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

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Treatment of $[RhCl_3(triphos)]$ or $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ [triphos = $MeC(CH_2PPh_2)_3$] with $Na(S_2CNEt_2)$ affords the complexes $[RhCl(S_2CNEt_2)(triphos)]Cl$ (**1**) and $[Rh(S_2CNEt_2)(MeCN)(triphos)](CF_3SO_3)_2$ (**2**). Whereas **1** is stereochemically rigid in solution at 25 °C, **2** and the analogous complex $[Rh(S_2CNBz_2)(MeCN)(triphos)](CF_3SO_3)_2$ (**3**) exhibit a rapid exchange of their phosphorus environments. In contrast, the ^{31}P-NMR spectra of both **2** and **3** at −30 °C consist of well-resolved A_2MX spin systems. κ^2P-coordinated complexes of the type $[Rh(S_2CNR_2)_2(triphos\text{-}\kappa^2P)]^+$ (R = Et **4**, R = Me **5**) with ABX spin systems may be obtained by treatment of the starting compounds with two equivalents of the respective dialkyl dithiocarbamate. The dangling phosphane arm can be readily oxidised to a phosphane oxide as in $[Rh(S_2CNEt_2)_2(triphosO\text{-}\kappa^2P)]Cl$ (**6**) [triphosO = $O{=}P(Ph)_2CH_2C(Me)(CH_2PPh_2)_2$]. The analogous compound $[Rh(mpy)_2(triphosO\text{-}\kappa^2P)]Cl$ (**7**) (Hmpy = 2-mercaptopyridine) was isolated as the *OC*-6-13 isomer with *trans*-positioned sulphur atoms, a siting which is in accordance with a reaction mechanism involving a phosphane arm-off $\kappa^3P \rightleftharpoons \kappa^2P$ dissociation equilibrium.

Recent interest in transition metal complexes of tripodal polyphosphanes such as $MeC(CH_2PPh_2)_3$ (triphos) has been triggered by their apparent potential as catalysts in homogeneous reactions such as the hydrogenation and hydroformylation of alkynes and alkenes[1–5]. Triphos is generally regarded as a typical innocent ligand that can occupy three facial sites in a square-pyramidal, trigonal-bipyramidal or octahedral coordination sphere. However, a series of examples have been reported of reactions involving triphos as a tripodal ligand in five-coordinate Rh(I) and Ir(I) complexes, which can only be explained on the basis of an "arm-off" $\kappa^3P \rightleftharpoons \kappa^2P$ dissocitation mechanism[6–12]. The kinetic lability of the M(I)−P bonds in such complexes can also lead to structural fluxionality at higher temperatures. For instance the ^{31}P-NMR spectrum of $[IrCl(CO)(triphos)]$ at 170 K exhibits two signals at $\delta = +1.1$ and -21.2 in an integral ratio of 2:1[13]. At room temperature dissociation of a triphosphane arm enables exchange between the two phosphorus environments, and the spectrum consists solely of a singlet at $\delta = -16.1$. This behaviour has been attributed to the pronounced reduction in ring strain that may be realised on going from the facial κ^3P geometry in an $18e^-$ trigonal-bipyramidal species to the open κ^2P geometry of a square-planar $16e^-$ species[11,14].

A phosphane arm-off process has also been proposed to explain the reaction of the octahedral Rh(III) complexes $[RhL_3(triphos)]$ (L = Me, H) with CO and H_2[7,14]. In addition, a $\kappa^3P \rightleftharpoons \kappa^2P$ equilibrium has been implicated for the triphosphane ligand of $[RhMe_2(MeCN)(triphos)]^+$, for solutions of this complex at room temperature[11]. ^1H-NMR studies in CD_3CN and CD_2Cl_2 indicate that exchange of free and coordinated acetonitrile molecules is rapid and first order in free CH_3CN. Evidence for the reaction mechanism is provided by the ^{31}P-NMR spectra (CD_2Cl_2) at −30 and 25 °C. Whereas a well-resolved A_2MX pattern may be recorded for the complex at the lower temperature, broadening prevents the resolution of the P-P coupling at room temperature. This fluxionality has been attributed to a $\kappa^3P \rightleftharpoons \kappa^2P$ equilibrium for the triphosphane ligand, which enables the addition of acetonitrile to the transient five-coordinated species in accordance with the ^1H-NMR data[11].

Such a phosphane arm dissociation in octahedral Rh(III) complexes can only partially be attributed to a relief of ring strain. The idealised octahedral P−Rh−P angles clearly provide a relatively unstrained triphos-κ^3P geometry so that the advantage of an open κ^2P geometry will be less pronounced than for five-coordinated Rh(I) complexes. The existing paucity of direct experimental evidence for $\kappa^3P \rightarrow \kappa^2P$ reactions of octahedral triphos complexes prompted us to investigate the treatment of $[RhCl_3(triphos)]$[7] and $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ with diorganyldithiocarbamates, $S_2CNR_2^-$ (R = Me, Et, Bz), and 2-mercaptopyridine, Hmpy (ligands L^-), with the goal of preparing complexes of the type $[RhCl(L)(triphos)]Cl$, $[RhL(MeCN)(triphos)](CF_3SO_3)_2$, and $[RhL_2(triphos)]X$ (X = Cl^-, $CF_3SO_3^-$) for NMR spectroscopic and X-ray structural studies. Our choice of the diorganyldithiocarbamates was motivated by their ability to coordinate in both a mono- and bidentate manner, by the pronounced *trans* effect of their sulphur donor atoms and by their relatively limited steric demands caused by the small chelating angle of bite. The ambidentate ligand mpy^-, which was employed for a

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mechanistic study of the formation of complex cations of the type $[RhL_2(triphos\text{-}\kappa^2P)]^+$ and $[RhL_2(triphosO\text{-}\kappa^2P)]^+$, exhibits similar properties.

Results

Treatment of $[RhCl_3(triphos)]$ with $Na(S_2CNEt_2)$ in methanol affords the octahedral complex $[RhCl(S_2CNEt_2)(triphos\text{-}\kappa^3P)]Cl$ (**1**), in which the κ^2S-coordinated diethyldithiocarbamate ligand participates in a four-membered chelate ring. The analogous mononuclear complexes $[RhCl(\eta^5\text{-}C_5Me_5)(S_2CNMe_2)]$ and $[RuCl(S_2PPh_2)(\eta^6\text{-}C_6H_6)]$ are known for the half-sandwich $(\eta^5\text{-}C_5Me_5)Rh(III)$ and $(\eta^6\text{-}C_6H_6)Ru(II)$[16,17] fragments. In contrast, the reduced steric demands of the facially coordinated cyclic thioether 1,4,7-trithiacyclononane ([9]aneS$_3$) allow the adoption of a tridentate $1\kappa^2S,S':2\kappa S$ bridging mode by the dimethyldithiocarbamate ligands in the dinuclear complex $[\{Ru(\mu\text{-}S_2CNMe_2)([9]aneS_3)\}_2](CF_3SO_3)_2$[18].

