Fluxionality and Phosphane Arm-off Reactions of Octahedral Ruthenium(II) Complexes with the Tripodal Polyphosphane MeC(CH₂PPh₂)₃

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Structural fluxionality is apparent in the ¹H- and ³¹P-NMR spectra of compounds of the type [Ru(L)(MeCN)(triphos)](CF₃SO₃), **2**–**5**, at 25 °C, where L represents a diorganyldithiocarbamate or a heterocyclic $\kappa^2 N$, *S* coordinating thioamide. In contrast, complexes [Ru(Et₂NCS₂)(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)](CF₃SO₃)₂, **1**, with Na(Et₂NCS₂) at a 1:2 molar ratio yields [Ru(Et₂NCS₂- $\kappa^2 S$)(Et₂NCS₂- κS)(triphos)], **9**, which slowly converts to [Ru(Et₂NCS₂- $\kappa^2 S$)₂(triphosO- $\kappa^2 P$)],

The employment of transition metal complexes of tripodal polyphosphanes such as CH₃C(CH₂PPh₂)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 CH₃C(CH₂)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 $\kappa^2 P$ binding mode has been implicated for a number of five-coordinate RhI and IrI 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 ³¹P-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 $\kappa^3 P$ geometry in an $18e^{-}$ trigonal-bipyramidal complex to the open $\kappa^2 P$ 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 $\kappa^3 P$ geometry for a tripodal polyphosphane, so that the energetic advantage of an open $\kappa^2 P$ 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 [RhL₃(triphos)] (L = Me, H) with CO and H₂^{[7][15]} and ¹H- and ³¹P-NMR evidence have been presented for a $\kappa^3 P \rightleftharpoons \kappa^2 P$ equilibrium of the triphosphane ligand in solutions of [RhMe₂(MeCN)-(triphos)]⁺ at room temperature^[11]. We ourselves have re-

10. on recrystallization from ethanol/acetone under air [triphosO is O=P(Ph)₂CH₂C(CH₃)(CH₂PPh₂)₂]. A similar $\kappa^{3}P \rightarrow \kappa^{2}P$ arm-off dissociation leads to the formation of $[\operatorname{Ru}(\operatorname{mpy}-\kappa^2 N,S)_2(\operatorname{triphosO}-\kappa^2 P)]$ (13) and [Ru(mmim- $\kappa^2 N_{,S}$ (triphosO- $\kappa^2 P$)] (14) (Hmpy = 2-mercaptopyridine, Hmmim = 2-mercapto-1-methylimidazole). Crystal structures reported for $[Ru(mbt-\kappa^2 N,S)(MeCN)(triphos$ are $\kappa^{3}P$](CF₃SO₃) (4) (Hmbt = 2-mercaptobenzothiazole), [Ru(mpym- $\kappa^2 N$, S)(mpym- κ S)(triphos- $\kappa^3 P$)] (11) (Hmpym = 2-mercaptopyrimidine) and 14, the latter of which is present as the OC-6-13 isomer.

cently 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 CH₃CN and phosphane arm-off dissociation processes can be proposed to explain the fluxional behavior of such species. $\kappa^2 P$ coordinated complexes of the type [RhL₂(triphos- $\kappa^2 P$)]⁺ (L = $Et_2NCS_2^-$, Me₂NCS₂⁻ 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 $[RuL_2(triphos-\kappa^2 P)]^+$ and [triphosO is $O=P(Ph)_2CH_2$ - $[RuL_2(triphosO-\kappa^2 P)]^+$ $C(CH_3)(CH_2PPh_2)_2].$

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) $(pyrdtc^- = pyrrolidindithi-$

