

Metalloligands: Rhodium(III) Cyclometallated Compounds Containing Multitopological Binucleating Ligands

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The reaction of $[\text{Rh}(\text{2-phenylpyridine})_2\text{Cl}]_2$ with secondary dithiooxamides $\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$ (R = isoamyl, isopropyl, $\{\text{S}\}$ -phenylethyl, *meso*-phenylethyl) affords the contact ion pair $[\text{Rh}(\text{2-phenylpyridine})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$, which can be transformed into the neutral complexes $[\text{Rh}(\text{2-phenylpyridine})_2(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$. The HCl exchange between the ion pairs and the corresponding neutral complexes has been studied by means of dynamic NMR spectroscopy techniques, and a mechanism for this exchange has been proposed. $[\text{Rh}(\text{2-phenylpyridine})_2(\text{H}(\text{isoamyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$ reacts with chlorido-bridged dimers $[\text{ML}_n\text{Cl}]_2$ (ML_n = $\text{Pd}(\eta^3\text{-allyl})$, $\text{Rh}(\text{cyclooctadiene})$, $(n\text{-propyl})_3\text{PClPd}$) and provides the heterobimetallic complexes $[\text{Rh}(\text{2-phenylpyridine})_2\text{-}$

$\mu\text{-(isoamyl)}_2\text{C}_2\text{N}_2\text{S}_2\text{ML}_n]$. Heterobimetallic complexes having the same formula and the same structure are obtained by reaction of $[\text{ML}_n\{\text{H}(\text{isoamyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-M}\}]$ species $[\text{ML}_n$ = $\text{Rh}(1,5\text{-cyclooctadiene})$, $\text{Pd}(\eta^3\text{-allyl})$, $\text{PdCl}(\text{tri-}n\text{-propylphosphane})$, $\text{PtCl}(\text{diphenyl-2-pyridylphosphane})]$ with $[\text{Rh}(\text{2-phenylpyridine})_2\text{Cl}]_2$. The connectivity of the binucleating ligand diisoamylidithiooxamidate within the bimetallic complexes has been assessed. The linkage isomer obtained is $[\text{Rh}(\text{2-phenylpyridine})_2\{\mu\text{-(isoamyl)}_2\text{C}_2\text{N}_2\text{S}_2\text{ML}_n\}]$ ($\kappa\text{-N,N-Rh}^{\text{III}}$, $\kappa\text{-S,S-M}$).

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Introduction

A number of donor sites conveniently placed in a molecular skeleton can give rise to a binucleating ligand, i.e. a multitopological ligand that can link metal fragments in a sequential way. In other words, when a metal coordinates one or more of the said donor sites, a mononuclear complex is formed with other uncoordinated donor atoms, which could link another metal fragment in a successive step. This is the essence of the synthetic strategy to achieve heteropolymetallic systems based on the use of “metalloligands” (i.e. metal complexes used as ligands). We have favoured the strategy of using “metal–dithiooxamidate” building blocks as a ligand to synthesize various heteropolymetallic complexes,^[1–4] by taking advantage of the fact that metal fragments coordinated to the donor sulfur atoms of a deprotonated secondary dithiooxamide can function as a ligand complex. In fact, the N–H...N frame of an *S,S*-coordinated dithiooxamidate is nucleophilic enough to split chlorido-bridged dimers so that heterobimetallic complexes can easily be obtained.

We are now interested in preparing “metal–dithiooxamidate” synthons containing a rhodium(III) cyclometall-

ated fragment, an interesting photoelectrochemical probe,^[5] and in exploring their reactivity toward other metal fragments. The aim is to get heteropolymetallic complexes in which the electronic communication between the metals is propagated through bridging atoms. Molecules containing different metals with diverse electronic properties are key structures that could display peculiar electronic^[6–9] and magnetic properties^[10] and are therefore potentially useful for developing molecular-based devices.^[11]

We report in this paper: (i) the synthesis of the mononuclear $[\text{Rh}(\text{2-phenylpyridine})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ species ($\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$ = diisoamylidithiooxamide, **1**; diisopropylidithiooxamide, **2**; di- $\{\text{S}\}$ -phenylethylidithiooxamide, **3**; *meso*-phenylethylidithiooxamide, **4**) and of their dehydrohalogenated counterparts $[\text{Rh}(\text{2-phenylpyridine})_2(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$ ($\text{HR}_2\text{C}_2\text{N}_2\text{S}_2$ = diisoamylidithiooxamidate, **5**; diisopropylidithiooxamidate, **6**; di- $\{\text{S}\}$ -phenylethylidithiooxamidate, **7**; *meso*-phenylethylidithiooxamidate, **8**); (ii) the reaction of $[\text{Rh}(\text{2-phenylpyridine})_2\{\text{H}(\text{isoamyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh}\}]$ with some chlorido-bridged dimers $[\text{ML}_n\text{Cl}]_2$ (M = di or trivalent metal ion, L_n = set of neutral and anionic ligands such that the charge of the ML_n fragment is 1+); (iii) the reaction of $[\text{ML}_n\{\text{H}(\text{isoamyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-M}\}]$ [ML_n = (1,5-cod)rhodium(I), **9** (cod = cyclooctadiene); $(\eta^3\text{-allyl})$ palladium(II), **10**; (tri-*n*-propylphosphane)palladium(II), **11**; (diphenyl-2-pyridylphosphane)-(chlorido)platinum(II), **12**] with the chlorido-bridged $[\text{Rh}(\text{2-phenylpyridine})_2\text{Cl}]_2$; (iv) the assessment of the struc-

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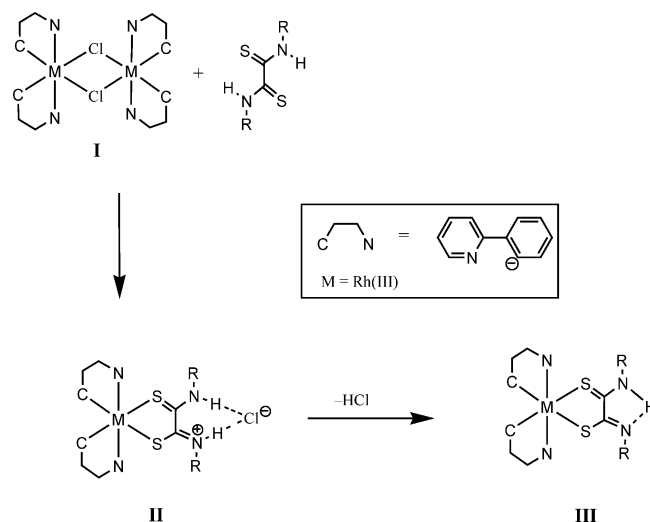
ture of the heterobimetallic compounds $[\text{Rh}(\text{2-phenylpyridine})_2\{\mu\text{-(isoamyl)}_2\text{C}_2\text{N}_2\text{S}_2\}\text{ML}_n]$ [$\text{ML}_n = (1,5\text{-cod})\text{rhodium(I)}$, **13**; $(\eta^3\text{-allyl})\text{palladium(II)}$, **14**; $(\text{tri-}n\text{-propylphosphane})\text{palladium(II)}$, **15**; $(\text{diphenyl-2-pyridylphosphane})\text{-(chlorido)platinum(II)}$, **16**].