Figure 1. Molecular structure of the cation of **1**. Phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–Cl 2.436(3), Rh–S(1) 2.423(2), Rh–S(2) 2.390(2), Rh–P(1) 2.355(2), Rh–P(2) 2.293(3), Rh–P(3) 2.341(2), S(1)–C(1) 1.708(8), S(2)–C(1) 1.683(9); S(1)–Rh–S(2) 72.0(1), S(1)–Rh–P(3) 166.3(1), S(2)–Rh–P(1) 178.8(1), Cl–Rh–P(2) 169.4(1), P(1)–Rh–P(2) 88.3(1), P(1)–Rh–P(3) 86.7(1), P(2)–Rh–P(3) 90.2(1)

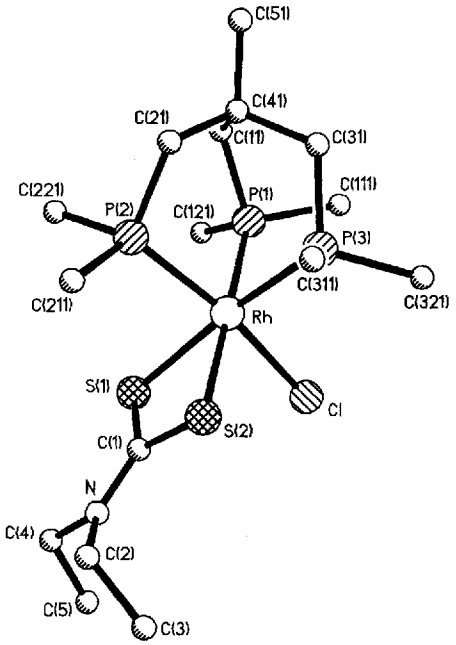
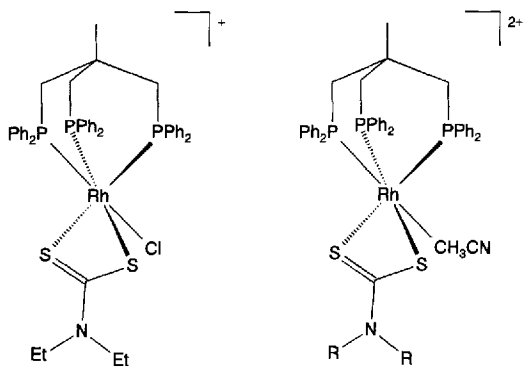


Figure 1 depicts the molecular structure of the monocation of **1**. The narrow angle of bite of the κ^2S-coordinated ligand [72.0(1)°] leads to a significant decrease in the opposite P(1)–Rh–P(3) angle from the idealised octahedral angle to 86.7(1)°. Whereas P(1) adopts a coordination site in an effectively ideal *trans* position to S(2) [S(2)–Rh–P(1) = 178.8(1)°] a marked deviation from linearity is observed for the S(1)–Rh–P(3) angle of 166.3(1)°. This angular difference is also reflected in the extent of the *trans* influence of the diethyldithiocarbamate S atoms on the opposite Rh–P bond lengths of 2.355(2) [Rh–P(1)] and 2.341(2) Å [Rh–P(3)]. The importance of this *trans* influence is indicated by a comparison of these distances with the markedly shorter Rh–P(2) bond length of 2.293(3) Å.

The ^{31}P-NMR spectrum of **1** at room temperature consists of a typical A_2MX spin system and provides no evidence for fluxional behaviour of the coordination sphere in $CDCl_3$ solution. Both the ^{103}Rh-^{31}P and the ^{31}P-^{31}P couplings are well resolved. The phosphorus atoms *trans* to the diethyldithiocarbamate ligand are responsible for the doublet of doublets ($J_{Rh\text{-}P}$ = 97.5, $J_{P\text{-}P}$ = 26.5 Hz) at $\delta = -1.53$, the unique phosphorus *trans* to the chloride ligand for the doublet of triplets ($J_{Rh\text{-}P}$ = 103.1 Hz) at δ = 27.01.

Scheme 1. $[RhCl(S_2CNEt_2)(triphos)]^+$ cation of **1**, $[Rh(S_2CNR_2)(MeCN)(triphos)]^{2+}$ cations of **2** (R = Et) and **3** (R = Bz)

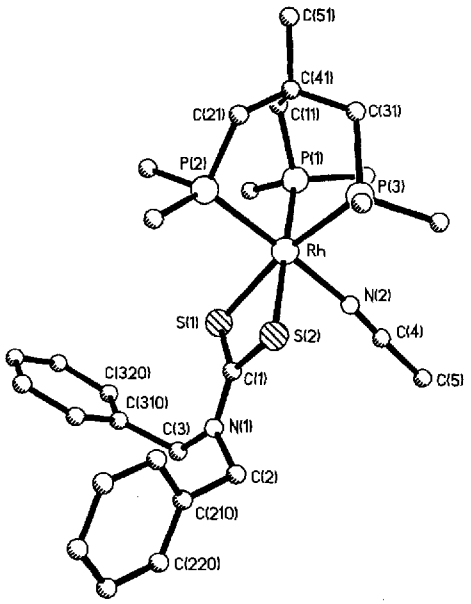


1 R = Et **2**, Bz **3**

Cationic complexes of the type $[Rh(S_2CNR_2)(MeCN)(triphos\text{-}\kappa^3P)](CF_3SO_3)_2$ (R = Et **2**, R = Bz **3**) may be prepared by the reaction of $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ with $Na(S_2CNR_2)$ in acetonitrile. Figure 2 depicts the molecular structure of the dication of the dibenzyldithiocarbamate derivative **3**. The P(1)–Rh–P(3) angle *trans* to the four-membered RhSCS chelate ring exhibits a smaller deviation (1.8°) from the idealised octahedral angle than the analogous angle in **1** (3.3°). A pronounced *trans* influence of the donor S atoms with an associated correlation of the S–Rh–P angles S(1)–Rh–P(3) [166.5(1)°] and S(2)–Rh–P(1) [175.5(1)°] and the Rh–P(3) [2.342(2) Å] and Rh–P(1) [2.361(2) Å] distances is once again apparent for complex **3**. As to be expected on the basis of the relative *trans* influences, the Rh–P(2) bond opposite to the coordinated acetonitrile ligand displays a distance [2.318(2) Å] intermediate between that of the analogous bond in **1** (*trans* to Cl) and the Rh–P distances *trans* to dithiocarbamate S atoms in **1** and **3**. It is interesting to contrast the formation of octahedral mono- and dications of the types $[RhCl(S_2CNEt_2)(triphos)]^+$ in **1** and $[Rh(S_2CNEt_2)(MeCN)(triphos)]^{2+}$ in **2** 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–)][19]. The angle of bite of the κ^2S-coordinated *o*-benzenedithiolate ligand is 14.4° wider than in **1** (14.0° in comparison to **3**). It is, therefore, apparent that the steric demands of the bulky triphos phenyl groups pre-

vent the occupation of the potential sixth octahedral coordination site. The Rh–P bonds opposite to the bdt^{2-} sulphur atoms in the distorted square-planar coordination sphere of $[Rh(bdt)(triphos)]^+$ are markedly shorter [2.300(3), 2.312(3) Å] than the analogous bonds in **1** and **3** [2.341(2)–2.361(2) Å].