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[Ru(mbt)(MeCN)(triphos)](CF₃SO₃) ocarbamate), (4)(Hmbt = 2-mercaptobenzothiazole), and [Ru(mpym)-(MeCN)(triphos)](CF₃SO₃) (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]aneS₃) allow the adoption of tridentate μ -1 κ S:2 κ ²S,S' and μ -1 κ S:2 κ ²N,S bridging modes by respectively Me₂NCS₂⁻ and mbt⁻ in the dinuclear complexes $[{Ru(\mu-Me_2NCS_2)([9]aneS_3)}_2]$ - $(CF_3SO_3)_2^{[20]}$ and $[{Ru(\mu-mbt)([9]aneS_3)}_2](CF_3SO_3)_2^{[21]}$. The latter coordination pattern has also been reported for organometallic half-sandwich complex [{Ru(µthe mtz)(C₆H₆)}₂Cl]Cl^[18] (Hmtz = 2-mercapto-2-thiazoline).







Figure 1 depicts the molecular structure of the monocation of **4**. As a result of the very small angle of bite $[S(1)-Ru-N(1) = 66.1(2)^{\circ}]$ 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 [Rh(bdt)(triphos)]⁺ product of the reaction of $[RhCl_3(triphos)]$ with $Na_2(bdt)$ [bdt = o-benzenedithiolate(2-)]^[22]. The angle of bite of the $\kappa^2 S$ coordinated obenzenedithiolate ligand is no less than 20.3° wider than that of the $\kappa^2 N_s S$ 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 ³¹P-NMR spectra in various solvents (CDCl₃, MeOD, [D₆]acetone) consist of a single broad uncontoured resonance (in CDCl₃ 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 ³¹P-NMR resonance. In fact, the fluxional behavior of **4** in CDCl₃ 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 $\delta = 20.92, 31.52, 36.53; 5 \delta = 19.89, 28.05, 37.59$) appear in the ³¹P-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 $\delta = 2.43$ can be observed for the triphos CH_2 protons of 2 at 25°C, three multiplets can be identified in CDCl₃ solution at -30° C: $\delta = 2.19, 2.30, 2.68$). Restricted rotation about the diorganyldithiocarbamate C-N bond also leads to the observation of two signals for the ethyl CH₂ protons of this cation at -30° C ($\delta = 3.64, 3.84$), which then coalesce to a single resonance ($\delta = 3.82$) at ambient temperature.





Both CH₃CN 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 CDCl₃ (-30°C: **2** $\delta = 1.80$, **3** $\delta = 1.87$, **4** $\delta = 1.87$, **5** $\delta = 1.61$) remain effectively un-

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changed 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(Et₂NCS₂)(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 ³¹P NMR spectra for 6-8 in [D₆]DMSO or CDCl₃ 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, $\delta = 3.54$) and the hydride complex 8 ($\delta = 5.29$).

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 $\kappa^2 P$ 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]} $\kappa^2 P$ coordinated complexes such as $[Rh(R_2NCS_2-\kappa^2 S)_2(triphos \kappa^2 P$)][CF₃SO₃] (R = Et, Me) or [Rh(mpym- $\kappa^2 N, S_2$ (triphos- $\kappa^2 P$)][CF₃SO₃]. In contrast, retention of a $\kappa^3 S$ facial coordination mode has been reported for the cyclic thioether [9]aneS₃ in [Rh(mpym- $\kappa^2 N$,S)(mpymScheme 3. $[Ru(Et_2dtc)(CO)(triphos)]^+$ cation of 6 and molecules $[Ru(Et_2dtc)(L)(triphos)]^+$ [(L = CN (7), H (8)]



 κS)([9]aneS₃- $\kappa^3 S$)][CF₃SO₃]^[19] and [Ru(mbt- $\kappa^2 N, S$)(mbt- κS)([9]aneS₃- $\kappa^3 S$]^[21]. The presence of both mono- and bidentate dimethyldithiocarbamate ligands has been confirmed for the organometallic half-sandwich complex [Rh(η^5 -C₅Me₅)(Me₂NCS₂- $\kappa^2 S$)(Me₂NCS₂- κS)]^[24].