Results and Discussion

Mononuclear Complexes

We prepared the metalloligands **III** according to Scheme 1. It is not surprising that treatment of **I** with bidentate sulfur ligands results in the cleavage of the chlorido-bridges and the formation of mononuclear complexes.^[12] However, the HN(R)C-C(R)NH frame of a secondary dithiooxamide should work more as a chelating system; thus the reaction of $\text{H}_2\text{C}_2\text{N}_2\text{S}_2$ with a chlorido-bridged dimer often results in reaction products that depend on the steric hindrance on the amidic nitrogen atom,^[13a] on the nature of the chlorido-bridged dimers and on the reaction temperature and time.^[13b] Actually, treatment of $[(\text{phpy})_2\text{MCl}]_2$ ($\text{phpy} = 2\text{-phenylpyridine}$; $\text{M} = \text{Rh}^{\text{III}}$, Ir^{III} , **I**) with a secondary dithiooxamide $\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$ in chloroform provides **II**, and **III** after dehydrohalogenation, independently of the structural complexity of the alkyl substituent R in $\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$, of the reaction duration and of the reaction temperature. In the absence of structural data, we can infer that the neutral dithiooxamide in **II**, as well as the anionic rubeanate in **III**, is bound to a M^{III} central ion through the S,S -chelating system of the ligand on the basis of the following. (i) Both type **II** and type **III** complexes have a C_2 symmetry axis. This is evidenced by the NMR spectra, which exhibit only one set of signals in all complexes, except in **4** and in **8**. In these complexes, the twofold axis is lost as a result of the *meso* ligand so that all resonances appear doubled. The NMR signals are doubled also in the spectra of compounds **3** and **7**, but these compounds are equimolar mixtures of $\Delta\text{-(S,S)}$ and $\Lambda\text{-(S,S)}$ diastereomers. (ii) The ^1H NMR shift of the NH signal indicates that amidic hydrogen atoms are engaged in a strong hydrogen bond of the type $^+\text{N-H}\cdots\text{Cl}^-$.^[14] (iii) The IR absorptions at 3400 and 3180 cm^{-1} in complexes **1–4** and at 3350 and 3180 cm^{-1} (shoulder) in complexes **5–8** are typical of N-H stretching frequencies. (iv) NMR NOESY experiments do not show dipolar interactions between the α -hydrogen atoms of the alkyl substituents and H^6 of the 2-phenylpyridine system that is N,C -chelated to the M^{III} central ions. These interactions should have been detectable if the dithiooxamide ligand had been bound to M^{III} through the N,N -chelating system; actually, this is the case for heterobimetallic complexes $[(\text{phpy})_2\text{Rh}(\mu\text{-R}_2\text{C}_2\text{N}_2\text{S}_2\text{ } \kappa\text{-N,N-Rh, } \kappa\text{-S,S-M})\text{ML}_n]$ (vide infra). (v) The nitrogen chelating system of the dithiooxamide ligands, being uncoordinated, is engaged in a $\text{N-H}\cdots\text{Cl}$ interaction, which plays an important role in the stabilization of contact ion pairs such as $[\text{Rh}(\text{phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2\text{ } \kappa\text{-S,S-Rh})]^+\text{Cl}^-$.^[15] Such an ion pair can easily be dehydrohalogenated to give the neutral complexes **III**; species **III** can incorporate gaseous HCl , thus restoring

the ion pair **II**. It is worth mentioning that the reversible loss of HCl from complex ion pairs similar to **II** has already been exploited to obtain molecular systems capable of exhibiting the on/off switching of luminescence both in the solid state and in solution.^[16]



Scheme 1.

The reversible exchange of HCl was investigated by means of VT ^1H NMR experiments. Thus, equimolar quantities of $[\text{Rh}(\text{2-phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2\text{ } \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ and $[(\text{2-phpy})_2\text{Rh}(\mu\text{-R}_2\text{C}_2\text{N}_2\text{S}_2\text{ } \kappa\text{-S,S-Rh})]$ were dissolved in deuteriochloroform, and the ^1H NMR spectra were recorded at various temperatures. When $\text{R} = \text{isoamyl}$, the signals corresponding to one species appear in the spectrum at room temperature, but the frequencies of such signals differ from those of both the $[\text{Rh}(\text{2-phpy})_2\{\text{H}_2(\text{isoamyl})_2\text{dithiooxamide } \kappa\text{-S,S-Rh}\}]^+\text{Cl}^-$ ion pair and the $[\text{Rh}(\text{2-phpy})_2\{\text{H}(\text{isoamyl})_2\text{dithiooxamide } \kappa\text{-S,S-Rh}\}]$ neutral complex. By lowering the temperature, the signals broadened, but coalescence was not reached, even at a temperature as low as 190 K . The isopropyl complexes **2** and **6** gave the results shown in Figure 1. The doublet, which is quite broadened at room temperature, at first coalesces and then splits into two well-resolved doublets by lowering the temperature. These doublets correspond to the H^6 2-phenylpyridine proton in **2** and **6**.

The room-temperature spectrum of the equimolar mixture of the $\{\text{S}\}$ -phenylethyl complexes (**3** and **7**) exhibits well-resolved signals for both species **3** and **7**. This mixture was warmed up to 330 K , but the signals of each diastereomer were scarcely affected; nevertheless, HCl exchange between species **3** and **7** was evidenced by means of a NOESY experiment.

