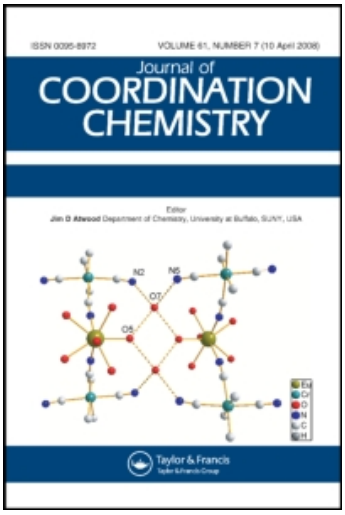

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CYCLORHODATION OF (1-PYRROLIDINOTHIOCARBONYL)-AROMATICS

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CYCLORHODATION OF (1-PYRROLIDINOTHIOCARBONYL)-AROMATICS

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Pyrrolidinothiocarbonyl groups promote cyclorhodation of an aromatic ring with $[RhCl_3(PBu_3)_2]$ (PBu_3 = tri-*n*-butylphosphine): thus *p*-(1-pyrrolidinothiocarbonyl)toluene (Htpr), 2-(1-pyrrolidinothiocarbonyl)naphthalene (Hbnr), 2-(1-pyrrolidinothiocarbonyl)benzo[*b*]thiophene (Htnp) and 1,3-*bis*(1-pyrrolidinothiocarbonyl)benzene (Hmpr) gave, respectively, $[RhCl_2(tpr)(PBu_3)_2]$, $[RhCl_2(bnr)(PBu_3)_2]$, $[RhCl_2(tnp)(PBu_3)_2]$, and $[RhCl_2(mpr)(PBu_3)_2]$. These complexes were characterized spectroscopically. The two PBu_3 ligands are *trans* to each other and the thioamides behave as uninegative, bidentate C–S donors. Htpr was rhodated at the *ortho* position, Hbnr at position 3, Htnp at position 3, and Hmpr at position 4 against the expected position 2 in which case it could act as an S–C–S terdentate ligand. Reactions of Htpr, Htnp, and Hbnr with $RhCl_3(H_2O)_3$ gave no definite cyclorhodated product but Hmpr afforded $[RhCl_2(mpr)(H_2O)]$ where mpr was cyclorhodated at position 2 and chelated as an S–C–S terdentate ligand.

Keywords: Cyclometallation; cyclorhodation; organorhodium(III) compounds; thioamide derivatives; (1-pyrrolidinothiocarbonyl)aromatics

INTRODUCTION

Cyclopalladation of furan and thiophene rings is promoted by an *N*,*N*-dimethylthiocarbamoyl group as an auxiliary coordinating substituent, but the same reaction of a benzene ring is not and one of the *N*-methyl groups is cyclopalladated instead.[1] When the *N*,*N*-dimethylthiocarbamoyl group is replaced with the 1-pyrrolidinothiocarbonyl group, the benzene ring is cyclopalladated.[2] The 1-pyrrolidinothiocarbonyl group is sterically less demanding than the *N*,*N*-dimethylthiocarbamoyl group as has been shown

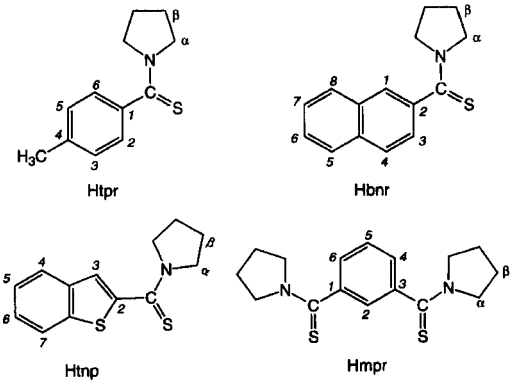


FIGURE 1 Abbreviations of ligands and atom-labelling for NMR spectra.