Figure 2. Molecular structure of the cation of **3**. Phenyl rings and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–N(2) 2.088(6), Rh–S(1) 2.409(2), Rh–S(2) 2.405(2), Rh–P(1) 2.361(2), Rh–P(2) 2.318(2), Rh–P(3) 2.342(2), S(1)–C(1) 1.714(8), S(2)–C(1) 1.726(8); S(1)–Rh–S(2) 72.35(7), S(1)–Rh–P(3) 166.48(7), S(2)–Rh–P(1) 175.51(7), N(2)–Rh–P(2) 176.1(2), P(1)–Rh–P(2) 85.82(7), P(1)–Rh–P(3) 88.22(7), P(2)–Rh–P(3) 92.38(7)



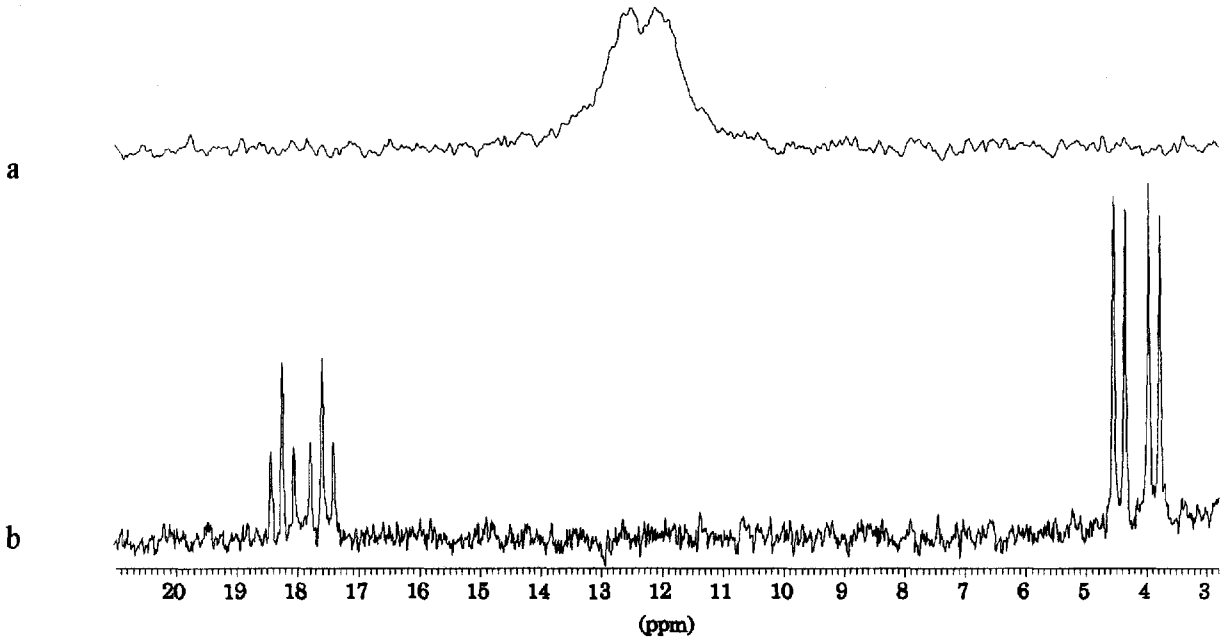
Both **2** and **3** exhibit the molecular ion $\{[Rh(S_2CNR_2)(triphos)]CF_3SO_3\}^+$ as the first peak in their FAB mass spectra. Facile exchange of coordinated and free acetonitrile is indicated by ^{1}H-NMR studies of **2** in CD_3CN. The spectrum at room temperature contains a broad singlet at $\delta = 2.92$ for the triphos CH_2 protons and a single multiplet at $\delta = 3.68$ for the ethyl CH_2 protons, which suggest a fluxional process. On cooling to −30 °C individual signals can be assigned to the triphos CH_3 ($\delta = 1.87$, d, $^4J_{P\text{-}H} = 3$ Hz) and CH_2 protons ($\delta = 2.69$, 2.82, 3.17), but only a broad resonance for free CH_3CN can be observed ($\delta = 1.94$) indicating that exchange with the solvent must be rapid. As the poor solubility of **2** prevented the registration of a resolved ^{1}H-NMR spectrum in $CDCl_3$ (or CD_2Cl_2), studies in this non-exchanging solvent were restricted to **3**. Fluxionality once again leads to equivalence of the triphos and benzyl CH_2 protons ($\delta = 2.90$ and 4.68) in the ^{1}H-NMR spectrum at room temperature. At −30 °C in $CDCl_3$, however, resolution is possible with signals appearing for the triphos ($\delta = 2.04$, q, $^4J_{P\text{-}H} = 5$ Hz) and acetonitrile methyl groups ($\delta = 2.14$, s). The ^{31}P-NMR spectra provide further evidence for the fluxional behaviour of **2** and **3** in solution at room temperature. Both complexes provide well-resolved A_2MX patterns at −30 °C with the unique phosphorus resonance (*trans* to MeCN) shifted to higher field ($\delta = 17.92$) in **3** in comparison to **1** ($\delta = 27.01$, $CDCl_3$). The ^{31}P-NMR spectrum of **2** in CD_3CN at 25 °C provides two very broad resonances without fine structure at $\delta = 6$ and 20, that of **3** in $CDCl_3$ is depicted in Figure 3(a). It consists of only one broad unstructured resonance without ^{103}Rh-^{31}P coupling in the range of $\delta = 11-14$. Both dissociative and associative CH_3CN exchange processes can be discussed for the cations of **2** and **3**. The associative exchange process proposed[11] for $[RhMe_2(MeCN)(triphos)]^+$ and plausible for **2** and **3** requires an initial phosphane arm-off dissociation, and such a mechanism is indeed suggested for the latter complexes by their lack of ^{103}Rh-^{31}P coupling. In contrast to $[RhMe_2(MeCN)(triphos)]^+$ a rapid averaging of the phosphorus environments is apparent for **2** and particularly **3** at room temperature. This should be a low-energy process for the required five-coordinated intermediate whether this be κ^3P- or κ^2P-coordinated; for instance exchange of the phosphorus environments has been observed for κ^3P-coordinated triphos $[RhMe_2(triphos)]^+$ in CD_2Cl_2[11]. The present NMR spectroscopic findings suggest that the arm-off process for κ^3P-coordinated triphos could be more general in octahedral complexes than previously supposed. An apparent prerequisite for the labilisation of the Rh–P bond would be the presence of an opposite ligand with a pronounced *trans* effect, e.g. Me^-, H^-, $S_2CNR_2^-$.

Phosphane Arm-off Reactions

The established fluxionality of the cations of **2** and **3** led us to consider whether the postulated κ^2P-coordinated triphos complexes with a dangling phosphane arm can be stabilised by the presence of an excess of a small bite chelating ligand such as $S_2CNR_2^-$ or mpy^-. Retention of the κ^2P environment would also be possible in complex cations of the type $[RhL_2(triphos)]^+$, if one of the ligands L adopts a monodentate coordination mode, as has been established for $[Rh(\eta^5\text{-}C_5Me_5)(S_2CNMe_2\text{-}\kappa^2S)(S_2CNMe_2\text{-}\kappa S)]$[16,17] and $[Rh(mpym\text{-}\kappa^2N,S)(mpym\text{-}\kappa S)([9]aneS_3)]$[20] (Hmpym = 2-mercaptopyrimidine).