Activation parameters for the above exchange processes were achieved only for isopropyl derivatives, as the other processes were too fast (species **1** and **5**) or too slow (species **3** and **7**). It has been found that $\Delta H = 27.1 \pm 1.0\text{ kJ/mol}$, $\Delta G = 59.9 \pm 0.1\text{ kJ/mol}$, $\Delta S = -110.0 \pm 3.8\text{ J/K mol}$. The negative value for the activation entropy, as well as the lowering of the exchange rate as a result of the progressively bulkier α -carbon atoms on going from isoamyl to phenyl-

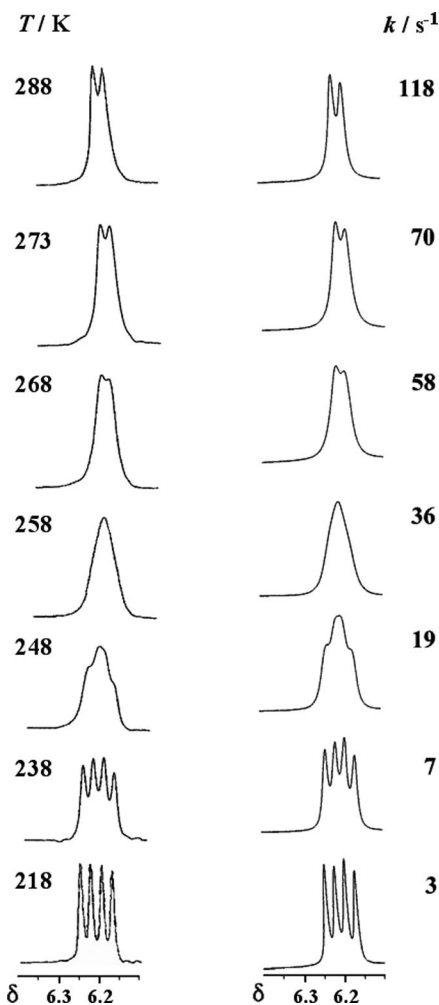


Figure 1. Variable-temperature spectra of an equimolar mixture of $[\text{Rh}(\text{phpy})_2\{\text{H}_2(\text{isopropyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh}\}]^+\text{Cl}^-$ (**2**) and $[\text{Rh}(\text{phpy})_2\{\text{H}(\text{isopropyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh}\}]$ (**6**) in the 6.1–6.4 ppm region. Computer-synthesized spectra are shown on the right.

ethyl groups, agrees with an exchange mechanism, which implies a congested transition state in which two $[(2\text{-phenylpyridine})_2\text{Rh}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2)]$ units interact with a HCl molecule as suggested in Figure 2.

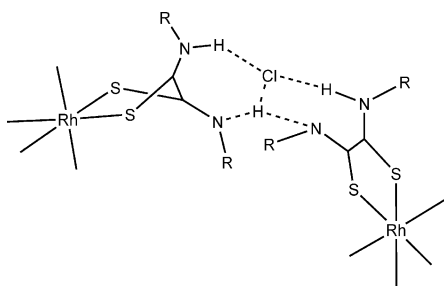
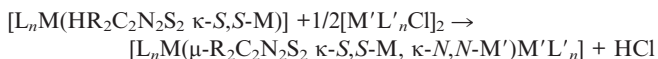


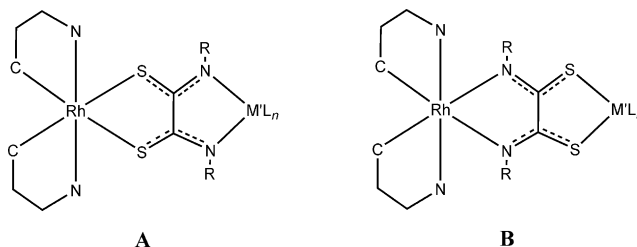
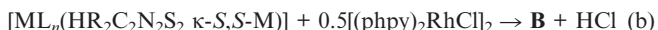
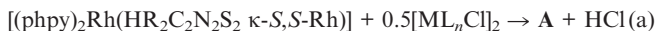
Figure 2. Proposed transition state for the HCl exchange process between the ion pair $[\text{Rh}(\text{phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ ($\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$ = dialkyldithiooxamide) and $[\text{Rh}(\text{phpy})_2(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$.

Binuclear Complexes

We have already synthesized a number of binuclear heterobimetallic,^[1,2,4] trinuclear heterobimetallic^[3,4] and trinuclear heterotrimetallic complexes^[4] by using $[\text{L}_n\text{M}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2)]$ (M = bi- or trivalent metal ion; L_n = various ligands, including dithiooxamate, that leave a positive charge in the fragment ML_n). All the complexes were obtained in one step or in a sequential synthesis, and in all cases, the metal fragment $\text{M}'\text{L}'_n$ was added to the $[\text{L}_n\text{M}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2)]$ ligand complex according to the following process ($[\text{M}'\text{L}'_n\text{Cl}]_2$ is any symmetrical chlorido-bridged dimer).

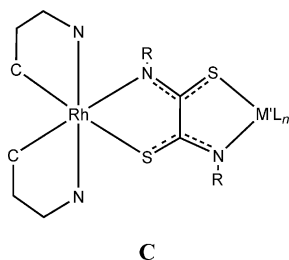


Thus, one could expect that a bis(2-phenylpyridine)rhodium(III) moiety could be connected to a ML_n fragment through a binucleating dithiooxamide ligand in two ways, so that the following linkage isomers **A** and **B** could be formed (Scheme 2). The formation of isomer **A**, rather than isomer **B**, depends on whether bis(2-phenylpyridine)rhodium(III) $[(\text{phpy})_2\text{Rh}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$ is added to $[\text{ML}_n\text{Cl}]_2$ in a ratio of 1:0.5 [procedure (a)] or $[\text{ML}_n(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-M})]$ is added to $[(\text{phpy})_2\text{RhCl}]_2$ in the same ratio [procedure (b)].



Scheme 2.

In contrast to what we expected, either procedure (a) or procedure (b) gave the same compound, which can be formulated as a heterobimetallic compound with the formula $[\text{Rh}(\text{phpy})_2(\mu\text{-R}_2\text{C}_2\text{N}_2\text{S}_2)\text{ML}_n]$. In such a compound, the binucleating dithiooxamide group could be linked through the sulfur atoms to rhodium and through the nitrogen atoms to the ML_n fragment as in isomer **A** or vice versa as in isomer **B**. Finally, the unique compound obtained could be isomer **C**, which contains the binucleating dithiooxamide group in an N,S coordination mode (Scheme 3). Complexes in which a dithiooxamide group links two metals in an N,S coordination mode are well known.^[17–20] Structure **C** can be ruled out because the NMR spectrum of **13** evidences a twofold axis in the $\text{Rh}^{\text{III}}\text{--Rh}^{\text{I}}$ bimetallic complex. Furthermore, the 2D NOESY spectrum shows polar interactions between the α protons of the alkyl substituents of the dithiooxamide group and both the H^6 and $\text{H}^{6'}$ protons of the N,C -chelated 2-phenylpyridine (Figure 3).



