \rightarrow \kappa^2 P$ arm-off reaction will be provided by the thermodynamic advantage of $\kappa^2 S$ chelation of both $Et_2NCS_2^-$ ligands. However, this process proceeds much more slowly than for the analogous Rh^{III} complexes, for which intermediate products of the type [Rh(R_2NCS_2-$\kappa^2 S$)(R_2NCS_2-κS)(triphos-$\kappa^3 P$)]$^+$ cannot be isolated[16].

Scheme 4. [Ru(Et_2dtc)$_2$(triphos)] (**9**) and [Ru(Et_2dtc)$_2$(triphosO)] (**10**)

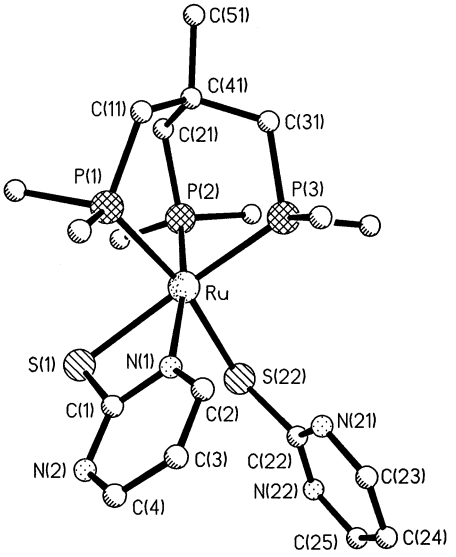


9 **10**

The reaction of **1** with 2 equivalents of the ambidentate heterocyclic thioamides $mpym^-$, mpy^-, and $mmim^-$ was studied to provide information on possible preferred isomer formation for products of the type [Ru(L)$_2$(triphosO-$\kappa^2 P$)]. As for diethyldithiocarbamate $Et_2NCS_2^-$, $\kappa^3 P$-triphos coordinated complexes [Ru(mpym-$\kappa^2 N,S$)(mpym-κS)-(triphos)] (**11**) and [Ru(mpy-$\kappa^2 N,S$(mpy-κS)(triphos)] (**12**) can be isolated in high yield at room temperature. Both are once again stereochemically rigid in solution at 25°C and may be characterized by their FAB MS basis peaks $[M]^+$ and the presence of three ^{31}P NMR triplets in the range δ = 21.5−29.2. In contrast to **10** or **12**, the 2-mercaptopyrimidinate complex **11** is stable in solution under air and may be recrystallized from $CHCl_3$/MeOH to afford crystals suitable for X-ray analysis (Figure 4). The small angle of bite [S(1)−Ru−N(1) 65.9(2)°] of the coordinating thioamide causes a marked narrowing of the opposite P(2)−Ru−P(3) angle to 85.0(1)°. As a result of the weaker *trans* influence of N, the Ru−P(2) distance of 2.291(2) Å is somewhat shorter than for the remaining triphos P atoms [2.301(2), 2.322(2) Å]. On leaving **12** to stand in $CHCl_3$ solution under air a color change from yellow to orange may be followed over a period of 3 d and the triphosO-$\kappa^2 P$ complex [Ru(mpy-$\kappa^2 N,S$)$_2$(triphosO-$\kappa^2 P$)] (**13**) may be isolated in effectively quantitative yield after 14 d. Rapid oxidation of the dangling phosphane arm is typical for analogous $\kappa^2 P$ coordinated Rh^{III} complexes[16][17] and has also been reported for square-planar Rh^I and Ni^{II} complexes[6][25]. Whereas **12** exhibits three triplets for its magnetically inequivalent P (δ 21.55, 26.60, 29.17 ppm) atoms, a singlet at δ = 25.89 and an AB pattern at δ = 42.45 for two nuclei with closely similar chemical shifts were recorded for **13**. The position of the former resonance is typical for the oxid-

ized phosphorus of triphosO and the latter spin system would be expected for either the OC-6-22 (N *trans* to N) or OC-6-13 (S *trans* to S) isomer but not the third possible OC-6-32 (S *trans* to N) isomer of Scheme 6. Although attempts to obtain crystals suitable for X-ray analysis remained unsuccessful, the molecular structure of the analogous κ^2P-triphosO complex [Ru(mmim-$\kappa^2N,S)_2$(triphosO-κ^2P)] (**14**) was determined. As previously also established for two Rh^{III} complexes [Rh(mpy-$\kappa^2N,S)_2$(triphosO-κ^2P)]Cl[16] and [Rh(mmim-$\kappa^2N,S)_2$(triphosO-κ^2P)]-[CF_3SO_3][17], **14** is present as the OC-6-13 isomer. The observation of individual resonances for the coordinated triphosO P atoms (δ = 47.8, 49.9) and the duplication of the $mmim^-$ methyl singlet (δ = 2.94, 2.98) and aromatic proton doublets (δ = 5.93, 6.09, 6.52, 6.61) indicates that the molecular geometry of **14** must deviate significantly from an idealized C_2 symmetry. This is confirmed by the observed distortions in the Ru^{II} coordination sphere of the X-ray structure (Figure 5). In view of the similarity of the ^{31}P NMR data for **13** and **14** it seems reasonable to assume that the former complex is also present as the OC-6-13 isomer with S atoms in *trans* position to one another.