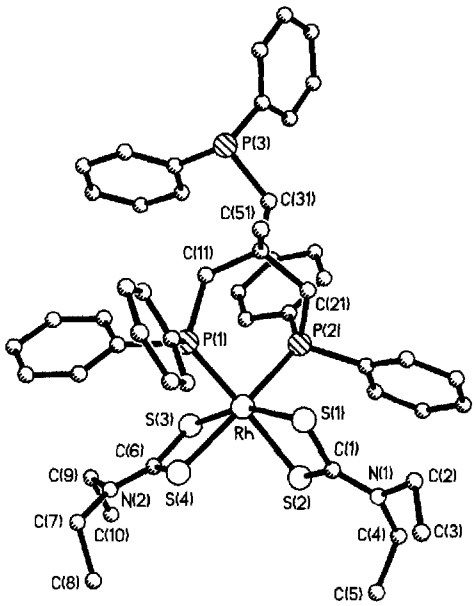
Treatment of either $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ or $[RhCl_3(triphos)]$ with $Na(S_2CNR_2)$ leads to the formation of complexes of the type $[Rh(S_2CNR_2\text{-}\kappa^2S)_2(triphos\text{-}\kappa^2P)]X$ (X = CF_3SO_3, Cl). The presence of a dangling phosphane arm is confirmed in the ^{31}P-NMR spectra of $[Rh(S_2CNEt_2)_2(triphos)]CF_3SO_3$ (**4**) and $[Rh(S_2CNMe_2)_2(triphos)]Cl$ (**5**) by the observation of a singlet at very high field for the uncoordinated phosphorus atom ($\delta = -27.08$ **4**, −28.04 **5**). The phosphorus atoms *trans* to dialkyldithiocarbamate sulphur atoms experience a marked shift to lower field ($\delta = 16.59$, 16.81 **4**; 16.34, 16.72 **5**) in comparison to the κ^3P-coordinated complexes **1**–**3**. Both **4** and **5** are stereochemically rigid species with an ABX pattern in solution at 25 °C. A further indication of the change in the triphosphane coordination mode is provided by the highfield shift of the triphos CH_3 protons to $\delta = 0.85$ (**4**) and 0.87 (**5**). The molecular structure of **4** is depicted in Figure 4. A degree of ring strain relief on going from κ^3P- to κ^2P-coordinated triphos is indicated by the significant decrease in the Rh-P

Figure 3. $^{31}P\{^1H\}$-NMR spectrum of **3** in $CDCl_3$: (a) at 25°C, (b) at −30°C



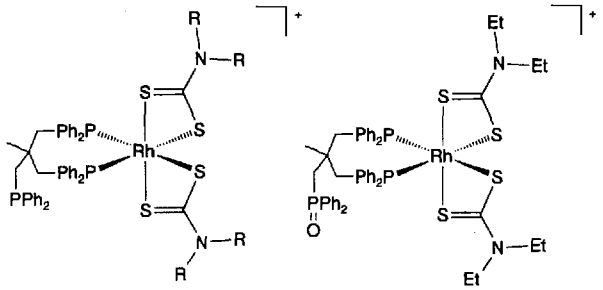
distances [2.314(7), 2.328(7) Å] in comparison to those of **1** and **3** and by the closeness of the P(1)−Rh−P(2) angle [90.7(2)°] to the idealised octahedral value. As previously discussed for **1** and **3** a correlation between the Rh−P bond lengths and the relevant bond angles [172.6(2), 177.3(2)°] can also be established for **4**.

Figure 4. Molecular structure of the cation of **4**. Selected bond lengths [Å] and angles [°]: Rh−S(1) 2.385(7), Rh−S(2) 2.400(7), Rh−S(3) 2.390(7), Rh−S(4) 2.386(6), Rh−P(1) 2.314(7), Rh−P(2) 2.328(7), S(1)−C(1) 1.73(2), S(2)−C(1) 1.70(2), S(3)−C(6) 1.72(2), S(4)−C(6) 1.71(2); S(1)−Rh−S(2) 72.9(2), S(3)−Rh−S(4) 73.0(2), S(1)−Rh−S(3) 160.7(3), S(2)−Rh−P(1) 172.6(2), S(4)−Rh−P(2) 177.3(2), P(1)−Rh−P(2) 90.7(2)



During the course of our ^{31}P-NMR investigations of **4** we noticed the presence of a minor singlet at δ = 27, that

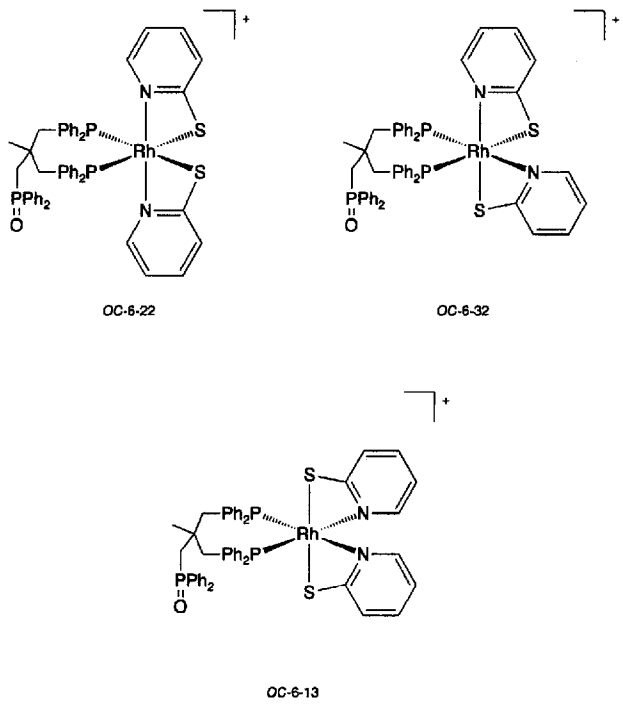
Scheme 2. $[Rh(S_2CNR_2)_2(triphos\text{-}\kappa^2P)]^+$ cations of **4** (R = Et) and **5** (R = Me), $[Rh(S_2CNEt_2)_2(triphosO\text{-}\kappa^2P)]^+$ cation of **6**



can be attributed to the oxidation of the uncoordinated phosphorus atom to afford $[Rh(S_2CNEt_2)_2(triphosO\text{-}\kappa^2P)]^+$ [triphosO = $O{=}P(Ph)_2CH_2C(CH_3)(CH_2PPh_2)_2$]. This signal grows with time on leaving the NMR tube in contact with air. The oxidation proceeds more rapidly in methanol than in acetonitrile or chloroform, and the presence of a phosphane oxide impurity is difficult to avoid when the synthesis of κ^2P-coordinated cations of the type $[Rh(S_2CNR_2)_2(triphos\text{-}\kappa^2P)]^+$ is performed in this solvent. We prepared $[Rh(S_2CNEt_2)_2(triphosO\text{-}\kappa^2P)]Cl$ (**6**) in effectively quantitative yield by treatment of $[RhCl_3(triphos)]$ with $Na(S_2CNEt_2)$ in methanol followed by slow recrystallisation of the raw product from a CH_2Cl_2/hexane solution under air. The facile oxidation of one phosphane arm has been reported by Bianchini and co-workers for five-coordinated nickel complexes containing κ^3P-coordinated triphos[21,22]. For instance, exposure of $[Ni(CS_2\text{-}\kappa^2C,S)(triphos\text{-}\kappa^3P)]$ to air yields the square-planar complex $[Ni(S_2CO\text{-}\kappa^2S)(triphosO\text{-}\kappa^2P)]$. As attempts to syn-

thesise the possible five-coordinated intermediate [Ni(S_2CO-κ^2S)(triphos-κ^3P)] were unsuccessful the nature of the reaction mechanism remains unclear. However, Collman et al. have demonstrated that κ^3P-coordinated triphos in [RhCl(CO)(triphos-κ^3P)] can be oxidised with H_2O_2 to afford square-planar [RhCl(CO)(triphos-κ^2P)][6]. A κ^2P-coordinated triphosO complex [ReCl(CO)$_3$(triphosO-κ^2P)] · H_2O was also obtained as a minor product of the reaction of [$Re_2(CO)_{10}$] with triphos in CH_2Cl_2 under photolysing conditions[23].