Scheme 3.

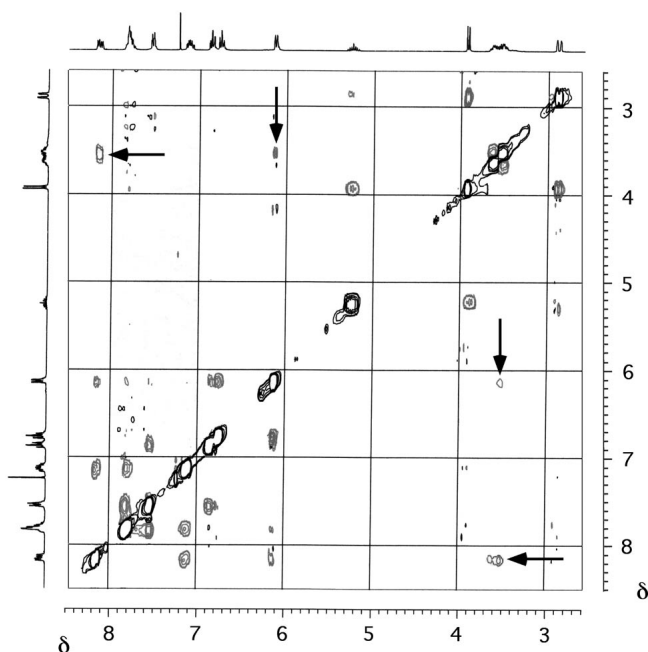


Figure 3. NOESY spectrum of $[\text{Rh}(\text{phpy})_2\{\mu\text{-(isoamyl)}_2\text{-C}_2\text{N}_2\text{S}_2\}\text{Pd}(\eta^3\text{-allyl})\kappa\text{-N,N-Rh}\kappa\text{-S,S-Pd}]\text{ (14)}$. Cross peaks marked with horizontal arrows indicate the proximity of the N-CH_2 protons to H^6 of 2-phenylpyridine; the peaks indicated by vertical arrows refer to the polar interaction between N-CH_2 and $\text{H}^{6'}$ of 2-phenylpyridine.

Such interactions are not present in the mononuclear complex $[(\text{phpy})_2\text{Rh}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2\kappa\text{-S,S-Rh})]$, in which the dithiooxamide ligand is chelated in an S,S fashion to rhodium and the NCH_2 protons are too far from H^6 of the 2-phenylpyridine rings. These facts suggest that the probable structure of the heterobimetallic species is **B** (Figure 4).

In order to strengthen the theory proposed by NMR spectroscopy, several attempts to obtain crystals of complexes **13–16** suitable for an X-ray analysis were made. Unfortunately, very thin needles of the only Ru–Pt complex (**16**) were obtained, which provided diffraction data of very poor quality. Nevertheless such data appeared to be sufficient in providing us with some information, i.e. the binucleating dithiooxamide ligand is linked to platinum through the sulfur atoms and to rhodium through the nitrogen atoms, as shown in Figure 5.

As a matter of fact, a change in the connectivity of the dithiooxamide ligand on going from the mononuclear species $[\kappa\text{-S,S-Rh}^{\text{III}}]$ to the binuclear complex $[\kappa\text{-N,N-Rh}^{\text{III}}]$

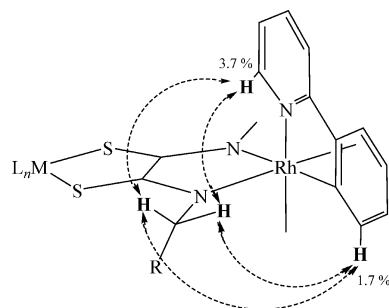


Figure 4. Schematic view of the polar interactions between the α hydrogen atoms of the alkyl substituents of the dithiooxamide ligand and the H^6 and $\text{H}^{6'}$ protons of the N,C -coordinated 2-phenylpyridine. Each N-CH_2 group is equidistant from the H^6 and $\text{H}^{6'}$ protons of both 2-phenylpyridine moieties. Irradiation of the N-CH_2 protons enhances the signal for H^6 (ca. 3.7%) and that for $\text{H}^{6'}$ (ca. 1.7%) in all the bimetallic complexes **13–16**.

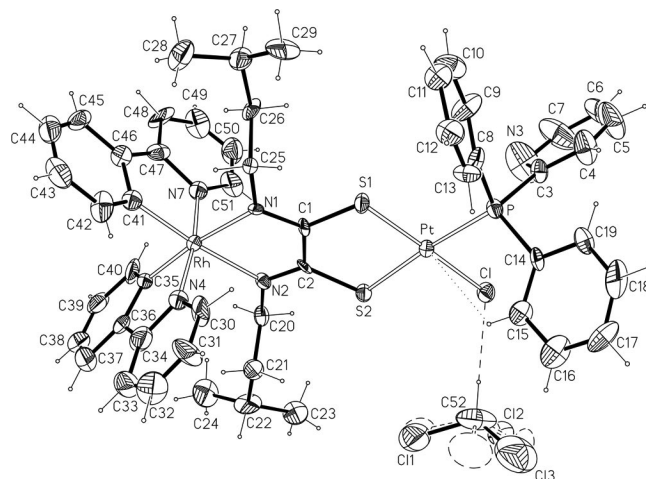
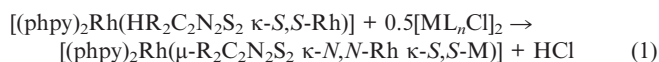


Figure 5. Asymmetric unit of the crystal model of **16** obtained by single-crystal X-ray diffraction, showing the molecular geometry and co-crystallized chloroform in a ratio of 1:1. Thermal ellipsoids are at the 25% probability level, while the H size is arbitrary. Selected bond lengths [Å] and angles [°]: $\text{Pt-P} = 2.258(6)$, $\text{Pt-S1} = 2.271(5)$, $\text{Pt-S2} = 2.315(5)$, $\text{Pt-Cl} = 2.336(5)$, $\text{Rh-C35} = 1.97(2)$, $\text{Rh-N4} = 2.00(2)$, $\text{Rh-N7} = 2.01(2)$, $\text{Rh-C41} = 2.01(2)$, $\text{Rh-N1} = 2.15(2)$, $\text{Rh-N2} = 2.17(1)$, $\text{S1-Pt-S2} = 89.6(2)$, $\text{N1-Rh-N2} = 75.9(6)$, $\text{N7-Rh-C41} = 84.3(8)$, $\text{C35-Rh-N4} = 84.2(8)$, $\text{S1-Cl} = 1.74(2)$, $\text{S2-C2} = 1.77(2)$, $\text{C1-N1} = 1.33(2)$, $\text{C1-C2} = 1.44(2)$, $\text{S1-C1-C2-S2} = 2(2)$.

occurs when the bimetallic complexes **13–15** were prepared according to the following reaction.