by X-ray analysis[2] and the former is recommended as a more favourable substituent for cyclopalladation than the latter. We have, therefore, extended studies on cyclometallation of *p*-(1-pyrrolidinothiocarbonyl)toluene (abbreviated as Htpr, Figure 1, where atom-labelling is given), which is cyclopalladated, to other metals and have found cyclorhodation to occur, the results of which are reported in this paper. Three related 1-pyrrolidinothiocarbonyl derivatives (Figure 1), 2-(1-pyrrolidinothiocarbonyl)naphthalene (Hbnr), 2-(1-pyrrolidinothiocarbonyl)benzo[*b*]thiophene (Htnp), and 1,3-*bis*(1-pyrrolidinothiocarbonyl)benzene (Hmpr) are also found to be cyclorhodated. The corresponding *N*,*N*-dimethylthiocarbamoyl derivatives of the four 1-pyrrolidinothiocarbonyl derivatives are not cyclorhodated under the same experimental conditions employed here.

RESULTS AND DISCUSSION

The three 1-pyrrolidinothiocarbonyl derivatives, Htpr, Hbnr, and Hmpr (Figure 1), were prepared from the corresponding aldehydes and pyrrolidine by reported methods.[2] Htnp was synthesized as follows. Benzo[*b*]thiophene-2-carboxylic acid[3] was first treated with *tris*(*N*,*N*-tetramethylene)phosphoric acid triamide to convert it to 2-(1-pyrrolidinocarbonyl)benzo[*b*]thiophene $C_8H_5S{-}CONC_4H_8$, (1)

$$3C_8H_5S{-}CO_2H + (C_4H_8N)_3PO \rightarrow 3C_8H_5S{-}CONC_4H_8 + H_3PO_4 \quad (1)$$

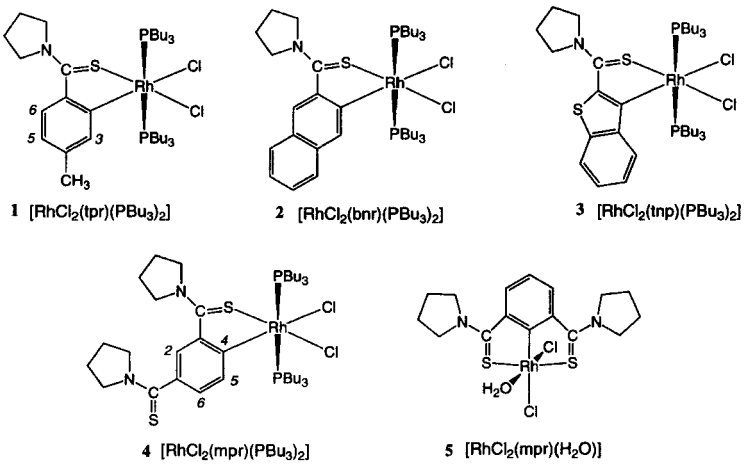
$$2C_8H_5S{-}CONC_4H_8 + C_{14}H_{14}O_2P_2S_4 \rightarrow 2C_8H_5S{-}CSNC_4H_8 + C_{14}H_{14}O_4P_2S_2 \quad (2)$$

and then thionation of the amide was effected with Lawesson's Reagent {2,4-*bis*(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide} (2).[4] The strong amide-characteristic band, ν(C=O), at 1591 cm^{-1} of C_8H_5S–$CONC_4H_8$ disappeared in the IR spectra of Htnp. The ν(C=O) value is lower than the normal range, 1670–1630 cm^{-1}, of a tertiary carboxamide[5] but the trend of low frequency is observed for other 1-pyrrolidinocarbonyl derivatives.[‡] The amide carbon signal at $\delta(^{13}C) = 162.2$ ppm of 2-(1-pyrrolidinocarbonyl)benzo[*b*]thiophene shifts to $\delta(^{13}C) = 187.3$ ppm upon formation of the thioamide, Htnp. Broad ^1H and ^{13}C signals of the pyrrolidine moiety of the former amide suggest that the amide C–N bond rotates near the NMR time scale.[6] Four separate ^{13}C signals are observed for the pyrrolidine moiety of the thioamide, Htnp, indicating slowdown of the rotation making the two α- and β-carbons inequivalent.[6]