Scheme 3. Possible isomers of the [Rh(mpy)$_2$(triphosO-κ^2P)]$^+$ cation of **7**

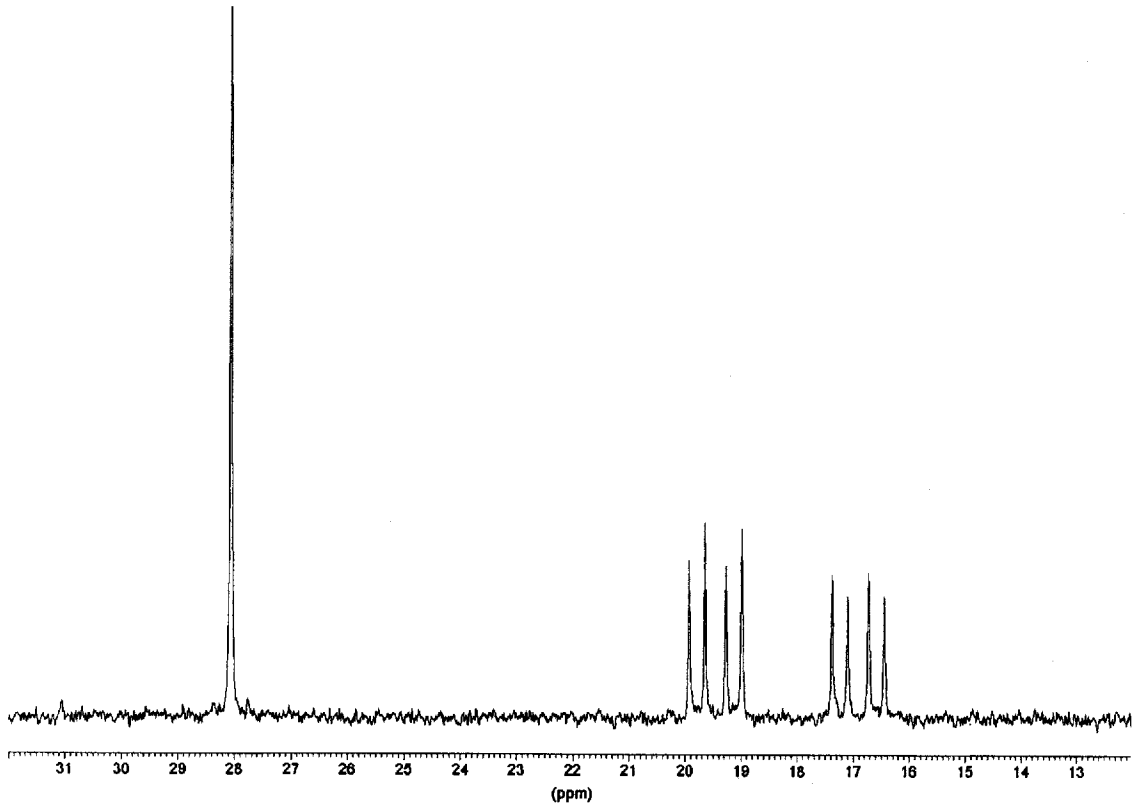


A phosphane arm-off reaction for [$RhCl_3$(triphos)] or [Rh(MeCN)$_3$(triphos)](CF_3SO_3)$_3$ with the ambidentate ligand mpy$^-$ could lead to one of three potential isomeric products with respectively N *trans* to N (*OC*-6-22), N *trans* to S (*OC*-6-32) or S *trans* to S (*OC*-6-13).

If it is assumed that the first stage of the reaction will afford a complex cation of the type [RhCl(mpy-κ^2N,S)(triphos-κ^3P)]$^+$ or [Rh(mpy-κ^2N,S)(MeCN)(triphos-κ^3P)]$^{2+}$, then the necessary subsequent dissociation process will determine which of the isomers will be formed. A chloride or acetonitrile dissociation followed by a nucleophilic attack of the preferred sulphur atom of mpy$^-$ in the vacant octahedral coordination position could lead to the *OC*-6-22 or *OC*-6-32 isomer. In contrast, a $\kappa^3P \rightleftharpoons \kappa^2P$ phosphane arm dissociation in the position opposite to the sulphur atom of the coordinated ligand, as plausible for the fluxional behaviour of **2** and **3**, must lead to nucleophilic attack of the sulphur atom of the second ligand at just this site. This mechanism would lead to formation of the third *OC*-6-13 isomer with the sulphur atoms in *trans* position to one another.

Complex **7**, [Rh(mpy-κ^2N,S)$_2$(triphosO-κ^2P)]Cl, was synthesised by treatment of [$RhCl_3$(triphos)] with two equival-

Figure 5. $^{31}P\{^1H\}$-NMR spectrum of **7** at 25°C in $CDCl_3$

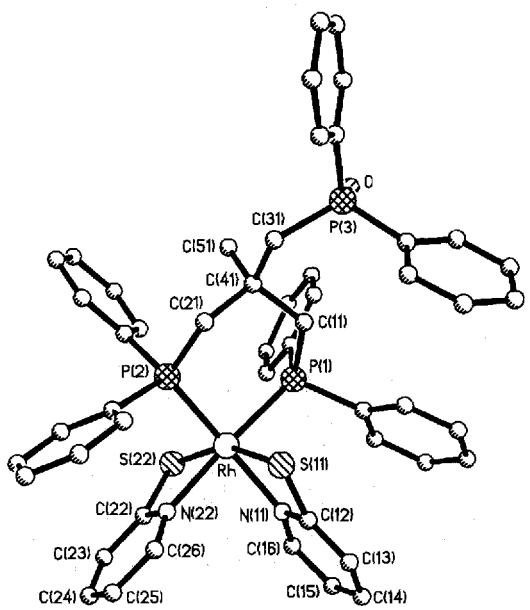


ents of Hmpy in methanol. As preliminary NMR studies of the raw product indicated the presence of a phosphane oxide impurity, it was decided to optimise the yield of this κ^2P-coordinated triphosO complex by slow crystallisation under air. The NMR spectra of **7** and the product of the analogous reaction of $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ with Hmpy are effectively identical and consist of a typical AMX pattern for the coordinated phosphorous atoms (Figure 5). The dangling P(V) atom exhibits a resonance at δ = 28.07 in similar position to the analogous atom in **6** (δ = 27.18).

Confirmation of an *OC*-6-13 (S *trans* to S) coordination sphere in **7** is provided by the X-ray structural analysis (Figure 6). The reduced *trans* influence of the mpy^- N atoms as opposed to the diethyldithiocarbamate S atoms is apparent from the shortening of the Rh–P distances [2.303(5), 2.273(5) Å] in comparison to **4** [2.328(7), 2.314(7) Å]. These bond lengths are once again correlated with the N–Rh–P angles of respectively 174.0(5) and 164.7(7)°. The bite angles [67.4(7), 66.1(6)°] of the chelating mpy^- ligands are markedly narrower than those of the dithiocarbamate ligands in **1**, **3** and **4**.