Treatment of 1 with Na(Et₂NCS₂) at a 1:2 or 1:3 ratio affords the $\kappa^3 P$ -triphos coordinated complex [Ru(Et₂NCS₂- $\kappa^2 S$)(Et₂NCS₂- 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 $\delta = 19.06$ for the P atoms *trans* to the $\kappa^2 S$ coordinated chelating ligand and a triplet at $\delta = 32.37$ 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 ¹H- and ³¹P-NMR spectra are in accordance with stereochemical rigidity of 9 in CDCl₃ 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 $[\operatorname{Ru}(\operatorname{EtNCS}_2 - \kappa^2 S)_2(\operatorname{triphosO} - \kappa^2 P)]$ (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 $\tilde{v}(PO)$ at 547 cm⁻¹, and by the presence of a typical ³¹P-NMR resonance at $\delta = 26.86$, a value very similar to that of 27.18 found for the analogous Rh^{III} complex [Rh(Et₂NCS₂- $\kappa^2 S$)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 ³¹P NMR spectroscopy. After 2d, respective singlets at $\delta = -26.00$ 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 the ³¹P-NMR spectrum of the mixture in of $[Ru(Et_2NCS_2)_2(triphos-\kappa^2 P)]$ and $[Ru(Et_2NCS_2)_2(triphos-\kappa^2 P)]$ $O(\kappa^2 P)$] present after 7 d in a CDCl₃ solution of 9 exposed to air. Whereas overlapping signals for the coordinated P atoms of these complexes may be located in the range $\delta =$

38–40, the phosphorus resonances of **9** ($\delta = 19.06, 32.37$) 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 Et₂NCS₂⁻ ligands. However, this process proceeds much more slowly than for the analogous Rh^{III} complexes, for which intermediate products of the type [Rh(R₂NCS₂- $\kappa^2 S$)(R₂NCS₂- κS)(triphos- $\kappa^3 P$)]⁺ cannot be isolated^[16].

Scheme 4. $[Ru(Et_2dtc)_2(triphos)]$ (9) and $[Ru(Et_2dtc)_2(triphosO)]$ (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 $Et_2NCS_2^-$, κ^3P -triphos co-[Ru(mpym- $\kappa^2 N, S$)(mpym- κS)ordinated complexes (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 ³¹P NMR triplets in the range $\delta = 21.5 - 29.2$. In contrast to 10 or 12, the 2-mercaptopyrimidinate complex 11 is stable in solution under air and may be recrystallized from CHCl₃/MeOH to afford crystals suitable for X-ray analysis (Figure 4). The small angle of bite $[S(1)-Ru-N(1) 65.9(2)^{\circ}]$ 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) A]. On leaving 12 to stand in CHCl₃ 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 $[\operatorname{Ru}(\operatorname{mpy-}\kappa^2 N, S)_2(\operatorname{triphosO-}\kappa^2 P)]$ (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 (& 21.55, 26.60, 29.17 ppm) atoms, a singlet at $\delta = 25.89$ and an AB pattern at $\delta = 42.45$ 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 $\kappa^2 P$ -triphosO complex [Ru(mmim- $\kappa^2 N, S)_2$ (triphosO- $\kappa^2 P$)] (14) was determined. As previously also established for two Rh^{III} complexes $[Rh(mpy-\kappa^2N,S)_2(triphosO \kappa^2 P$]Cl^[16] $[Rh(mmim-\kappa^2 N, S)_2(triphosO-\kappa^2 P)]$ and $[CF_3SO_3]^{[17]}$, 14 is present as the OC-6-13 isomer. The observation of individual resonances for the coordinated triphosO P atoms ($\delta = 47.8, 49.9$) and the duplication of the mmim⁻ methyl singlet ($\delta = 2.94, 2.98$) and aromatic proton doublets ($\delta = 5.93, 6.09, 6.52, 6.61$) 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