Reflux of an equimolar mixture of the 1-pyrrolidinothiocarbonyl derivatives and $[RhCl_3(PBu_3)_2]$ (PBu_3 = tri-*n*-butylphosphine)[7] in toluene yielded $[RhCl_2(L)(PBu_3)_2]$ (L = tpr, **1**; bnr, **2**; tnp, **3**; and mpr, **4**; Figure 2) (3) while for reactions with $RhCl_3(H_2O)_3$, only Hmpr gave the definite product $[RhCl_2(mpr)(H_2O)]$, **5**, (4).

$$[RhCl_3(PBu_3)_2] + HL \rightarrow [RhCl_2(L)(PBu_3)_2] + HCl \quad (3)$$

$$RhCl_3(H_2O)_3 + Hmpr \rightarrow [RhCl_2(mpr)(H_2O)] + HCl + 2H_2O \quad (4)$$



1 $[RhCl_2(tpr)(PBu_3)_2]$ **2** $[RhCl_2(bnr)(PBu_3)_2]$ **3** $[RhCl_2(tnp)(PBu_3)_2]$

4 $[RhCl_2(mpr)(PBu_3)_2]$ **5** $[RhCl_2(mpr)(H_2O)]$

FIGURE 2 Proposed structures for the complexes.

[‡] Examples of low frequency ν(C=O) of tertiary carboxamides: *N*-(2-thenoyl)pyrrolidine, 1580; *N*-(3-furoyl)pyrrolidine, 1599 and *N*-(*p*-toluoyl)pyrrolidine, 1610 cm^{-1}.

The thioamides act as uninegative ligands (Figure 2) on the basis of the elemental analysis and this fact is supported by the ^{1}H NMR spectra; in the aromatic proton resonance region, the number of protons is reduced by one.

The ^{1}H signals {7.19(m) ppm} due to four protons of free Htpr are replaced with one singlet at 8.53 ppm and a pair of doublets ($J = 8.3$ Hz) at 6.84 and 7.51 ppm (each intensity of 1H). This pattern is very similar to that of the previously reported cyclopalladated tpr complex.[2] The deshielded singlet is assigned to H-3 *ortho* to the Rh–C bond and the deshielding is caused by the coordinated Cl ligand[8] as in the palladium complexes.[2] The naphthyl derivative, $[RhCl_2(bnr)(PBu_3)_2]$, shows two singlets indicating rhodation at C-3 and the deshielded singlet at 8.99 ppm is similarly assigned to H-4 *ortho* to the Rh–C bond. The singlet due to H-3 of free Htnp disappears upon formation of $[RhCl_2(tnp)(PBu_3)_2]$ and the H-4 signal is strongly deshielded. Molecular models suggests that H-4 is close to the Cl ligand because of the rigid structure of the planar benzo[*b*]thiophene ring and the deshielding effect of Cl strongly affects the H-4 chemical shift.

There are two possibilities for the site of cyclometallation of Hmpr, C-2 and C-4, and both are indeed found in the two complexes, $[RhCl_2(mpr)(PBu_3)_2]$ and $[RhCl_2(mpr)(H_2O)]$. The ^{1}H NMR spectra of the two in the aromatic proton resonance region are shown in Figure 3 and the pattern (Figure 3, **4**) of $[RhCl_2(mpr)(PBu_3)_2]$ suggests the presence of one isolated {7.99 ppm (d, $J = 1.5$ Hz)} and a pair of *ortho* protons {8.74 (d, 8.3) and 7.08 ppm (dd, 8.3, 1.5 Hz)}; that is, rhodation occurred at C-4 (Figure 2). In the spectrum of $[RhCl_2(mpr)(H_2O)]$ at room temperature (Figure 3, **5**) the number of signals is double the anticipated one and at 373 K (Figure 3, **5***) the intensities of the signals become unequal (integration ratio = *ca.* 74/26) suggesting that two isomers exist and the ratio of the two is temperature-dependent. The pattern {a doublet and a triplet ($J = 8.0$ Hz)} is consistent with the presence of three adjacent protons with C_2 symmetry and the structure shown in Figure 2 is a satisfactory one. Cyclometallation at C-2 has already been confirmed for a palladium(II) complex, [PdCl(mpr)], the structure being determined by X-ray analysis.[2]