The stereochemical non-rigidity of $[Rh(S_2CNR_2)(MeCN)(triphos\text{-}\kappa^3P)]^{2+}$ (R = Et, Bz) in solution at room temperature and the preferred formation of the κ^2P-coordinated *OC*-6-13 isomer of $[Rh(mpy)_2(triphosO\text{-}\kappa^2P)]^+$ are in agreement with a facile phosphane arm-off dissociation, a process, which may be more general for octahedral (triphos)Rh(III) complexes than previously supposed. It seems probable that relief of ring strain and steric crowding will be responsible for this coordination change, which could be characteristic for complexes in which Rh–P bonds are labilised by ligands such as H^-, CH_3^-, or $S_2CNR_2^-$ with a pronounced *trans* effect. The dynamic behaviour of complexes of the type $[Fe(MeCN)_3(triphos)]^{2+}$ has recently been studied by Huttner et al.[24], who interpreted NOESY-EXSY spectra as providing evidence for triphos rotation at 308 K. The observation of a $\kappa^3P \rightleftharpoons \kappa^2P$ arm-off reaction for the (triphos-κ^3P)Rh(III) fragment with $S_2CNR_2^-$ and mpy^- would contrast with the behaviour of the analogous facial $6e^-$ coligand 1,4,7-trithiacyclononane in ([9]aneS$_3$-κ^3S)Rh(III), for which the κ^3S coordination mode is retained in $[Rh(mpym\text{-}\kappa^2N,S)(mpym\text{-}\kappa S)([9]aneS_3\text{-}\kappa^3S)]^+$[20]. Treatment of $[RhCl(MeCN)_2([9]aneS_3)]^{2+}$ with $S_2CNEt_2^-$ leads to a base-induced opening of the macrocycle, so that a direct comparison is not possible for the dialkyldithiocarbamates.

Figure 6. Molecular structure of the cation of **7**. Selected bond lengths [Å] and angles [°]: Rh–S(11) 2.367(6), Rh–S(22) 2.413(7), Rh–N(11) 2.07(2), Rh–N(22) 2.09(2), Rh–P(1) 2.303(5), Rh–P(2) 2.273(5), S(11)–C(12) 1.77(2), S(22)–C(22) 1.74(3); S(11)–Rh–S(22) 158.6(2), N(11)–Rh–P(2) 164.7(7), N(22)–Rh–P(1) 174.0(5), P(1)–Rh–P(2) 91.1(2), S(11)–Rh–N(11) 67.4(7), S(22)–Rh–N(22) 66.1(6)



7 $[Rh(mpy\text{-}\kappa^2N,S)_2(triphosO\text{-}\kappa^2P)]Cl$

Experimental

All reactions and manipulations were carried out under Ar. Solvents were dried and distilled before use. – FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as the matrix. – FT-IR[25]: KBr, Perkin-Elmer 1760. – ^1H and $^{31}P\{^1H\}$ NMR: Bruker AM 400; chemical shifts are given in δ values relative to the signal of the deuterated solvent (for ^1H) and relative to 85% H_3PO_4 as external standard (for ^{31}P); ABX spin systems were simulated by an iterative process with the program WIN-DAISY 2.0 (Bruker). – Elemental analyses: Carlo Erba 1106. – The starting materials $[RhCl_3(triphos)]$[7] and $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$[15] were prepared according to the literature procedures.

[RhCl(S$_2$CNEt$_2$)(triphos)]Cl (**1**): $[RhCl_3(triphos)]$ (125 mg, 0.15 mmol) was added to a solution of $Na(S_2CNEt_2) \cdot 3\,H_2O$ (34 mg, 0.30 mmol) in 15 ml of MeOH and the reaction mixture refluxed for 3 h. After removal of the solvent, addition of 3 ml of CH_2Cl_2 and filtration of NaCl, the resulting solution was covered with hexane to yield yellow crystals of **1** suitable for the X-ray analysis. Yield 102 mg (69%). – $C_{46}H_{49}Cl_2NP_3RhS_2 \cdot 1/2\,CH_2Cl_2$ (989.2): calcd. C 56.5, H 5.1, N 1.4; found C 55.7, H 5.1, N 1.2. – FAB MS, *m/z* (%): 910 (100) $[RhCl(S_2CNEt_2)(triphos)]^+$, 875 (29) $[Rh(S_2CNEt_2)(triphos)]^+$. – ^1H NMR ($CDCl_3$): δ = 1.08 (t, 6H, CH_2CH_3), 2.07 (s, 3H, CH_3 of triphos), 2.77 (br, 2H, CH_2 of triphos), 2.98 (m, 4H, CH_2 of triphos), 3.34, 3.58 (2 q, 4H, CH_2CH_3), 6.72–7.92 (m, 30H, C_6H_5). – ^{31}P NMR ($CDCl_3$): δ = –1.53 (dd, $J_{Rh\text{-}P}$ = 97.5, $J_{P\text{-}P}$ = 26.5 Hz, 2 P, *trans* to S_2CNEt_2-κ^2S), 27.01 (dt, $J_{Rh\text{-}P}$ = 103.1, $J_{P\text{-}P}$ = 26.5 Hz, 1 P, *trans* to Cl). – IR: $\tilde{\nu}$ = 1511 cm^{-1} (CN).

[Rh(S$_2$CNEt$_2$)(MeCN)(triphos)](CF$_3$SO$_3$)$_2$ (**2**): $[Rh(MeCN)_3(triphos)](CF_3SO_3)_2$ (195 mg, 0.15 mmol) and $Na(S_2CNEt_2) \cdot 3\,H_2O$ (34 mg, 0.15 mmol) were refluxed for 3 h in 15 ml MeCN. After filtration and removal of solvent, the resulting solid was dissolved in CH_2Cl_2 and covered with hexane to afford **2**. Yield 111 mg (59%). – $C_{50}H_{52}F_6N_2O_6P_3RhS_4 \cdot 1/2\,CH_2Cl_2$ (1257.5): calcd. C 48.2, H 4.2, N 2.2; found C 48.0, H 3.8, N 2.5. – FAB MS, *m/z* (%): 1024 (37) $\{[Rh(S_2CNEt_2)(triphos)]CF_3SO_3\}^+$, 875 (100) $[Rh(S_2CNEt_2)(triphos)]^+$. – ^1H NMR (CD_3CN, –30°C): δ = 1.18 (t, 6H, CH_2CH_3), 1.87 (d, $^4J_{P\text{-}H}$ = 3 Hz, 3H, CH_3 of triphos), 1.94 (s, 3H, CH_3 of MeCN), 2.69, 2.82 (2 m, 4H, CH_2 of triphos), 3.17 (m, 2H, CH_2 of triphos), 3.54, 3.70 (2 q, 4H, CH_2CH_3), 6.99–7.61 (m, 30H, C_6H_5). – ^{31}P NMR (CD_3CN, –30°C): δ = 2.72 (dd, $J_{Rh\text{-}P}$ = 93.8, $J_{P\text{-}P}$ =

30.5 Hz, 2 P, *trans* to S_2CNEt_2-κ^2S), 19.70 (dt, J_{Rh-P} = 105.3, J_{P-P} = 30.5 Hz, 1 P, *trans* to N). – IR: $\tilde{\nu}$ = 1526 cm^{-1} (CN).