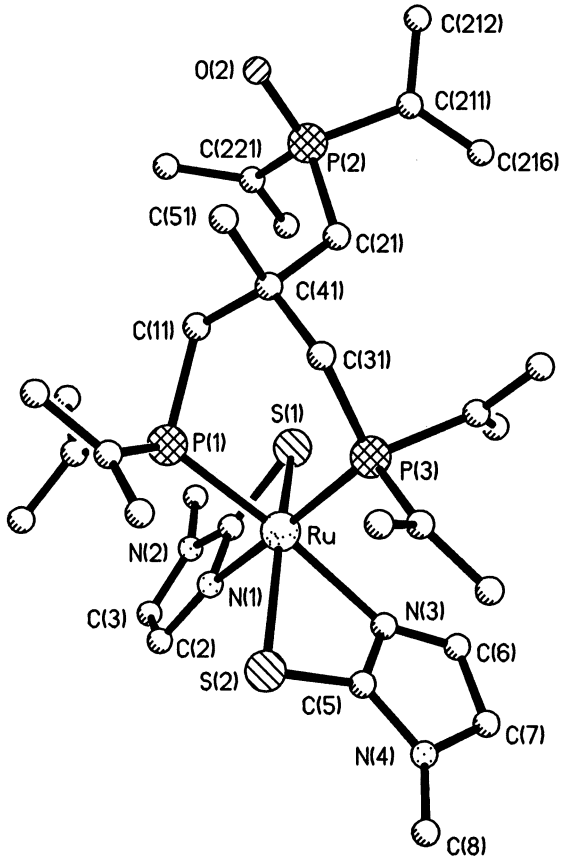
Figure 4. Molecular structure of **11**. Phenyl rings are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: Ru−P(1) 2.301(2), Ru−P(2) 2.291(2), Ru−P(3) 2.322(2), Ru−S(1) 2.488(2), Ru−S(22) 2.451(2), Ru−N(1) 2.142(7), S(22)−Ru−P(1) 168.3(1), N(1)−Ru−P(2) 170.3(1), S(1)−Ru−P(3) 170.3(1), P(1)−Ru−P(2) 89.3(1), P(1)−Ru−P(3) 91.0(1), P(2)−Ru−P(3) 85.0(1), S(1)−Ru−N(1) 65.9(2).

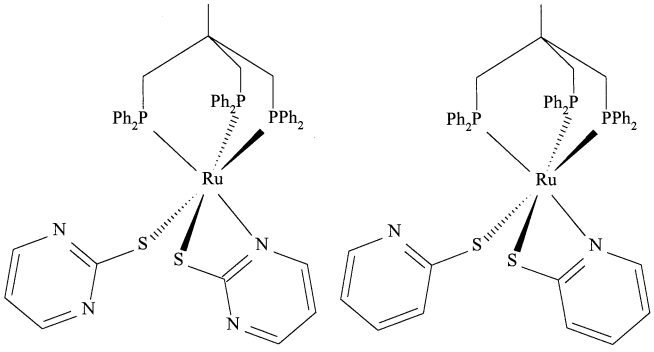
Our present results indicate that the fluxionality of octahedral Ru^{II} complexes [Ru(L)(MeCN)(triphos-κ^3P)]$^+$ of bidentate ligands L^- results from a facile acetonitrile dissociation to a five-coordinate species [Ru(L)(triphos-κ^3P)]$^+$. In contrast to the analogous acetonitrile complexes, κ^3P-triphos compounds of the type [Ru(L)(Y)(triphos-κ^3P)]$^{n+}$ (n = 1, Y = CO; n = 0, Y = CN^-, H^-) are stereochemically rigid in solution at both 25°C and 60°C. Arm-off $\kappa^3P \rightarrow \kappa^2P$ reactions are apparently less favorable for Ru^{II} than for Rh^{III}, thereby allowing the isolation of com-

Figure 5. Molecular structure of **14**. Phenyl rings are omitted for clarity[a]