$^{13}C\{^1H\}$ NMR spectra of $[RhCl_2(L)(PBu_3)_2]$ give a doublet of triplets {J(Rh–C) = 29.0–33.2 and J(P–C) = 8.8–9.8 Hz} characteristic of a rhodated carbon at a low field and that of $[RhCl_2(mpr)(H_2O)]$ a doublet {J(Rh–C) = 26.8, 26.3 Hz}. Rhodation of C-4 of mpr in $[RhCl_2(mpr)(PBu_3)_2]$ also agrees with the ^{13}C NMR spectrum in that the six carbon signals of the benzene ring and the two inequivalent thiocarbonyl carbon signals are observed. The number of the ^{13}C signals of $[RhCl_2(mpr)(H_2O)]$ is

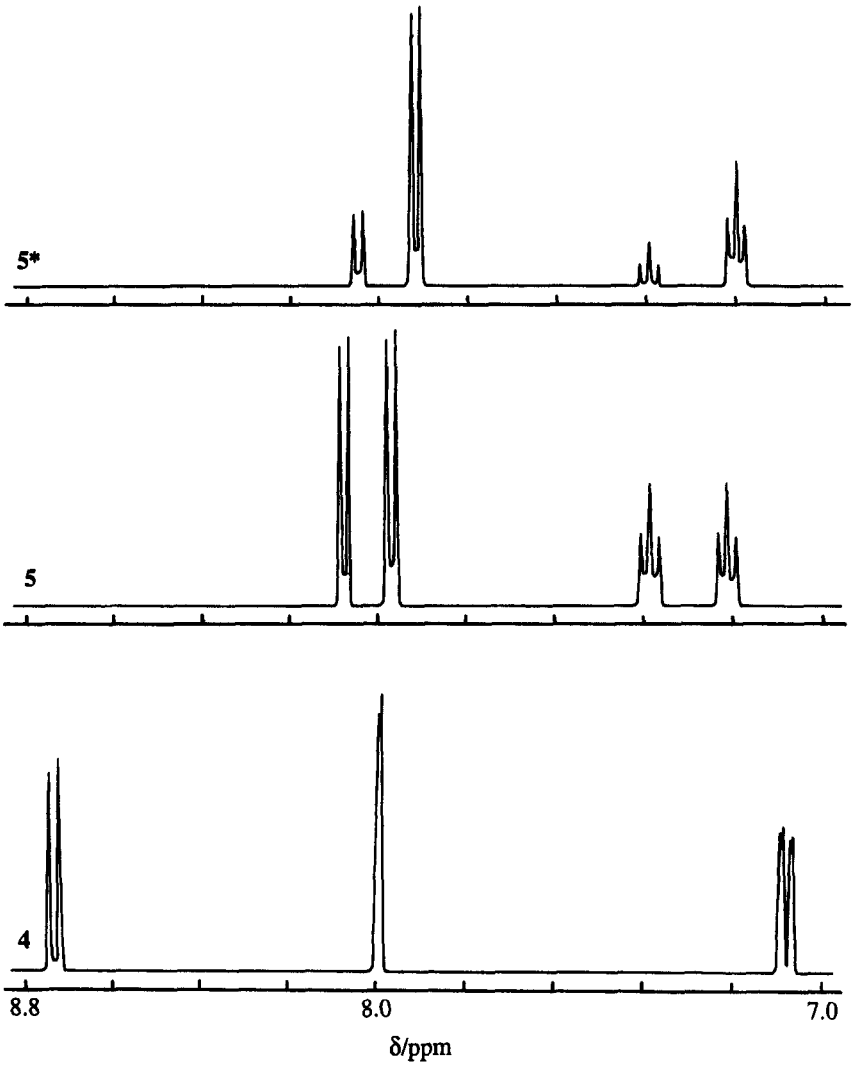


FIGURE 3 ^{1}H NMR spectra of (**4**) $[RhCl_2(mpr)(PBu_3)_2]$ in $CDCl_3$, (**5**) $[RhCl_2(mpr)(H_2O)]$ in dmso-d_6 at room temperature, and (**5***) $[RhCl_2(mpr)(H_2O)]$ in dmso-d_6 at 373 K in the aromatic proton resonance region.

double that expected for the C-2 metallated mpr ligand with C_2 symmetry, suggesting the presence of two isomers in dmso-d_6 solution.