[Rh(S_2CNBz_2)(MeCN)(triphos)](CF_3SO_3)$_2$ (**3**): A solution of [Rh(MeCN)$_3$(triphos)](CF_3SO_3)$_3$ (194.7 mg, 0.15 mmol) and Na(S_2CNBz_2) (44.3 mg, 0.15 mmol) in 15 ml of MeCN was stirred at reflux for 3 h. After removal of the solvent, addition of 2 ml of $CHCl_3$ and subsequent filtration of $NaCF_3SO_3$, slow evaporation of the filtrate provided yellow crystals of **3**. Yield 146 mg (61%). – $C_{60}H_{56}F_6N_2O_6P_3RhS_4 \cdot 2\,CHCl_3 \cdot H_2O$ (1595.9): calcd. C 46.8, H 3.5, N 1.7; found C 47.4, H 3.3, N 1.0. – FAB MS, *m/z* (%): 1148 (38) {[Rh(S_2CNBz_2)(triphos)]CF_3SO_3}$^+$, 999 (100) [Rh(S_2CNBz_2)(triphos)]$^+$, 922 (7) [Rh($S_2CN(CH_2)Bz$)(triphos)]$^+$. – ^{1}H NMR ($CDCl_3$, –30°C): 2.04 (s, $^4J_{P-H}$ = 5 Hz, 3H, CH_3 of triphos), 2.14 (s, 3H, CH_3 of MeCN), 2.70–3.27 (m, 6H, CH_2 of triphos), 4.66, 5.00 (2 d, 4H, CH_2Ph), 6.84–7.85 (m, 40H, C_6H_5 of triphos and S_2CNBz_2). – ^{31}P NMR ($CDCl_3$, –30°C): 4.16 (dd, J_{Rh-P} = 94.0, J_{P-P} = 31.0 Hz, 2 P, *trans* to S_2CNBz_2-κ^2S), 17.92 (dt, J_{Rh-P} = 105.3, J_{P-P} = 31.0 Hz, 1 P, *trans* to N). – IR: $\tilde{\nu}$ = 1512 cm^{-1} (CN).

[Rh(S_2CNEt_2)$_2$(triphos)](CF_3SO_3) (**4**): [Rh(MeCN)$_3$(triphos)](CF_3SO_3)$_3$ (195 mg, 0.15 mmol) was refluxed with Na(S_2CNEt_2) · 3 H_2O (68 mg, 0.30 mmol) in 15 ml of MeCN for 3 h. The volume was reduced to 4 ml and **4** precipitated by addition of diethyl ether. Crystals suitable for X-ray structural analysis were obtained by recrystallisation from CH_2Cl_2 covered with hexane. Yield 143 mg (81%). – $C_{52}H_{59}F_3N_2O_3P_3RhS_5$ (1173.2): calcd. C 53.2, H 5.1, N 2.4; found C 52.2, H 5.0, N 2.1. – FAB MS, *m/z* (%): 1023 (100) [Rh(S_2CNEt_2)$_2$(triphos)]$^+$, 875 (19) [Rh(S_2CNEt_2)(triphos)]$^+$. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, CH_3 of triphos), 0.98, 1.06 (2 t, 12H, CH_2CH_3), 1.78–3.00 (m, 6H, CH_2 of triphos), 3.21–3.45 (m, 8H, CH_2CH_3), 6.93–7.66 (m, 30H, C_6H_5). – ^{31}P NMR ($CDCl_3$): δ = –27.08 (s, 1 P, non-coordinated), 16.59, 16.81 (ABX system, J_{Rh-P} = 107.6, 107.3, J_{P-P} = 31.0 Hz, 2 P, *trans* to S_2CNEt_2-κ^2S). – IR: $\tilde{\nu}$ = 1511 cm^{-1} (CN).

[Rh(S_2CNMe_2)$_2$(triphos)]Cl (**5**): A solution of Na(S_2CNMe_2) · 2 H_2O (54 mg, 0.30 mmol) in 5 ml of MeCN was added to a suspension of [$RhCl_3$(triphos)] (125 mg, 0.15 mmol) in 10 ml of MeCN and stirred for 3 h at reflux. After filtration the solvent was removed and the residue dissolved in 2 ml of CH_2Cl_2. Addition of hexane led to formation of **5** as a yellow precipitate. Yield 121 mg (77%). – $C_{47}H_{51}ClN_2P_3RhS_4 \cdot 1/2\,CH_2Cl_2$ (1045.9): calcd. C 54.5, H 5.0, N 2.7; found C 53.8, H 5.3, N 2.4. – FAB MS, *m/z* (%): 967 (100) [Rh(S_2CNMe_2)$_2$(triphos)]$^+$, 847 (20) [Rh(S_2CNMe_2)(triphos)]$^+$. – ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 3H, CH_3 of triphos), 1.70–3.04 (m, 18H, CH_2 of triphos and S_2CNMe_2), 6.88–7.68 (m, 30H, C_6H_5). – ^{31}P NMR ($CDCl_3$): δ = –28.04 (s, 1 P, non-coordinated), 16.34, 16.72 (ABX system, J_{Rh-P} = 107.7, 107.5, J_{P-P} = 29.7 Hz, 2 P, *trans* to S_2CNMe_2-κ^2S). – IR: $\tilde{\nu}$ = 1538 cm^{-1} (CN).

[Rh(S_2CNEt_2)$_2$(triphosO)]Cl (**6**): A solution of Na(S_2CNEt_2) · 3 H_2O (68 mg, 0.30 mmol) in 5 ml of MeOH was added to a suspension of [$RhCl_3$(triphos)] (125 mg, 0.15 mmol) in 10 ml of MeOH. The reaction mixture was refluxed for 3 h and the solvent removed. Recrystallisation from CH_2Cl_2/hexane under air afforded **6** as a yellow crystalline product. Yield 138 mg (79%). – $C_{51}H_{59}ClN_2OP_3RhS_4 \cdot CH_2Cl_2$ (1160.5): calcd. C 53.8, H 5.3, N 2.4; found C 52.6, H 5.4, N 1.9. – FAB MS, *m/z* (%): 1039 (100) [Rh(S_2CNEt_2)$_2$(triphosO)]$^+$, 891 (15) [Rh(S_2CNEt_2)(triphosO)]$^+$. – ^{1}H NMR ($CDCl_3$): δ = 0.84–1.08 (m, 15H, CH_3 of triphosO and CH_2CH_3), 2.11–3.72 (m, 14H, CH_2 of triphosO and CH_2CH_3), 6.94–7.78 (m, 30H, C_6H_5). – ^{31}P NMR ($CDCl_3$): δ = 15.53, 16.41 (ABX system, J_{Rh-P} = 107.3, 107.0, J_{P-P} = 30.2 Hz, 2 P, *trans* to S_2CNEt_2-κ^2S), 27.18 (s, 1 P, P=O). – IR: $\tilde{\nu}$ = 1511 cm^{-1} (CN), 577 (δPO).