^[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- $\kappa^3 P$)]⁺ of bidentate ligands L⁻ results from a facile acetonitrile dissociation to a five-coordinate species [Ru(L)(triphos- $\kappa^3 P$)]⁺. In contrast to the analogous acetonitrile complexes, $\kappa^3 P$ -triphos compounds of the type [Ru(L)(Y)(triphos- $\kappa^3 P$)]ⁿ⁺ (n = 1, Y = CO; n = 0, Y = CN⁻, H⁻) are stereochemically rigid in solution at both 25°C and 60°C. Armoff $\kappa^3 P \rightarrow \kappa^2 P$ reactions are apparently less favorable for Ru^{II} than for Rh^{III}, thereby allowing the isolation of comFigure 5. Molecular structure of 14. Phenyl rings are omitted for $clarity^{\left[a\right]}$

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 $\stackrel{[a]}{=}$ Selected bond lengths $\stackrel{[A]}{=}$ and angles $\stackrel{[\circ]}{=}$: 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 $[\operatorname{Ru}(\operatorname{Et}_2\operatorname{NCS}_2-\kappa^2 S)(\operatorname{Et}_2\operatorname{NCS}_2-\kappa S)(\operatorname{triphos}_{\kappa^3} P)]$ (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 $[\operatorname{Ru}(\operatorname{Et}_2\operatorname{NCS}_2-\kappa^2 S)_2(\operatorname{triphosO-}\kappa^2 P)]$ (10) and $[\operatorname{Ru}(\operatorname{mpy-}\kappa^2 N,S)_2(\operatorname{triphosO-}_{\kappa^2} P)]$ 13. As 13 and 14 are both formed from $\kappa^3 P$ -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 $\kappa^3 P \rightleftharpoons \kappa^2 P$ 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 $\kappa^2 P$ -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 $\kappa^2 S$ or $\kappa^2 S, N$ 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. – ¹H and ³¹P{¹H} NMR: Bruker AM 400; chemical shifts are reported as δ values relative to the signal of the deuterated solvent (for ¹H) or relative to 85% H₃PO₄ as external standard (for ³¹P). – Elemental analyses: Carlo Erba 1106. – The starting compound [Ru(MeCN)₃(triphos)][CF₃SO₃] (1) was prepared according to the literature procedure^[26] from RuCl₃·x H₂O, which was a gift from Degussa AG.