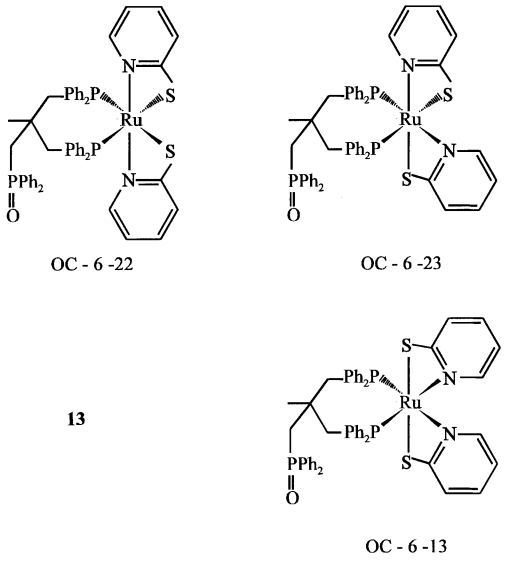
[a] Selected bond lengths [Å] and angles [°]: Ru−P(1) 2.239(5), Ru−P(3) 2.242(5), Ru−S(1) 2.480(6), Ru−S(2) 2.457(6), Ru−N(1) 2.155(4), Ru−N(3) 2.21(2), N(3)−Ru−P(1) 172.8(5), N(1)−Ru−P(3) 169.6(5), S(1)−Ru−S(2) 156.1(2), P(1)−Ru−P(3) 89.2(5), N(1)−Ru−S(1) 66.9(5), N(3)−Ru−S(2) 68.1(5).

Scheme 5. [Ru(mpym)$_2$(triphos)] (**11**) and [Ru(mpy)$_2$(triphos)] (**12**)



plexes such as [Ru(Et_2NCS_2-κ^2S)(Et_2NCS_2-κS)(triphos-κ^3P)] (**9**) or the analogous $mpym^-$ and mpy^- complexes **11** and **12**. However **9** and **12** do exhibit a slow arm-off phosphane dissociation and subsequent oxidation to afford the thermodynamically favorable bis-chelates [Ru(Et_2NCS_2-$\kappa^2S)_2$(triphosO-κ^2P)] (**10**) and [Ru(mpy-$\kappa^2N,S)_2$(triphosO-κ^2P)] **13**. As **13** and **14** are both formed from κ^3P-triphos

Scheme 6. Possible isomers of [Ru(mpy)$_2$(triphosO)] **13**



complexes it may be assumed that the first reaction stage will involve a slow $\kappa^3P \rightleftharpoons \kappa^2P$ dissociation. This must be followed by rapid isomerisation of the five-coordinated intermediate to allow nucleophilic attack of the N atom of the previously κS coordinated thioamide at a site *trans* to a κ^2P-triphos phosphorus. The resulting octahedral complex will then exhibit the observed OC-6-13 geometry. Relief of steric crowding and the energetic advantage of the associated formation of a second κ^2S or κ^2S,N chelate may be presumed to provide the driving force behind such a triphos arm-off dissociation.

Experimental Section

Where not otherwise stated reactions were performed under Ar in carefully dried solvents. − FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as the matrix. − FT-IR: KBr, Perkin-Elmer 1760. − ^{1}H and ^{31}P{^{1}H} NMR: Bruker AM 400; chemical shifts are reported as δ values relative to the signal of the deuterated solvent (for ^{1}H) or relative to 85% H_3PO_4 as external standard (for ^{31}P). − Elemental analyses: Carlo Erba 1106. − The starting compound [Ru(MeCN)$_3$(triphos)][CF_3SO_3] (**1**) was prepared according to the literature procedure[26] from $RuCl_3 \cdot x\ H_2O$, which was a gift from Degussa AG.

[Ru(Et$_2$NCS$_2$)(MeCN)(triphos)](CF$_3$SO$_3$) (**2**): Na(Et$_2$NCS$_2$)·3 H_2O (33.8 mg, 0,15 mmol) was added to a solution of **1** (172.0 mg, 0.15 mmol) in 10 ml of MeOH and the reaction mixture heated at reflux for 3 h. After filtration the red solution was reduced in volume to 3 ml and left to stand at room temperature to afford a yellow precipitate of **2** within 24 h. Recrystallisation from ethanol provided **2**·0.5 C_2H_5OH. Yield 111.0 mg (68%). − FAB MS, *m/z* (%): 874 (100) [M − MeCN − CF_3SO_3]$^+$. − ^{1}H NMR ($CDCl_3$, −30°C): δ = 1.24 (t, 6 H, CH_3 Et$_2$NCS$_2$), 1.58 (s, 3 H, CH_3 triphos), 1.80 (s, 3 H, MeCN), 2.19 (m, 2 H, CH_2 triphos), 2.30 (m, 2 H, CH_2 triphos), 2.68 (m, 2 H, CH_2 triphos), 3.64 (m, 2 H, CH_2 Et$_2$NCS$_2$), 3.84 (m, 2 H, CH_2 Et$_2$NCS$_2$), 6.87−7.38 (m, 30 H, Ph triphos). − ^{31}P NMR ($CDCl_3$, −30°C): δ = 26.10 (d, 2 P, *trans* to Et$_2$NCS$_2$), 27.44 (t, 1 P, *trans* to MeCN). − $C_{49}H_{52}F_3N_2O_3P_3RuS_3 \cdot 0.5\ C_2H_5OH$ (1088.2): calcd. C 55.2, H 5.1, N 2.6; found C 55.0, H 5.4, N 2.3.