[Rh(mpy)$_2$(triphosO)]Cl (**7**): 2-Mercaptopyridine (Hmpy) (33 mg, 0.30 mmol) was dissolved in 15 ml of MeOH by addition of 1 M NaOH (0.3 ml). The resulting solution was refluxed with [$RhCl_3$(triphos)] (125 mg, 0.15 mmol) for 3 h. The solvent was removed and the resulting solid dissolved in 2 ml of CH_2Cl_2. After filtration the solution was covered with hexane under air to afford orange crystals of **7**. Yield 121 mg (81%). – $C_{51}H_{47}ClN_2OP_3RhS_2$ (999.3): calcd. C 61.3, H 4.7, N 2.8; found C 61.0, H 5.3, N 2.7. – FAB MS, *m/z* (%): 963 (100) [Rh(mpy)$_2$(triphosO)]$^+$, 853 (14) [Rh(mpy)(triphosO)]$^+$. – ^{1}H NMR (CD_2Cl_2): δ = 0.54 (s, 3H, CH_3 of triphos), 2.81–3.02 (m, 4H, CH_2 of triphos), 3.53, 3.91 (2 m, 2H, CH_2 of triphos), 6.25, 6.41 (2 t, 2H, mpy), 6.46, 6.73 (2 d, 2H, mpy), 6.87–8.02 (m, 34H, C_6H_5 and mpy). – ^{31}P NMR ($CDCl_3$): δ = 16.92, 19.45 (2 dd, J_{Rh-P} = 105.5, 106.1, J_{P-P} = 45.6 Hz, 2 P, *trans* to mpy-κ^2N,S), 28.07 (s, 1 P, P=O). – IR: $\tilde{\nu}$ = 1582 cm^{-1} (CN), 581 (δPO).

X-ray Structural Analyses: Siemens P4 diffractometer, graphite-monochromated Mo-K_α 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 **1** and **4** and **8** (SHELXTL PLUS programs[26]) and against F^2 for **3** (SHELXL-93[27]). Hydrogen atoms were included where possible at calculated positions with isotropic temperature factors[28].

1 · 1/2 CH_2Cl_2: $C_{46}H_{49}Cl_2NP_3RhS_2 \cdot 1/2\,CH_2Cl_2$, M = 989.2, monoclinic, space group $P2_1/n$ (No. 14), a = 19.980(4), b = 10.535(2), c = 22.837(5) Å, β = 107.96(3)°, V = 4578(2) Å^3, Z = 4, D_{calc} = 1.435 g cm^{-3}, μ = 0.778 mm^{-1}. Crystal size: 0.15 × 0.23 × 0.59 mm; ω scan, scan range: 2Θ ≤ 50° (0 ≤ h ≤ 23, 0 ≤ k ≤ 12, –27 ≤ l ≤ 27), 8680 reflections collected, 7954 symmetry-independent reflections (R_{int} = 0.023); max./min. transmission: 0.627/0.548; 536 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0004\,F_o^2$, R = 0.056, R_w = 0.053 for 4221 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 0.88 eÅ^{-3}. Anisotropic temperature factors for all nonhydrogen atoms with the exception of the disordered solvent molecule. Rotational disorder is observed for the chlorine atoms of the CH_2Cl_2 molecule with a site occupation factor (s.o.f.) of 0.50 for the atom C and s.o.f.s of 0.25 for the atoms Cl1–Cl4.

3 · 2 $CHCl_3$ · H_2O: $C_{60}H_{56}F_6N_2O_6P_3RhS_4 \cdot 2\,CHCl_3 \cdot H_2O$, M = 1595.9, triclinic, space group $P\bar{1}$ (No. 2), a = 13.060(3), b = 15.227(3), c = 19.693(4) Å, α = 93.48(3), β = 90.98(3), γ = 115.02(3)°, V = 3538(1) Å^3, Z = 2, D_{calc} = 1.498 g cm^{-3}, μ = 0.720 mm^{-1}. Crystal size: 0.42 × 0.48 × 0.66 mm; Θ-2Θ scan, scan range: 2Θ ≤ 47.5° (–14 ≤ h ≤ 0, –15 ≤ k ≤ 17, –22 ≤ l ≤ 22), 10780 reflections collected, 10313 symmetry-independent reflections (R_{int} = 0.050); max./min. transmission: 0.667/0.447; 752 parameters refined; $w^{-1} = [\sigma^2(F_o^2) + (0.1371 \cdot P)^2 + 11.62 \cdot P]$ where $P = [\mathrm{Max}(F_o^2, 0) + 2 \cdot F_c^2]/3$, R = 0.076 for 7748 reflections with $I > 2\sigma(I)$, $wR2 = [[\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)^2]]]^{1/2}$ = 0.228 (all data); largest difference peak: 2.04 eÅ^{-3}. Anisotropic temperature factors for all non-hydrogen atoms. The chlorine atoms of the second $CHCl_3$ molecule are disordered with s.o.f.s of 0.50.

4 · CH_2Cl_2: $C_{52}H_{59}F_3N_2O_3P_3RhS_5 \cdot CH_2Cl_2$, M = 1258.1, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 10.027(2), b = 18.110(4), c = 32.284(6) Å, V = 5862(2) Å^3, Z = 4, D_{calc} = 1.425 g cm^{-3}, μ = 0.694 mm^{-1}. Crystal size: 0.23 × 0.33 × 0.51 mm; ω scan, scan range: 2Θ ≤ 45° (–11 ≤ h ≤ 0, –20 ≤ k ≤ 0, –35 ≤ l ≤ 0), 4294 reflections collected, 4267 symmetry-independent reflections; max./min. transmission: 0.504/0.462; 333 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0006\,F_o^2$, R = 0.081, R_w = 0.078 for 2279

reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 0.70 eÅ^{-3}. Anisotropic temperature factors for the Rh, P, S, Cl, and N atoms, for the C atoms of the diethyldithiocarbamate ligands and the solvent. Rotational disorder about the S–C bond for the $CF_3SO_3^-$ anion, the relevant s.o.f.s being 0.70 for O1′, O2′, O3′, F1′, F2′, F3′ and correspondingly 0.30 for O1″, O2″, O3″, F1″, F2″, and F3″.

7 · 1/2 CH_2Cl_2 · 1/2 CH_3OH · 1/2 H_2O: $C_{51}H_{47}ClN_2OP_3RhS_2$ · 1/2 CH_2Cl_2 · 1/2 CH_3OH · 1/2 H_2O, M = 1066.8, monoclinic, space group $P2_1/n$ (No. 14), a = 10.554(2), b = 24.730(5), c = 22.170(4) Å, β = 96.11(3)°, V = 5753(2) Å^3, Z = 4, D_{calc} = 1.232 g cm^{-3}, μ = 0.582 mm^{-1}. Crystal size: 0.27 × 0.31 × 0.56 mm; ω scan, scan range: $2\Theta \leq 45°$ ($0 \leq h \leq 12$, $0 \leq k \leq 27$, $-24 \leq l \leq 24$), 8100 reflections collected, 7401 symmetry-independent reflections (R_{int} = 0.034); max./min. transmission: 0.648/0.568; 325 parameters refined; $w^{-1} = \sigma^2(F_o) + 0.0005\,F_o^2$, R = 0.094, R_w = 0.092 for 2991 reflections with $F_o^2 > 2\sigma(F_o^2)$; largest difference peak: 0.92 eÅ^{-3}. Anisotropic temperature factors for all non-hydrogen atoms with the exception of the C atoms of the solvent molecules.

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[28] Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, with specification of deposition numbers CSD-404790 to -404793, the names of the authors, and the journal reference.

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