This implies that a favourable hard–hard interaction between the nitrogen chelating system of the binucleating ligand and the proton in the mononuclear $[(\text{phpy})_2\text{Rh}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2\kappa\text{-S,S-Rh})]$ changes with a probable stable $\text{N-Rh}^{\text{III}}\text{-N}$ interaction in the binuclear complexes. At the same time, the rearrangement of the binucleating ligand also produces a stable $\text{S-M}(\text{L}_n)\text{-S}$ soft–soft interaction, since all ML_n^+ are soft metal fragments.^[21]

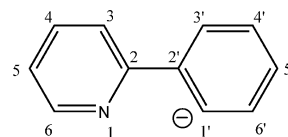
Finally, it should be noted that in $[(\text{phpy})_2\text{Rh}(\text{HR}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]$, the high *trans* influence exerted by the σ -bonded $\text{C}^{1'}$ atom destabilizes the $\text{Rh}^{\text{III}}\text{-S}$ bond.^[22] This could be a concomitant cause favouring the change in the coordination mode of the binucleating ligand observed in process (1).

Conclusions

This work shows that metalloligand $[(2\text{-phenylpyridine})_2\text{Rh}\{\text{H}(\text{isoamyl})_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh}\}]$ changes the coordination mode of the dithiooxamide group when it is linked to a second metal fragment. Such a change mainly depends on the stability of the interaction between each of the metals and the different chelating sites of the binucleating ligand, other than on the *trans* influence, and presumably, on the *trans* effect of the ancillary ligands surrounding both metal centres. Steric effects have not been investigated in the course of the present study, although one can suppose that bulkier alkyl groups in the species $\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2$ causes further effects either in the reactions indicated as procedure (a) or in those indicated as procedure (b). Consequently, further studies are required to achieve a complete comprehension of the stereoelectronic factors that rule the step-wise formation of polymetallic complexes.

Experimental Section

General Remarks: Solvents were purified by standard procedures and distilled before use. Secondary dithiooxamides,^[23] *cis*- $\text{Pt}(\text{Me}_2\text{SO})_2\text{Cl}_2$ ^[24] and *cis*- $\text{Pt}(\text{Me}_2\text{SO})(\text{diphenyl-2-pyridylphosphane})\text{Cl}_2$ ^[25] and $[\text{Pd}(\text{tri-}n\text{-propylphosphane})\text{Cl}_2]$ ^[26] were prepared according to literature methods. $[\text{Rh}(1,5\text{-cyclooctadiene})\text{Cl}]_2$, $[(\eta^3\text{-allyl})\text{PdCl}]_2$ and $[\text{Rh}(2\text{-phenylpyridine})_2\text{Cl}]_2$ were obtained commercially and were used as purchased. The reactions were performed under laboratory atmosphere, since both reagents and reaction products are stable in air. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 298°K on a Bruker ARX-300, equipped with a broad band probe operating at 300.13 and 75.56 MHz, respectively. Chemical shifts (δ , ppm) were referenced to SiMe_4 . The simulation of static and dynamic spectra was performed with a gNMR program. IR spectra were obtained as Nujol mulls on KBr plates by using a Perkin–Elmer FTIR 1720 spectrometer. Diffraction analysis was performed with a four-circle single-crystal Siemens P4 diffractometer by using graphite monochromated Mo-K_α radiation. Thin needles of complex **16** were obtained by slow evaporation of the solvent from a chloroform/petroleum ether solution. The diffraction data were collected up to $2\theta = 50^\circ$, and the reflection intensities were evaluated by a learnt-profile procedure^[27] among 2θ shells and then corrected for Lorentz-polarization and absorption effects. Data collection and reduction were performed with a SHELXTL^[28] package, but the quality of the 9036 independent reflection set was very poor [$R(\text{int}) = 0.124$]. The atom labelling scheme for 2-phenylpyridine[−] is shown in Scheme 4. CCDC-730891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme 4.

$[\text{Rh}(\text{phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ ($\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 = N,N'$ -diisoamylidithiooxamide) (1**):** The chloridobis(2-phenyl-pyridine)rhodium(III) dimer (446.7 mg, 0.5 mmol) was suspended in chloroform (75 mL) and a twofold quantity of *N,N'*-diisoamylidithiooxamide (260.5 mg, 1 mmol) was added to the resulting suspension. The mixture was magnetically stirred for 24 h at room temperature. After this period, the resulting red solution was concentrated to 10 mL, after which petroleum ether (50 mL) was added. The ion pair $[\text{Rh}(2\text{-phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ precipitated as an orange–red powder; the solvent removed by filtration, and the powder was allowed to dry in air. Yield: 495.0 mg (70%). $\text{C}_{34}\text{H}_{40}\text{ClN}_4\text{RhS}_2$ (707.21): calcd. H 5.70, C 57.75, N 7.92, S 9.07; found H 5.70, C 57.90, N 7.90, S 9.00. ^1H NMR (CDCl_3 , 27 °C): $\delta = 0.83, 0.86$ [2d, $J = 6.60$ Hz, 12 H, $\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 1.58 [seven lines, $J = 6.6$ Hz, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 1.74 [m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 3.70 [m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 6.21 (d, $J = 7.8$ Hz, 2 H, H^6), 6.83 (t, $J = 7.8$ Hz, 2 H, H^5), 6.95 (t, $J = 7.8$ Hz, 2 H, H^4), 7.19 (t, $J = 6.2$ Hz, 2 H, H^5), 7.63 (d, $J = 7.8$ Hz, 2 H, H^3), 7.84 (t, $J = 8.2$ Hz, 2 H, H^4), 7.87 (d, $J = 8.2$ Hz, 2 H, H^3), 8.84 (d, $J = 6.0$ Hz, 2 H, H^6), 12.43 (br. s, 2 H, $\text{NH}\cdots\text{Cl}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): $\delta = 22.21, 22.33$ [$\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 26.34 [$\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 35.00 [$\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 48.20 [$\text{NCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$], 118.40 (C^3), 122.50 (C^4), 123.10 (C^5), 124.00 (C^3'), 129.80 (C^5'), 132.00 (C^6'), 137.27 (C^4), 143.23 (C^2), 150.66 (C^6), 153.96 (d, $^2J_{\text{Rh-C}} = 2.1$ Hz, C^2), 166.86 (d, $J_{\text{Rh-C}} = 31.6$ Hz, $\text{C}^{1'}$) ppm.