[Ru(pyrdtc)(MeCN)(triphos)](CF$_3$SO$_3$) (**3**): The preparation of **3** was performed using **1** and NH_4(pyrdtc) (pyrdtc$^-$ = pyrrolidinedithiocarbamate) under conditions analogous to those for **2**. Yield 119.5 mg (75%). − FAB MS, *m/z* (%): 872 (100) [M − MeCN − CF_3SO_3]$^+$. − ^{1}H NMR ($CDCl_3$, −30°C): δ = 58 (s, 3 H, CH_3 triphos), 1.87 (s, 3 H, MeCN), 1.97, 2.08, 2.14 (3×2 H, 3 m, CH_2 pyrdtc$^-$ and triphos), 2.32 (m, 2 H, CH_2 triphos), 2.64 (m, 2 H, CH_2 triphos), 3.64 (m, 4 H, CH_2 pyrdtc$^-$), 6.87−7.39 (m, 30 H, Ph triphos). − ^{31}P NMR ($CDCl_3$, −30°C): δ = 5.70 (d, 2 P, *trans* to pyrdtc$^-$), 28.56 (t, 1 P, *trans* to MeCN). − $C_{49}H_{50}F_3N_2O_3P_3RuS_3$ (1062.1): calcd. C 55.4, H 4.7, N 2.6; found C 54.5, H 5.1, N 2.3.

[Ru(mbt)(MeCN)(triphos)](CF$_3$SO$_3$) (**4**): 2-Mercaptobenzothiazole Hmbt (25.2 mg, 0.15 mmol) was dissolved in 10 ml MeOH in the presence of 0.15 mmol 1 M NaOH. After addition of **1** (172.0 mg, 0.15 mmol) the reaction mixture was heated for 2 h at reflux and subsequently filtered; the volume of the red-brown solution was then reduced to 1 ml. Standing at −18°C led to crystallization of yellow-brown prisms of **4**·1/2 MeOH suitable for X-ray analysis. Yield 120.2 mg (73%). − FAB MS, *m/z* (%): 892 (100) [M − MeCN − CF_3SO_3]$^+$. − ^{1}H NMR ($CDCl_3$, −30°C): δ = 1.59 (s, 3 H, CH_3 triphos), 1.87 (s, 3 H, MeCN), 2.27 (m, 2 H, CH_2 triphos), 2.46 (m, 3 H, CH_2 triphos), 2.60 (m, 1 H, CH_2 triphos), 6.30 (d, 1 H, mbt), 6.80−7.39 (m, 32 H, Ph triphos and mbt), 7.68 (d, 1 H, mbt). − ^{31}P NMR ($CDCl_3$, −30°C): δ = 20.92 (t, 1 P), 31.52 (t, 1 P), 36.43 (t, 1 P). − $C_{51}H_{46}F_3N_2O_3P_3RuS_3 \cdot 0.5$ MeOH (1098.1): calcd. C 56.3, H 4.4, N 2.6; found C 55.9, H 4.4, N 2.4.

[Ru(mpym)(MeCN)(triphos)](CF$_3$SO$_3$) (**5**): The preparation of **5** was carried out with **1** and 2-mercaptopyrimidine (Hmpym) in a manner analogous to that employed for **4**. Yield 126.3 mg (82%). − FAB MS, *m/z* (%): 986 (2) [M$^+$], 837 (100) [M − MeCN − CF_3SO_3]$^+$. − ^{1}H NMR ($CDCl_3$, −30°C): δ = 1.61 (s, 3 H, MeCN), 1.63 (s, 3 H, CH_3 triphos), 2.05 (m, 1 H, CH_2 triphos), 2.26 (m, 2 H, CH_2 triphos), 2.78 (m, 3 H, CH_2 triphos), 6.60−7.56 (m, 31 H, Ph triphos and mpym), 7.78 (d, 1 H, mpym), 8.45 (d, 1 H, mpym). − ^{31}P NMR ($CDCl_3$, −30°C): δ = 19.89 (t, 1 P), 28.05 (t, 1 P), 37.59 (t, 1 P). − $C_{48}H_{45}F_3N_3O_3P_3RuS_2$ (1027.0): calcd. C 56.1, H 4.4, N 4.1; found C 55.4, H 5.1, N 3.6.