In the ^{31}P NMR spectra of $[RhCl_2(L)(PBu_3)_2]$ one doublet $\{J(Rh-P) = 87.3-90.7\,Hz)\}$ is observed, confirming mutual *trans* coordination of the two PBu_3 ligands and the equivalence of the two PBu_3 groups is also

supported by the ^{13}C spectra: only one set of *n*-butyl group signals is detected. The observed J(Rh–P) values are similar to that reported for *trans*-(*P*,*P*)-$[RhCl_2(C–S)(PBu_3)_2]$ where HC–S is *N*,*N*-dimethylpyrrole-1-thiocarboxamide.[9] The *cis* disposition of the two Cl ligands agrees with the presence of two strong ν(Rh–Cl) bands in the far IR spectra and the significantly low frequency of one of the two reveals the strong *trans* influence of the carbon donor coordinated *trans* to it.

Two isomers are possible for $[RhCl_2(mpr)(H_2O)]$ and one is depicted in Figure 2, **5**; the other is that where H_2O is bound *trans* to the C-2 donor and the two Cl ligands are mutually *trans*. Which isomer is preferred at 373 K in dmso-d_6 solution is unknown at present. It is interesting that the site of cyclorhodation of Hmpr is discriminated by metallating reagents, $[RhCl_3(PBu_3)_2]$ or $RhCl_3(H_2O)_3$. In a recent review[10] relevant to this question several factors are discussed. At present the factors determining the metallation site of Hmpr are difficult to predict. Further studies will be required to answer the question.

EXPERIMENTAL

Measurements

^1H and ^{13}C NMR spectra were recorded on Hitachi R-90H and Brucker AMX 400 spectrometers with tetramethylsilane (TMS) as internal standard and ^{31}P NMR with 85% H_3PO_4 as external reference. ^{13}C signals are singlets unless otherwise noted (abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad). IR spectra were measured on a Perkin-Elmer System 2000 FTIR spectrophotometer and the nujol mull method was employed.

Preparation of the Ligands

The three thioamides Htpr, Hbnr, and Hmpr were prepared from *p*-tolualdehyde, 2-naphthaldehyde and isophthalaldehyde, respectively, by the methods reported previously[2] and spectroscopic data were reported in the paper.

2-(1-*Pyrrolidinothiocarbonyl*)*benzo*[*b*]*thiophene*, *Htnp*

A mixture of 5.56 g (21.6 mmol) of *tris*(*N*,*N*-tetramethylene)phosphoric acid triamide (Fluka) and 7.70 g (43.2 mmol) of benzo[*b*]thiophene-2-carboxylic

acid, prepared by a method in the literature,[3] was heated at 180°C for 3.5 h. After cooling to room temperature the reaction product was dissolved in a mixture of dichloromethane and diethyl ether and undissolved material removed by filtration. The filtrate was washed with 10% aqueous potassium carbonate to remove unreacted carboxylic acid, filtered, and concentrated to small volume. Upon addition of *n*-hexane a white powder was obtained; it was collected by air filtration, washed with *n*-hexane, and dried in air; 6.87 g (68%) of 2-(1-pyrrolidinothiocarbonyl)benzo[*b*]thiophene was obtained. Mp: 95–96°C. Cacld. for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.06%. Found: C, 67.26; H, 5.78; N, 6.00%. IR: 1591{ν(C=O)} cm^{-1}. ^1H NMR ($CDCl_3$): 1.95br(4H, CH_2-β), 3.75br(4H, CH_2-α), 7.34–7.41m(2H), 7.68s(H-3), 7.80–7.85m(2H) ppm. $^{13}C\{^1H\}$ NMR: 25.5br(C-β), 48.2br(C-α); 122.3, 124.6, 124.9, 125.9, 126.0 (*C*H); 139.1, 139.5, 140.6(quaternary C); 162.2(C=O) ppm.