 $[Ru(Et_2NCS_2)(MeCN)(triphos)](CF_3SO_3)$ (2): Na(Et₂-NCS₂) · 3 H₂O (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 C₂H₅OH. Yield 111.0 mg (68%). - FAB MS, m/z (%): 874 (100) [M - MeCN - CF₃SO₃]⁺. - ¹H NMR $(CDCl_3, -30^{\circ}C): \delta = 1.24$ (t, 6 H, CH₃ Et₂NCS₂), 1.58 (s, 3 H, CH₃ triphos), 1.80 (s, 3 H, MeCN), 2.19 (m, 2 H, CH₂ triphos), 2.30 (m, 2 H, CH₂ triphos), 2.68 (m, 2 H, CH₂ triphos), 3.64 (m, 2 H, CH₂ Et₂NCS₂), 3.84 (m, 2 H, CH₂ Et₂NCS₂), 6.87-7.38 (m, 30 H, Ph triphos). – ³¹P NMR (CDCl₃, –30°C): δ = 26.10 (d, 2 P, trans to Et_2NCS_2), 27.44 (t, 1 P, trans to MeCN). C49H52F3N2O3P3RuS3 · 0.5 C2H5OH (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 NH₄(pyrdtc) (pyrdtc⁻ = pyrrolidinedithiocarbamate) under conditions analogous to those for **2**. Yield 119.5 mg (75%). – FAB MS, *m/z* (%): 872 (100) [M – MeCN – CF₃SO₃]⁺. – ¹H NMR (CDCl₃, –30°C): δ = 58 (s, 3 H, CH₃ triphos), 1.87 (s, 3 H, MeCN), 1.97, 2.08, 2.14 (3×2 H, 3 m, CH₂ pyrdtc⁻ and triphos), 2.32 (m, 2 H, CH₂ triphos), 2.64 (m, 2 H, CH₂ triphos), 3.64 (m, 4 H, CH₂ pyrdtc⁻), 6.87–7.39 (m, 30 H, Ph triphos). – ³¹P NMR (CDCl₃, –30°C): δ = 5.70 (d, 2 P, *trans* to pyrdtc⁻), 28.56 (t, 1 P, *trans* to MeCN). – C₄₉H₅₀F₃N₂O₃P₃RuS₃ (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 – CF₃SO₃]⁺. – ¹H NMR (CDCl₃, -30° C): $\delta = 1.59$ (s, 3 H, CH₃ triphos), 1.87 (s, 3 H, MeCN), 2.27 (m, 2 H, CH₂ triphos), 2.46 (m, 3 H, CH₂ triphos), 2.60 (m, 1 H, CH₂ triphos), 6.30 (d, 1 H, mbt), 6.80–7.39 (m, 32 H, Ph triphos and mbt), 7.68 (d, 1 H, mbt). – ³¹P NMR (CDCl₃, -30° C): $\delta = 20.92$ (t, 1 P), 31.52 (t, 1 P), 36.43 (t, 1 P). – C₅₁H₄₆F₃N₂O₃P₃RuS₃·0.5 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, *mlz* (%): 986 (2) [M⁺], 837 (100) [M – MeCN – CF₃SO₃]⁺. – ¹H NMR (CDCl₃, –30°C): δ = 1.61 (s, 3 H, MeCN), 1.63 (s, 3 H, CH₃ triphos), 2.05 (m, 1 H, CH₂ triphos), 2.26 (m, 2 H, CH₂ triphos), 2.78 (m, 3 H, CH₂ triphos), 6.60–7.56 (m, 31 H, Ph triphos and mpym), 7.78 (d, 1 H, mpym), 8.45 (d, 1 H, mpym). – ³¹P NMR (CDCl₃, –30°C): δ = 19.89 (t, 1 P), 28.05 (t, 1 P), 37.59 (t, 1 P). – C₄₈H₄₅F₃N₃O₃P₃RuS₂ (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 CH₂Cl₂ 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, *mlz* (%): 902 (26) [M – CF₃SO₃]⁺, 874 (87) [M – CO – CF₃SO₃]⁺. – ¹H NMR ([D₆]DMSO): δ = 1.14 (t, 6 H, CH₃ Et₂NCS₂), 1.70 (s, 3 H, CH₃ triphos), 2.53–2.85 (m, 6 H, CH₂ triphos), 3.54 (m, 2 H, CH₂ Et₂NCS₂), 3.71 (m, 2 H, CH₂ Et₂NCS₂), 6.94–7.49 (m, 30 H, Ph triphos). – ³¹P NMR ([D₆]DMSO): δ = 3.54 (t, 1 P, *trans* to CO), 21.20 (d, 2 P, *trans* to Et₂NCS₂). – IR: \tilde{v} = 2002 s cm⁻¹ (CO). – C₄₈H₄₉F₃NO₄P₃RuS₃ (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 CH₂Cl₂. 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 – Et₂dtc]⁺. – ¹H NMR ([D₆]DMSO): δ = 1.08 (t, 6 H, CH₃ Et₂NCS₂), 1.42 (s, 3 H, CH₃ triphos), 2.20–2.45 (m, 6 H, CH₂ triphos), 3.43 (m, 2 H, CH₂ Et₂NCS₂), 3.67 (m, 2 H, CH₂ Et₂NCS₂), 6.77–7.79 (m, 30 H, Ph triphos). – ³¹P NMR ([D₆]DMSO): δ = 19.26 (t, 1 P, *trans* to CN),