[Ru(Et$_2$NCS$_2$)(CO)(triphos)](CF$_3$SO$_3$) (**6**): CO was bubbled through a solution of **2** (119.7 mg, 0.11 mmol) in 20 ml CH_2Cl_2 leading to loss of the initial deep red color. After filtration and reduction in volume to 2 ml addition of 10 ml of diethyl ether led to precipitation of **6** which was centrifuged off and dried in vacuum. Yield 87.9 mg (76%). − FAB MS, *m/z* (%): 902 (26) [M − CF_3SO_3]$^+$, 874 (87) [M − CO − CF_3SO_3]$^+$. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.14 (t, 6 H, CH_3 Et$_2$NCS$_2$), 1.70 (s, 3 H, CH_3 triphos), 2.53−2.85 (m, 6 H, CH_2 triphos), 3.54 (m, 2 H, CH_2 Et$_2$NCS$_2$), 3.71 (m, 2 H, CH_2 Et$_2$NCS$_2$), 6.94−7.49 (m, 30 H, Ph triphos). − ^{31}P NMR ([D$_6$]DMSO): δ = 3.54 (t, 1 P, *trans* to CO), 21.20 (d, 2 P, *trans* to Et$_2$NCS$_2$). − IR: $\tilde{\nu}$ = 2002 s cm^{-1} (CO). − $C_{48}H_{49}F_3NO_4P_3RuS_3$ (1051.1): calcd. C 54.9, H 4.7, N 1.3; found C 53.4, H 4.6, N 1.7.

[Ru(CN)(Et$_2$NCS$_2$)(triphos)] (**7**): NaCN (4.4 mg, 0.09 mmol) was added to **1** (95.2 mg, 0.09 mmol) in 10 ml of ethanol and the reaction mixture stirred for 18 h at room temperature. The resulting solid was filtered off and redissolved in 2 ml of CH_2Cl_2. Addition of 10 ml of diethyl ether led to precipitation of **7** which was dried in vacuum. Yield 54.3 mg (67%). − FAB MS, *m/z* (%): 900 (26) [M]$^+$, 874 (14) [M − CN]$^+$, 752 (3) [M − Et$_2$dtc]$^+$. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.08 (t, 6 H, CH_3 Et$_2$NCS$_2$), 1.42 (s, 3 H, CH_3 triphos), 2.20−2.45 (m, 6 H, CH_2 triphos), 3.43 (m, 2 H, CH_2 Et$_2$NCS$_2$), 3.67 (m, 2 H, CH_2 Et$_2$NCS$_2$), 6.77−7.79 (m, 30 H, Ph triphos). − ^{31}P NMR ([D$_6$]DMSO): δ = 19.26 (t, 1 P, *trans* to CN),

27.40 (d, 2 P, *trans* to Et_2NCS_2). − IR: $\tilde{\nu}$ = 2094 s cm^{-1} (CN). − $C_{47}H_{49}N_2P_3RuS$ (900.0): calcd. C 62.7, H 5.5, N 3.1; found C 61.8, H 5.9, N 3.1.

[Ru(Et$_2$NCS$_2$)(H)(triphos)] (**8**): $NaBH_4$ (11.3 mg, 0.3 mmol) was added to **1** (108.8 mg, 0.1 mmol) in 20 ml at room temperature leading to gas formation and lightening of the solution color. After stirring at room temperature for 18 h the resulting solid was filtered off, washed with ethanol and ethyl ether and dried in vacuum. Yield 66.5 mg (76%). − FAB MS, *m/z* (%): 874 (100) $[M - H]^+$. − ^{1}H NMR ($CDCl_3$): δ = −5.47 (d, 1 H, $^2J_{PH}$ (*trans* to H) = 109.4 Hz, $^2J_{PH}$ (*trans* to S) = 16.6 Hz), 1.24 (t, 6 H, CH_3 Et_2NCS_2), 1.38 (s, 3 H, CH_3 triphos), 2.10−2.23 (m, 6 H, CH_2 triphos), 3.61 (m, 2 H, CH_2 Et_2NCS_2), 3.91 (m, 2 H, CH_2 Et_2NCS_2), 6.87−7.39 (m, 26 H, Ph triphos), 7.74 (s, 4 H, Ph triphos). − ^{31}P NMR ($CDCl_3$): δ = 5.29 (m, 1 P, *trans* to H), 47.10 (d, 2 P, *trans* to Et_2NCS_2). − IR: $\tilde{\nu}$ = 1846 s cm^{-1} (RuH). − $C_{46}H_{50}NP_3RuS_2$ (875.0): calcd. C 63.1, H 5.8, N 1.6; found C 61.9, H 5.8, N 1.4.

[Ru(Et$_2$NCS$_2$-κ^{2}S)(Et$_2$NCS$_2$-κS)(triphos)] (**8**): $Na(Et_2NCS_2)\cdot 3\ H_2O$ (67.0 mg, 0.3 mmol) was added to a solution of **1** (172.0 mg, 0.15 mmol) in 10 ml of MeOH and the reaction mixture heated at reflux for 3 h. After filtration and reduction in volume to 3 ml the resulting solution was left to stand at 4°C to afford a yellow precipitate of **9** within 24 h. Yield 127.3 mg (83%). − FAB MS, *m/z* (%): 874 (100) $[M - Et_2NCS_2]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.86, 1.01 (2 t, 2×6 H, CH_3 Et_2NCS_2), 1.52 (s, 3 H, CH_3 triphos), 2.23, 2.42 (m, 6 H, CH_2 triphos), 3.31, 3.54 (m, 8 H, CH_2 Et_2NCS_2), 6.60−7.70 (m, 30 H, Ph triphos). − ^{31}P NMR ($CDCl_3$): δ = 19.06 (d, 2 P, *trans* to Et_2NCS_2-κ^2*S*), 32.37 (t, 1 P, *trans* to Et_2NCS_2-κ*S*). − $C_{51}H_{59}N_2P_3RuS_4$ (1022.3): calcd. C 59.9, H 5.8, N 2.7; found C 59.8, H 5.0, N 2.6.