The amide was converted to the thioamide with Lawesson's Reagent using the standard method[4] and the yellow thioamide, Htnp, was recrystallized from ether and methanol. Mp: 113–114°C. Yield: 62%. Calcd. for $C_{13}H_{13}NS_2$: C, 63.12; H, 5.30; N, 5.66%. Found: C, 63.01; H, 5.38; N, 5.68%. ^1H NMR ($CDCl_3$): 2.05br(4H, CH_2-β), 3.89brt(2H, CH_2-α), 3.99brt(2H, CH_2-α'), 7.31–7.38m(2H), 7.41s(H-3), 7.73–7.79m(2H) ppm. $^{13}C\{^1H\}$ NMR: 24.4(C-β), 26.8(C-β'), 54.4(C-α), 55.0(C-α'); 122.0, 122.8, 124.8, 124.9, 125.8(CH); 139.1, 141.l(quaternary C); 145.5(C-2), 187.3(C=S) ppm.

Preparation of the Complexes

$[RhCl_3(PBu_3)_2]$ was obtained by a literature method.‡

[*RhCl*$_2$(*tpr*)(*PBu*$_3$)$_2$], 1

A mixture of 0.5 mmol (103 mg) of Htpr and 0.5 mmol (307 mg) of $[RhCl_3(PBu_3)_2]$ in 25 cm^3 of toluene was refluxed for 7 days with stirring. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was treated with Florisil and filtered. To the concentrated filtrate was added *n*-hexane to precipitate a yellow powder, which was filtered, washed with *n*-hexane, and dried in air. The yield was 208 mg (53%). Mp: 196–198°C. Cacld. for $C_{36}H_{68}NCl_2P_2SRh$: C, 55.24; H, 8.76; N, 1.79%. Found: C, 55.41; H, 8.37; N, 1.67%. IR: 1585{ν(C–N)}; 301, 223{ν(Rh–Cl)} cm^{-1}. ^1H NMR ($CDCl_3$): 0.82t, 1.21m, 1.71m ($PC_{12}H_{27}$); 2.17m(CH_2-β), 2.31s(CH_3), 4.08br(CH_2-α); 6.84d, 7.51d (H-5,6); 8.53s(H-3) ppm. $^{13}C\{^1H\}$ NMR: 13.7, 21.4t, 24.5t, 25.3($PC_{12}H_{27}$);

21.7(CH_3), 25.3br(C-β,β'), 55.1br(C-α,α'); 122.4, 126.2(C-5,6); 140.0(C-3); 140.7, 142.3(C-1,4); 171.5dt{C–Rh; J(Rh–C) = 29.0 and J(C–P) = 8.8 Hz}, 186.8(C=S) ppm. ^{31}P NMR: 1.5d ppm {J(P–Rh) = 90.7 Hz}.

[*RhCl*$_2$(*L*)(*PBu*$_3$)$_2$] (*L* = *bnr*, **2**; *tnp*, **3**; *mpr*, **4**)

The three complexes were obtained by the above method; **2**: 46% yield. Mp: 215°C (dec.). Calcd. for $C_{39}H_{68}NCl_2P_2SRh$: C, 57.21; H, 8.37; N, 1.71%. Found: C, 57.22; H, 8.38; N, 1.64%. IR: 1566{ν(C–N)}; 301, 218 {ν(Rh–Cl)} cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.69t, 1.10m, 1.72m($PC_{12}H_{27}$); 2.24br(CH_2-β), 4.22br(CH_2-α), 7.2–7.8m(C-5,6,7,8), 8.13s(H-1), 8.99s (H-4) ppm. ^{13}C{^{1}H} NMR: 13.6, 21.3t, 24.5t, 25.3t($PC_{12}H_{27}$); 25.3br (C-β,β'), 55.7br(C-α,α'); 124.4, 126.2(2C), 128.3, 129.2(CH); 128.4, 134.5(quaternary C); 137.0br(C-4), 143.8(C-2), 159.1dt{C–Rh; J(Rh–C) = 29.0 Hz and J(C–P) = 9.5 Hz}, 197.9(C=S) ppm. ^{31}P NMR: 2.3d ppm{J(P–Rh) = 89.7 Hz}.