27.40 (d, 2 P, *trans* to Et₂NCS₂). – IR: $\tilde{\nu} = 2094$ s cm⁻¹ (CN). – C₄₇H₄₉N₂P₃RuS (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): NaBH₄ (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]⁺. – ¹H NMR (CDCl₃): 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, CH₃ Et₂NCS₂), 1.38 (s, 3 H, CH₃ triphos), 2.10–2.23 (m, 6 H, CH₂ triphos), 3.61 (m, 2 H, CH₂ Et₂NCS₂), 3.91 (m, 2 H, CH₂ Et₂NCS₂), 6.87–7.39 (m, 26 H, Ph triphos), 7.74 (s, 4 H, Ph triphos). – ³¹P NMR (CDCl₃): δ = 5.29 (m, 1 P, *trans* to H), 47.10 (d, 2 P, *trans* to Et₂NCS₂). – IR: \tilde{v} = 1846 s cm⁻¹ (RuH). – C₄₆H₅₀NP₃RuS₂ (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(Et₂-NCS₂)· 3 H₂O (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 – Et₂NCS₂]⁺. – ¹H NMR (CDCl₃): δ = 0.86, 1.01 (2 t, 2×6 H, CH₃ Et₂NCS₂), 1.52 (s, 3 H, CH₃ triphos), 2.23, 2.42 (m, 6 H, CH₂ triphos), 3.31, 3.54 (m, 8 H, CH₂ Et₂NCS₂), 6.60–7.70 (m, 30 H, Ph triphos). – ³¹P NMR (CDCl₃): δ = 19.06 (d, 2 P, *trans* to Et₂NCS₂-*κ*²*S*), 32.37 (t, 1 P, *trans* to Et₂NCS₂-*κS*). – C₅₁H₅₉N₂P₃RuS₄ (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 – Et₂NCS₂]⁺. – ¹H NMR (CDCl₃): $\delta = 0.80-1.01$ (m, 15 H, CH₃ of Et₂NCS₂ and triphosO), 2.13–3.60 (m, 14 H, CH₂ of Et₂NCS₂ and triphosO), 6.80–7.80 (m, 30 H, Ph triphosO). – ³¹P NMR (CDCl₃): $\delta = 26.86$ (s, 1 P, P=O) 38.96, 40.38 (2d, 2 P, *trans* to Et₂NCS₂). – IR: $\tilde{v} = 574$ m cm⁻¹ (δ PO). – C₅₁H₅₉N₂OP₃RuS₄ (1038.3): calcd. C 59.0, H 5.7, N 2.7; found C 58.5, H 5.3, N 2.6.

[*Ru*(*mpym*- $\kappa^2 N$, *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 CHCl₃/MeOH mixture (2:3). Slow evaporation afforded yellow crystals of 11. Yield 122.0 mg (74%). – FAB MS, *mlz* (%): 948 (1) [M]⁺, 837 (100) [M – mpym]⁺. – ¹H NMR (CDCl₃): δ = 1.53 (s, 3 H, CH₃ triphos), 2.05 (m, 1 H, CH₂ triphos), 2.45 (m, 2 H, CH₂ triphos), 2.68 (m, 3 H, CH₂ triphos), 5.62 (s, 1 H, mpym), 6.25 (s, 1 H, mpym) 6.60–8.00 (m, 34 H, mpym and Ph triphos). – ³¹P NMR (CDCl₃): δ = 25.17 (t, 1 P), 26.39 (t, 1 P), 29.05 (t, 1 P). – C₄₉H₄₅N₄P₃RuS₂·MeOH·CHCl₃ (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*- κ *S*)(*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 CHCl₃ solution covered with hexane. Yield 100.7 mg (63%). – FAB MS, *m*/*z* (%): 947 (1) [M]⁺, 836 (100) [M – myp]⁺. – ¹H NMR (CDCl₃): δ = 1.43 (s, 3 H, CH₃ triphos), 2.39 (m, 6 H, CH₂ 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). – ³¹P NMR (CDCl₃): 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*- $\kappa^2 N$,*S*)₂(*triphosO*- $\kappa^2 P$) (13): On leaving a reaction solution of 12 in CHCl₃ 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. C₅₁H₄₇N₂OP₃RuS₂ (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]⁺. – ¹H NMR (CDCl₃) 0.63 (s, 3 H, CH₃ triphosO), 2.19 (m, 2 H, CH₂ triphosO), 2.58, 2.79, 2.86, 3.19 (m, 4 H, CH₂ 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). – ³¹P NMR (CDCl₃) 25.89 (s, 1 P, P=O), 42.45 (AB system, 2 P). – IR: $\tilde{v} = 1200$ m (vPO), 568 m cm⁻¹ (δ PO).