[Ru(Et$_2$NCS$_2$-κ^{2}S)$_2$(triphosO-κ^{2}P) (**10**): Slow crystallization of **9** from an ethanol/acetone solution at room temperature under air affords **10** in 50% yield over a period of 14 d. − FAB MS, *m/z* (%): 1038 (100) $[M]^+$, 890 (41) $[M - Et_2NCS_2]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.80−1.01 (m, 15 H, CH_3 of Et_2NCS_2 and triphosO), 2.13−3.60 (m, 14 H, CH_2 of Et_2NCS_2 and triphosO), 6.80−7.80 (m, 30 H, Ph triphosO). − ^{31}P NMR ($CDCl_3$): δ = 26.86 (s, 1 P, P=O) 38.96, 40.38 (2d, 2 P, *trans* to Et_2NCS_2). − IR: $\tilde{\nu}$ = 574 m cm^{-1} (δPO). − $C_{51}H_{59}N_2OP_3RuS_4$ (1038.3): calcd. C 59.0, H 5.7, N 2.7; found C 58.5, H 5.3, N 2.6.

[Ru(mpym-κ^{2}N,S)(mpym-κS)(triphos) (**11**): Hmpym (33.6 mg, 0.3 mmol) was dissolved in 10 ml of MeOH in the presence of 0.3 ml of 1 M NaOH. After addition of **1** (172.0 mg, 0.15 mmol) and refluxing for 3 h the solvent was removed and the resulting solid dissolved in a $CHCl_3$/MeOH mixture (2:3). Slow evaporation afforded yellow crystals of **11**. Yield 122.0 mg (74%). − FAB MS, *m/z* (%): 948 (1) $[M]^+$, 837 (100) $[M - mpym]^+$. − ^{1}H NMR ($CDCl_3$): δ = 1.53 (s, 3 H, CH_3 triphos), 2.05 (m, 1 H, CH_2 triphos), 2.45 (m, 2 H, CH_2 triphos), 2.68 (m, 3 H, CH_2 triphos), 5.62 (s, 1 H, mpym), 6.25 (s, 1 H, mpym) 6.60−8.00 (m, 34 H, mpym and Ph triphos). − ^{31}P NMR ($CDCl_3$): δ = 25.17 (t, 1 P), 26.39 (t, 1 P), 29.05 (t, 1 P). − $C_{49}H_{45}N_4P_3RuS_2\cdot MeOH\cdot CHCl_3$ (1099.4): calcd. C 55.7, H 4.6, N 5.1; found C 56.8, H 4.8, N 5.1.

[Ru(mpy-κ^{2}N,S)(mpy-κS)(triphos) (**12**): The preparation of **12** was performed with Hmpy and **1** under conditions analogous to those for **11**. It was recrystallized within 1 d from a $CHCl_3$ solution covered with hexane. Yield 100.7 mg (63%). − FAB MS, *m/z* (%): 947 (1) $[M]^+$, 836 (100) $[M - myp]^+$. − ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 3 H, CH_3 triphos), 2.39 (m, 6 H, CH_2 triphos), 5.94 (6, 1 H, mpy), 6.15 (d, 1 H, mpy), 6.53 (t, 1 H, mpy), 6.70−8.00 (m, 35 H, mpy and Ph triphos). − ^{31}P NMR ($CDCl_3$): δ = 21.55 (t, 1 P), 26.60 (t, 1 P), 29.17 (t, 1 P). − $C_{51}H_{47}N_2P_3RuS_2\cdot CHCl_3$ (1065.4): calcd: C 58.6, H 4.5, N 2.6; found C 58.0, H 4.9, N 2.6.