$[\text{Rh}(\text{phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ ($\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 = N,N'$ -diisopropylidithiooxamide) (2**):** This orange compound was obtained according to the above procedure by using *N,N'*-diisopropylidithiooxamide (204.4 mg, 1 mmol) in place of *N,N'*-diisoamylidithiooxamide. Yield: 462.3 mg (71%). $\text{C}_{30}\text{H}_{32}\text{ClN}_4\text{RhS}_2$ (651.09): calcd. H 4.95, C 55.34, N 8.61, S 9.85; found H 5.00, C 55.80, N 8.50, S 9.90. ^1H NMR (CDCl_3 , 27 °C): $\delta = 1.37, 1.46$ [2d, $J = 6.20$ Hz, 12 H, $\text{NCH}(\text{CH}_3)_2$], 4.50 [m, 2 H, $\text{NCH}(\text{CH}_3)_2$], 6.21 (d, $J = 7.7$ Hz, 2 H, H^6), 6.84 (t, $J = 7.8$ Hz, 2 H, H^5), 6.96 (t, $J = 7.7$ Hz, 2 H, H^4), 7.19 (t, $J = 6.2$ Hz, 2 H, H^5), 7.63 (d, $J = 7.8$ Hz, 2 H, H^3), 7.82 (t, $J = 8.2$ Hz, 2 H, H^4), 7.85 (d, $J = 8.2$ Hz, 2 H, H^3), 8.77 (d, $J = 6.0$ Hz, 2 H, H^6), 12.31 (br. s, 2 H, $\text{NH}\cdots\text{Cl}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): $\delta = 20.28, 20.40$ [$\text{NCH}(\text{CH}_3)_2$], 52.62 [$\text{NCH}(\text{CH}_3)_2$], 119.20 (C^3), 122.50 (C^4), 123.04 (C^5), 123.97 (C^3'), 129.80 (C^5'), 132.06 (C^6'), 137.26 (C^4), 143.20 (C^2'), 150.71 (C^6), 165.37 (d, $^2J_{\text{Rh-C}} = 2.1$ Hz, C^2), 166.90 (d, $J_{\text{Rh-C}} = 31.6$ Hz, $\text{C}^{1'}$) ppm.

$[\text{Rh}(\text{phpy})_2(\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 \kappa\text{-S,S-Rh})]^+\text{Cl}^-$ ($\text{H}_2\text{R}_2\text{C}_2\text{N}_2\text{S}_2 = N,N'$ -di- $\{S\}$ -phenylethylidithiooxamide) (3**):** This orange compound was prepared as described for **1** by using *N,N'*-di- $\{S\}$ -phenylethylidithiooxamide (328.5 mg, 1 mmol) in place of *N,N'*-diisoamylidithiooxamide. Yield: 535.0 mg (69%). $\text{C}_{40}\text{H}_{36}\text{ClN}_4\text{RhS}_2$ (775.23): calcd. H 4.68, C 61.97, N 7.23, S 8.27; found H 4.70, C 62.50, N 7.40, S 8.20. ^1H NMR (CDCl_3 , 27 °C): $\delta = 1.88, 1.93$ [2d, $J = 7.04$ Hz, 6 H, $\text{NCH}(\text{C}_6\text{H}_5)\text{CH}_3$], 5.33, 5.94 [2sl, $J = 7.0$ Hz, 2 H, $\text{NCH}(\text{C}_6\text{H}_5)\text{CH}_3$], 5.92, 6.14 (2d, $J = 7.8$ Hz, 2 H, H^6), 6.7–7.84 (overlapping signals due to $\text{H}^3, \text{H}^4, \text{H}^5, \text{H}^3', \text{H}^4', \text{H}^5'$, 22 H, phenylethyl- C_6H_5), 8.59, 9.19 (2d, $J = 6.0$ Hz, 2 H, H^6), 12.88, 13.04 (2d, $J = 6.2$ Hz, 2 H, $\text{NH}\cdots\text{Cl}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): $\delta = 21.33,$

22.08 [NCH(C₆H₅)CH₃], 60.04, 60.34 [NCH(C₆H₅)CH₃], 119.24 (C³), 122.25 (C⁴), 122.90 (C⁵), 123.90 (C^{3'}), 127.70 (*meta*-C₆H₅), 128.01 (*para*-C₆H₅), 128.40, 128.60 (*ortho*-C₆H₅), 129.70 (C^{5'}), 131.38, 132.04 (C^{6'}), 137.06, 137.18 (C⁴), 140.10, 141.00 (C^{2'}), 150.50 (C⁶), 165.30 (²J_{Rh-C} = 2.1 Hz, C²), 166.50, 166.90 (2d, ¹J_{Rh-C} = 31.6 Hz, C^{1'}) ppm.

[Rh(ppy)₂(HR₂C₂N₂S₂ κ-S,S-Rh)]⁺Cl⁻ (HR₂C₂N₂S₂ = *N,N'*-*meso*-diphenylethylidithiooxamide) (4): This orange compound was obtained according to the procedure described for **1** by using *N,N'*-*meso*-diphenylethylidithiooxamide (328.5 mg, 1 mmol) in place of *N,N'*-diisoamylidithiooxamide. Yield: 503.9 mg (65%). C₄₀H₃₆ClN₄RhS₂ (775.24): calcd. H 4.68, C 61.97, N 7.23, S 8.27; found H 4.65, C 62.40, N 7.20, S 8.15. ¹H NMR (CDCl₃, 27 °C): δ = 1.86, 1.94 [2d, *J* = 7.04 Hz, 6 H, N-CH(C₆H₅)CH₃], 5.34, 5.56 [2sl, *J* = 7.0 Hz, 2 H, NCH(C₆H₅)CH₃], 6.04, 6.17 (2d, *J* = 7.8 Hz, 2 H, H^{6'}), 6.68–7.90 (overlapped signals due to H³, H⁴, H⁵, H^{3'}, H^{4'}, H^{5'}, 22 H, phenylethyl-C₆H₅), 8.03, 8.76 (2d, *J* = 6.0 Hz, 2 H, H⁶), 12.90, 13.07 (2d, *J* = 6.2 Hz, 2 H, NH···Cl) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 21.62, 22.10 [NCH(C₆H₅)CH₃], 60.30 [NCH(C₆H₅)CH₃], 119.30, 119.50 (C³), 122.40, 122.60 (C⁴), 122.97 (C⁵), 123.90, 124.01 (C^{3'}), 127.68 (*meta*-C₆H₅), 127.89 (*para*-C₆H₅), 128.50, 128.60 (*ortho*-C₆H₅), 129.70 (C^{5'}), 131.90, 132.1 (C^{6'}), 137.16, 137.34 (C⁴), 140.10, 141.00 (C^{2'}), 150.47, 150.51 (C⁶), 165.05, 165.45 (C²), 166.64, 167.01 (2d, ¹J_{Rh-C} = 31.6 Hz, C^{1'}) ppm.