3: 74% yield. Mp: 176–178°C. Cacld. for $C_{37}H_{66}NCl_2P_2S_2Rh$: C, 53.88; H, 8.06; N, 1.70%. Found: C, 53.89; H, 7.69; N, 1.81%. IR: 303, 225 {ν(Rh–Cl)} cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.71t, 1.06m, 1.75m($PC_{12}H_{27}$); 2.18q(2H, CH_2-β), 2.25q(2H, CH_2-β'), 3.95brs(2H, CH_2-α), 4.30brs(2H, CH_2-α'); 7.35td, 7.40td (H-5,6); 7.77d(H-7), 10.02d(H-4) ppm. ^{13}C{^{1}H} NMR: 13.7, 21.5t, 24.3t, 25.3($PC_{12}H_{27}$); 24.8, 27.2(C-β,β'); 52.6, 53.7 (C-α,α'); 121.5(C-7); 124.1, 127.8(C-5,6); 133.0(C-4); 131.6, 142.2, 146.7(quaternary C); 177.3dt{C–Rh: J(Rh–C) = 33.2 and J(P–C) = 9.8 Hz}; 187.6(C=S) ppm. ^{31}P NMR: 4.1d ppm {J(Rh–P) = 87.3 Hz}.

4: 42% yield. Mp: 213–216°C. Cacld. for $C_{40}H_{73}N_2Cl_2P_2S_2Rh$: C, 54.48; H, 8.34; N, 3.18%. Found: C, 54.41; H, 8.01; N, 3.05% IR: 1580, 1497{ν(C–N)}; 307, 230{ν(Rh–Cl)} cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.83t, 1.26m, 1.71m($PC_{12}H_{27}$); 24.7br, 26.6br(CH_2-β); 54.1br, 55.5br(CH_2-α); 7.08dd(H-6), 7.99d(H-2), 8.74d(H-5) ppm. ^{13}C{^{1}H} NMR: 13.8, 21.6t, 24.5t, 25.3($PC_{12}H_{27}$); 24.7br, 26.6br(C-β,β'); 54.1br, 55.5br(C-α,α'); 125.7(C-6), 126.1(C-2), 137.0(C-1), 138.5(C-5), 144.5(C-3), 175.3dt {C–Rh; J(Rh–C) = 29.4 and J(P–C) = 8.9 Hz}; 196.6, 196.9(C=S) ppm. ^{31}P NMR: 1.2d ppm {J(Rh–P) = 90.0 Hz}.

[*RhCl*$_2$(*mpr*)(*H*$_2$*O*)], **5**

A mixture of 0.5 mmol (132 mg) of $RhCl_3 \cdot 3H_2O$ and 0.55 mmol (167 mg) of Hmpr in 25 cm^3 of 2-methoxyethanol was refluxed for 2 days with stirring. An orange precipitate was filtered, washed with ethanol, and dried in air.

The yield was 140 mg (59%). Mp: 280°C (dec.). Cacld. for $C_{16}H_{21}N_2Cl_2OS_2Rh$: C, 38.80; H, 4.27; N, 5.66%. Found: C, 38.56; H, 4.35; N, 5.34%. IR: 3601, 3461{$\nu(H_2O)$}; 1552{ν(C–N)}; 337, 309{ν(Rh–Cl)} cm^{-1}. The NMR spectra of [$RhCl_2$(mpr)(H_2O)] in dmso-d_6 are complicated because of the presence of two isomers. At room temperature the two isomers exist in a nearly equivalent amount but at 373 K the isomer ratio became *ca.* 74/26 (Figure 3). ^{1}H NMR (dmso-d_6, at room temperature): 2.13m(CH_2-β); 4.08m(2H), 4.19m(2H), 4.34m(4H)(CH_2-α); 7.22t, 7.39t (H-5); 7.97d, 8.08d(H-4,6) ppm. ^{13}C{^{1}H} NMR: 23.6, 23.8, 26.4, 26.6 ((C-β,β'); 56.0, 56.1, 56.8, 57.0(C-α,α'); 120.5, 122.5(C-5); 130.8, 132.2(C-4,6); 143.3, 144.3(C-1,3); 181.0d{J(Rh–C) = 26.8}, 187.2d(26.3 Hz)(C–Rh); 191.7, 194.3(C=S) ppm.

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