[Ru(mpy-κ^{2}N,S)$_2$(triphosO-κ^{2}P) (**13**): On leaving a reaction solution of **12** in $CHCl_3$ to stand under air the color changed over 3 d from yellow to orange. After 14 d the solution was reduced in volume to afford **13** as a yellow solid. $C_{51}H_{47}N_2OP_3RuS_2$ (962.1): calcd. C 63.7, H 4.9, N 2.9; found C 62.8, H 5.2, N 2.8. − FAB MS, *m/z* (%): 962 (84) $[M]^+$, 852 (30) $[M - mpy]^+$. − ^{1}H NMR ($CDCl_3$) 0.63 (s, 3 H, CH_3 triphosO), 2.19 (m, 2 H, CH_2 triphosO), 2.58, 2.79, 2.86, 3.19 (m, 4 H, CH_2 triphosO), 6.06 (m, 2 H, mpy), 6.22, 6.37 (d, 2 H, mpy), 6.76, 6.82 (m, 2 H, mpy) 6.90−7.70 (m, 32 H, Ph triphosO and mpy). − ^{31}P NMR ($CDCl_3$) 25.89 (s, 1 P, P=O), 42.45 (AB system, 2 P). − IR: $\tilde{\nu}$ = 1200 m (νPO), 568 m cm^{-1} (δPO).

[Ru(mmim-κ^{2}N,S)$_2$(triphosO-κ^{2}P) (**14**): Hmmim (34.2 mg, 0.3 mmol) was dissolved in 10 ml of MeOH in the presence of 0.3 ml of 1 M NaOH. After addition of **1** (172.0 mg, 0.15 mmol) the solution was refluxed for 4 h and then left to stand under air for 2 d. This was followed by filtration and reduction in volume to 1 ml to afford yellow-brown crystals of **14** at 4°C. Yield 100.2 mg (69%). − FAB MS, *m/z* (%): 968 (25) $[M]^+$, 855 (100) $[M - mmim]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 3 H, CH_2 triphosO), 2.94, 2.98 (s, 6 H, CH_3 mmim), 5.93, 6.09, 6.52, 6.61 (d, 4 H, CH mmim), 6.52 − 7.79 (m, 30 H, Ph triphosO). − ^{31}P NMR ($CDCl_3$): δ = 26.74 (s, 1 P, P=O), 47.8, 49.9 (AB system, 2 P). − IR: $\tilde{\nu}$ = 571 m cm $^{-1}$ (δPO). − $C_{49}H_{49}N_4OP_3RuS_2$ (968.1): calcd. C 60.8, H 5.1, N 5.8; found C 61.6, H 4.7, N 6.2.

X-Ray Structural Analyses Siemens P4 diffractometer, graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å). Semi-empirical absorption corrections were applied to the intensity data by use of ψ scans. The structures were solved by a combination of Patterson and Fourier difference syntheses and refined by full-matrix least squares against *F* for **4**, **11**, and **14** (SHELXTL PLUS programs[27]). Hydrogen atoms were included where possible at calculated positions with isotropic temperature factors[28].

4·1/2 CH_3OH: $C_{51}H_{46}F_3N_2O_3P_3RuS_3\cdot 1/2\ CH_3OH$, M = 1098.1, orthorhombic, space group $Pca2_1$ (No. 29), a = 17.3490(3), b = 11.315(4), c = 25.440(6) Å, V = 4994(2) Å^3, Z = 4, D_{calc} = 1.460 g·cm^{-3}, μ = 0.59 mm^{-1}. Crystal size 0.42 × 0.48 × 0.49 mm; ω scan , scan range: 4 ≤ 2θ ≤ 50°(−20 ≤ h ≤ 0, −13 ≤ k ≤ 0, 0 ≤ l ≤ 30), 4963 reflections collected, 4530 symmetry-independent reflections (R_{int} = 0.049); max./min. transmission: 0.516/0.470; 613 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.003\ F_o^2$, R = 0.040, R_w = 0.044 for 3896 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 0.55 eÅ^{-3}. The $CF_3SO_3^-$ anion exhibits rotational disorder about the C−S axis and site occupation factors (s.o.fs) of 0.50 were employed for the F and O atoms of the two observed orientations. Anisotropic temperature factors were introduced for all nonhydrogen atoms of the cation, the anion S atoms and the C and O atoms of a disordered methanol molecule (s.o.fs = 0.5).

11·$CHCl_3\cdot CH_3OH$: $C_{49}H_{45}N_4P_3RuS_2\cdot CHCl_3\cdot CH_3OH$, M = 1099.4, monoclinic, space group $P2_1/c$ (No. 14), a = 12.611(3), b = 21.605(4), c = 18.757(4) Å, β = 91.01(3)°, V = 5110(2) Å^3, Z = 4, D_{calc} = 1.429 g·cm^{-3}, μ = 0.68 mm^{-1}. Crystal size 0.32 × 0.39 × 0.42 mm; ω scan , scan range: 4 ≤ 2θ ≤ 50° (0 ≤ h ≤14, −25 ≤ k ≤ 0, −22 ≤ l ≤ 22), 9602 reflections collected, 8898 symmetry-independent reflections (R_{int} = 0.032); max./min. transmission: 0.497/0.445; 512 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.001\ F_o^2$, R = 0.061, R_w = 0.058 for 5639 refelctions with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.13 eÅ^{-3}. Anisotropic temperature factors were introduced for all nonhydrogen atoms.