[*Ru*(*mmin*- $\kappa^2 N$, *S*)₂(*triphosO*- $\kappa^2 P$) (14): Hmmim (34.2 mg, 0.3 mmol) was dissolved in 10 ml of MeOH in the presence of 0.3 ml of 1 м 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 – mmin]⁺. – ¹H NMR (CDCl₃): δ = 0.92 (s, 3 H, CH₂ triphosO), 2.94, 2.98 (s, 6 H, CH₃ mmin), 5.93, 6.09, 6.52, 6.61 (d, 4 H, CH mmin), 6.52 – 7.79 (m, 30 H, Ph triphosO). – ³¹P NMR (CDCl₃): δ = 26.74 (s, 1 P, P=O), 47.8, 49.9 (AB system, 2 P). – IR: $\tilde{\nu}$ = 571 m cm ⁻¹ (δPO). – C₄₉H₄₉N₄OP₃RuS₂ (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, graphitemonochromated Mo-*Ka* radiation ($\lambda = 0.71073$ 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 CH₃OH: C₅₁H₄₆F₃N₂O₃P₃RuS₃ · 1/2 CH₃OH, *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) Å³, *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 = σ²(*F*_o) + 0.003 *F*_o⁻², *R* = 0.040, *R*_w = 0.044 for 3896 reflections with *F*_o² > 2σ(*F*_o²); largest difference peak: 0.55 eÅ⁻³. The CF₃SO₃⁻ 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 · CHCl₃ · CH₃OH: $C_{49}H_{45}N_4P_3RuS_2 \cdot CHCl_3 \cdot CH_3OH$, M = 1099.4, monoclinic, space group $P2_1/c$ (No. 14), a = 12.611(3), b = 21.605(4), c = 18.757(4) Å, $\beta = 91.01(3)^\circ$, V = 5110(2) Å³, Z = 4, $D_{calc} = 1.429$ g·cm⁻³, $\mu = 0.68$ mm⁻¹. Crystal size $0.32 \times 0.39 \times 0.42$ mm; ω scan, scan range: $4 \le 2\theta \le 50^\circ$ ($0 \le h \le 14, -25 \le k \le 0, -22 \le l \le 22$), 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 reflections 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.

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14 \cdot CH₃OH \cdot 1/2 H₂O: C₄₉H₄₉N₄OP₃RuS₂ \cdot CH₃OH \cdot 1/2 H₂O, M = 1009.1, triclinic, space group $P\bar{1}$ (No. 2), a = 10.9610(4), b =13.944(6), c = 17.590(3) Å, $\alpha = 76.90(3)$, $\beta = 88.68(3)$, $\gamma =$ 88.94(3)°, V = 2618(2) Å³, Z = 2, $D_{calc} = 1.280$ g·cm⁻³, $\mu = 0.50$ mm⁻¹. Crystal size $0.28 \times 0.34 \times 0.40$ mm; ω scan , scan range: 3 $\leq 2\theta \leq 45^{\circ} \ (0 \leq h \leq 11, -15 \leq k \leq 15, -18 \leq l \leq 18), 7081$ reflections collected, 6659 symmetry-independent reflections (R_{int} = 0.050); max./min. transmission: 0.804/0.627; 305 parameters refined; $w^{-1} = \sigma^2(F_0) + 0.005 F_0^2$, R = 0.088, $R_w = 0.081$ for 2803 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 1.13 eA^{-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.

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- ^[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)

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