[Rh(ppy)₂(HR₂C₂N₂S₂ κ-S,S-Rh)] (HR₂C₂N₂S₂ = *N,N'*-diisoamylidithiooxamide) (5): Compound **1** (353.6 mg, 0.5 mmol) was dissolved in chloroform (75 mL), and the resulting orange solution was treated with sodium hydrogen carbonate (2 g). The mixture soon turned yellow and was left to stir for 0.5 h. After this time, the solution was filtered, concentrated to 10 mL and purified by chromatography [alumina column, chloroform/petroleum ether (4:1, v/v) as eluent]. The pure yellow product was finally obtained by precipitation from the addition of petroleum ether (40/60) to a concentrated portion (about 10 mL) of the eluate. Yield: 228.1 mg (68%). C₃₄H₃₉N₄RhS₂ (670.73): calcd. H 5.86, C 60.88, N 8.35, S 9.56; found H 5.90, C 61.00, N 8.25, S 9.50. ¹H NMR (CDCl₃, 27 °C): δ = 0.88, 0.89 [2d, 12 H, NCH₂CH₂CH(CH₃)₂], 1.60 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 3.58 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 6.27 (d, *J* = 7.3 Hz, 2 H, H^{6'}), 6.79 (t, *J* = 7.3 Hz, 2 H, H^{5'}), 6.88 (t, *J* = 7.3 Hz, 2 H, H^{4'}), 7.09 (t, *J* = 6.6 Hz, 2 H, H⁵), 7.59 (d, *J* = 8.0 Hz, 2 H, H^{3'}), 7.72 (t, *J* = 8.0 Hz, 2 H, H⁴), 7.82 (d, *J* = 8.0 Hz, 2 H, H³), 9.08 (d, *J* = 6.0 Hz, 2 H, H⁶) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 22.58 [NCH₂CH₂CH(CH₃)₂], 26.41 [NCH₂CH₂CH(CH₃)₂], 37.99 [NCH₂CH₂CH(CH₃)₂], 48.55 [NCH₂CH₂CH(CH₃)₂], 118.89 (C³), 121.81 (C⁴), 122.15 (C⁵), 123.63 (C^{3'}), 129.22 (C^{5'}), 132.26 (C^{6'}), 136.27 (C⁴), 143.39 (C^{2'}), 150.91 (C⁶), 165.70 (C²), 169.90 (d, ¹J_{Rh-C} = 31.9 Hz, C^{1'}) ppm.

[Rh(ppy)₂(HR₂C₂N₂S₂ κ-S,S-Rh)] (HR₂C₂N₂S₂ = *N,N'*-diisopropylidithiooxamide) (6): This yellow compound was obtained according to the above procedure by using **2** (325.6 mg, 0.5 mmol) in place of **1**. Yield: 215.1 mg (70%). C₃₀H₃₁N₄RhS₂ (614.63): calcd. H 5.08, C 58.63, N 9.12, S 10.43; found H 5.00, C 58.90, N 9.20, S 10.50. ¹H NMR (CDCl₃, 27 °C): δ = 1.13, 1.26 [2d, *J* = 6.10 Hz, 12 H, NCH(CH₃)₂], 4.33 [m, 2 H, NCH(CH₃)₂], 6.27 (d, *J* = 7.50 Hz, 2 H, H^{6'}), 6.76 (t, *J* = 7.78 Hz, 2 H, H^{5'}), 6.87 (t, *J* = 7.7 Hz, 2 H, H^{4'}), 7.08 (t, *J* = 6.16 Hz, 2 H, H⁵), 7.59 (d, *J* = 7.8 Hz, 2 H, H^{3'}), 7.75 (t, *J* = 8.2 Hz, 2 H, H⁴), 7.8 (d, *J* = 8.22 Hz, 2 H, H³), 9.12 (d, *J* = 6.0 Hz, 2 H, H⁶) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 21.75, 21.93 [NCH(CH₃)₂], 50.27, [NCH(CH₃)₂], 118.80 (C³), 121.63 (C⁴), 121.96 (C⁵), 123.55 (C^{3'}), 129.14 (C^{5'}), 132.27 (C^{6'}), 136.19 (C⁴), 143.37 (C^{2'}), 150.91 (C⁶), 165.00 (d, ²J_{Rh-C} = 2.1 Hz, C²), 170.00 (d, ¹J_{Rh-C} = 31.8 Hz, C^{1'}) ppm.

[Rh(ppy)₂(HR₂C₂N₂S₂ κ-S,S-Rh)] (HR₂C₂N₂S₂ = *N,N'*-di-*S*-phenylethylidithiooxamide) (7): This yellow compound was obtained according to the procedure described for **5** by using **3** (387.6 mg, 0.5 mmol) in place of **1**. Yield: 229.6 mg (62%). C₄₀H₃₅N₄RhS₂ (738.77): calcd. H 4.78, C 65.03, N 7.58, S 8.68; found H 4.90, C 64.90, N 7.50, S 8.65. ¹H NMR (CDCl₃, 27 °C): δ = 1.45, 1.55 [2d, *J* = 6.7 Hz, 6 H, NCH(C₆H₅)CH₃], 5.39, 5.38 [2q, *J* = 6.7 Hz, 2 H, NCH(C₆H₅)CH₃], 6.20, 6.28 (2d, *J* = 7.8 Hz, 2 H, H^{6'}), 6.62–7.83 (overlapping signals due to H³, H⁴, H⁵, H^{3'}, H^{4'}, H^{5'}, 22 H, phenylethyl-C₆H₅), 8.86, 9.12 (2d, *J* = 5.9 Hz, 2 H, H⁶) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 21.75, 21.93 [NCH(C₆H₅)CH₃], 58.15, 58.20 [NCH(C₆H₅)CH₃], 118.73, 118.84 (C³), 121.74 (C⁵), 122.05, 122.10 (C⁴), 123.43, 123.60 (C^{3'}), 126.47, 126.65 (*meta*-C₆H₅), 126.99 (*para*-C₆H₅), 128.47 (*ortho*-C₆H₅), 129.19, 129.21 (C^{5'}), 132.25 (C^{6'}), 136.10, 136.20 (C⁴), 143.40, 144.00 (C^{2'}), 151.91 (C⁶), 165.69, 170.00 (C²), 169.92, 170.00 (2d, ¹J_{Rh-C} = 31.6 Hz, C^{1'}) ppm.