14·CH_3OH·1/2 H_2O: $C_{49}H_{49}N_4OP_3RuS_2$·CH_3OH·1/2 H_2O, M = 1009.1, triclinic, space group $P\bar{1}$(No. 2), a = 10.9610(4), b = 13.944(6), c = 17.590(3) Å, α = 76.90(3), β = 88.68(3), γ = 88.94(3)°, V = 2618(2) Å^3, Z = 2, D_{calc} = 1.280 g·cm^{-3}, μ = 0.50 mm^{-1}. Crystal size 0.28 × 0.34 × 0.40 mm; ω scan , scan range: 3 ≤ 2θ ≤ 45° (0 ≤ h ≤ 11, −15 ≤ k ≤ 15, −18 ≤ l ≤ 18), 7081 reflections collected, 6659 symmetry-independent reflections (R_{int} = 0.050); max./min. transmission: 0.804/0.627; 305 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.005\ F_o^2$, R = 0.088, R_w = 0.081 for 2803 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.13 eÅ^{-3}. The asymmetric unit contains a disordered water molecule and two disordered solvent methanols. S.o.fs of 0.5 were employed for the relevant O and C atoms. Anisotropic temperature factors were introduced for the Ru, S, P, and O atoms of **15**.

[1] C. Bianchini, C. Mealli, A. Meli, M. Peruzzini, F. Zanobini, *J. Am. Chem. Soc.* **1988**, 8725.
[2] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, Y. Fujiwara, T. Tintoku, H. Taniguchi, *J. Chem. Soc., Chem. Commun.* **1988**, 210.
[3] C. Bianchini, A. Meli, F. Laschi, J. A. Ramirez, P. Zanello, *Inorg. Chem.* **1988**, *27*, 4429.
[4] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, P. Frediani, J. A. Ramirez, *Organometallics* **1990**, *9*, 226.
[5] H. A. Mayer, W. C. Kaska, *Chem. Rev.* **1994**, *94*, 1239.
[6] W. O. Siegl, S. J. Lapporte, J. P. Collmann, *Inorg. Chem.* **1971**, *10*, 2158.
[7] J. Ott, L. M. Venanzi, C. A. Ghilardi, S. Midollini, A. Orlandini, *J. Organomet. Chem.* **1985**, *291*, 89.
[8] G. G. Johnston, M. C. Baird, *Organometallics* **1989**, *8*, 1894.
[9] G. G. Johnston, M. C. Baird, *J. Chem. Soc., Chem. Commun.* **1989**, 1008.
[10] E. G. Thaler, K. G. Caulton, *Organometallics* **1990**, *9*, 1871.
[11] D. J. Rauscher, E. G. Thaler, J. C. Huffmann, K. G. Caulton, *Organometallics* **1991**, *10*, 2209.
[12] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, A. Albinati, *Organometallics* **1990**, *9*, 2283.
[13] G. Kiss, I. T. Horváth, *Organometallics* **1991**, *10*, 3798.
[14] P. Janser, L. M. Venanzi, F. Bachechi, *J. Organomet. Chem.* **1985**, *296*, 229.
[15] E. G. Thaler, K. Folting, K. G. Caulton, *J. Am. Chem. Soc.* **1990**, *112*, 2664.
[16] K. Brandt, W. S. Sheldrick, *Chem. Ber.* **1996**, *129*, 1199.
[17] K. Brandt, W. S. Sheldrick, *Inorg. Chim. Acta* **1997**, in press.
[18] W. S. Sheldrick, C. Landgrafe, *Inorg. Chim. Acta* **1993**, *208*, 145.
[19] K. Brandt, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans* **1996**, 1237.
[20] C. Landgrafe, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans* **1994**, 1885.
[21] C. Landgrafe, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans* **1996**, 989.
[22] C. A. Ghilardi, F. Laschi, S. Midollini, A. Orlandini, G. Scapacci, P. Zanello, *J. Chem. Soc., Dalton Trans* **1995**, 531.
[23] J. Ott, Dissertation, ETH Zürich, **1986**.
[24] D. R. Robertson, T. A. Stephenson, *J. Organomet. Chem.* **1976**, *107*, C46; D. R. Robertson, T. A. Stephenson, *J. Chem. Soc., Dalton Trans* **1994**, 1885.
[25] C. Bianchini, C. Mealli, A. Meli, M. Sabat, *Inorg. Chem.* **1984**, *23*, 2731; C. Bianchini, C. A. Ghilardi, A. Meli, A. Orlandini, *J. Organomet. Chem.* **1985**, *286*, 259.
[26] L. F. Rhodes, C. Sorato, L. M. Venanzi, F. Bachechi, *Inorg. Chem.* **1988**, *27*, 604.
[27] G. M. Sheldrick, *SHELXTL PLUS programs for use with Siemens X-ray systems, Göttingen, **1990***.
[28] Further details of the crystal structure investigations reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100819. Copies of the data may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44(0)1223/336−033, email: deposit@chemcrys.cam.ac.uk)

[97267]