[Rh(ppy)₂(HR₂C₂N₂S₂ κ-S,S-Rh)] (HR₂C₂N₂S₂ = *N,N'*-di-*meso*-phenylethylidithiooxamide) (8): This yellow compound was obtained according to the procedure described for **5** by using **4** (387.6 mg, 0.5 mmol) in place of **1**. Yield: 248.0 mg (67%). C₄₀H₃₅N₄RhS₂ (738.77): calcd. H 4.78, C 65.03, N 7.58, S 8.68; found H 4.70, C 65.00, N 7.50, S 8.50. ¹H NMR (CDCl₃, 27 °C): δ = 1.49, 1.67 [2d, *J* = 6.7 Hz, 6 H, NCH(C₆H₅)CH₃], 5.38, 5.39 [2q, *J* = 6.7 Hz, 2 H, NCH(C₆H₅)CH₃], 6.20, 6.23 (2d, *J* = 7.8 Hz, 2 H, H^{6'}), 6.66–7.93 (overlapping signals due to H³, H⁴, H⁵, H^{3'}, H^{4'}, H^{5'}, 22 H, phenylethyl-C₆H₅), 8.69, 9.24 (2d, *J* = 5.9 Hz, 2 H, H⁶) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 21.73, 22.46 [NCH(C₆H₅)CH₃], 58.00, 58.17 [NCH(C₆H₅)CH₃], 118.74, 118.86 (C³), 121.74 (C⁵), 122.06 (C⁴), 123.56 (C^{3'}), 126.35, 126.54 (*meta*-C₆H₅), 126.83/126.95 (*para*-C₆H₅), 128.50 (*ortho*-C₆H₅), 129.19, 129.21 (C^{5'}), 132.17, 132.35 (C^{6'}), 136.25 (C⁴), 143.40, 144.00 (C^{2'}), 151.91 (C⁶), 166.25 (C²), 169.32, 169.74 (2d, ¹J_{Rh-C} = 31.6 Hz, C^{1'}) ppm.

[Rh(1,5-cyclooctadiene)(HR₂C₂N₂S₂ κ-S,S-Rh)] (HR₂C₂N₂S₂ = *N,N'*-diisoamylidithiooxamide) (9): [Rh(1,5-cyclooctadiene)Cl]₂ (123.3 mg, 0.25 mmol) was dissolved in chloroform (40 mL), and sodium hydrogen carbonate (1.0 g) and *N,N'*-diisoamylidithiooxamide (130.2 mg, 0.5 mmol) were then added. The mixture was kept under magnetic stirring for 1 h. Sodium hydrogen carbonate was then removed, and the resulting solution was concentrated to a small volume (about 5 mL). Finally, petroleum light was added, and a pure yellow compound was obtained. Yield: 198.0 mg (84%). C₂₀H₃₅N₂RhS₂ (470.54): calcd. H 7.50, C 51.05, N 5.95, S 13.63; found H 7.60, C 51.10, N 6.00, S 13.50. ¹H NMR (CDCl₃, 27 °C): δ = 0.92 [d, *J* = 6.3 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.57–1.63 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 2.03 (m, 4 H, CH₂-cod), 2.44 (m, 4 H, CH₂-cod), 3.60 [t, *J* = 7.2 Hz, 4 H, NCH₂CH₂CH(CH₃)₂], 4.43 (br. s, 4 H, CH-cod) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): δ = 22.47, [NCH₂CH₂CH(CH₃)₂], 26.23 [NCH₂CH₂CH(CH₃)₂], 31.30 (CH₂-cod), 37.64 [NCH₂CH₂CH(CH₃)₂], 47.64 [NCH₂CH₂CH(CH₃)₂], 82.65 (¹J_{Rh-C} = 11.0 Hz, CH-cod) ppm.

[Pd(η³-allyl)(HR₂C₂N₂S₂ κ-S,S-Pd)] (HR₂C₂N₂S₂ = *N,N'*-diisoamylidithiooxamide) (10): This yellow compound was obtained according to the above procedure by using [Pd(η³-allyl)Cl]₂ (91.5 mg, 0.25 mmol) in place of [Rh(1,5-cyclooctadiene)Cl]₂. Yield: 175.0 mg (86%). C₁₅H₂₈N₂PdS₂ (406.94): calcd. H 6.94, C 44.27, N 6.88, S 15.76; found H 6.90, C 44.20, N 6.80, S 15.60. ¹H NMR (CDCl₃, 27 °C): δ = 0.90 [d, *J* = 6.45 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.60–1.70 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 3.00 (d, *J* = 12.7 Hz, 2 H, allyl *anti*), 3.68 [d, *J* = 7.2 Hz, 1 H, NCH₂CH₂CH(CH₃)₂], 4.15 (d, *J* = 6.9 Hz, 2 H, allyl *syn*), 5.32 (m,

4 H, *CH*-allyl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 22.50, [NCH₂CH₂CH(CH₃)₂], 26.3 [NCH₂CH₂CH(CH₃)₂], 37.6 [NCH₂CH₂CH(CH₃)₂], 48.30 [NCH₂CH₂CH(CH₃)₂], 61.80 (allyl-CH₂), 113.8 (allyl-CH) ppm.

[PdCl(tri-*n*-propylphosphane)(HR₂C₂N₂S₂ κ-S,S-Pd)] (HR₂C₂N₂S₂ = *N,N'*-diisoamylidithiooxamidate) (11): This yellow compound was obtained according to the procedure described for **9** by using [Pd(tri-*n*-propylphosphane)Cl₂]₂ (168.8 mg, 0.25 mmol) in place of [Rh(1,5-cyclooctadiene)Cl]₂. Yield: 235.9 mg (84%). C₂₁H₄₄ClN₂PPdS₂ (561.56): calcd. H 7.90, C 44.92, N 4.99, S 11.42; found H 7.90, C 44.20, N 4.80, S 11.60. ^1H NMR (CDCl_3 , 27 °C): δ = 0.93 [d, *J* = 6.1 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.05 (t, $^3J_{\text{H-H}}$ = 6.6 Hz, PCH₂CH₂CH₃), 1.562–1.925 [m, NCH₂CH₂CH(CH₃)₂, PCH₂CH₂CH₃], 3.5 [t, $J_{\text{H-H}}$ = 7.2 Hz, NCH₂CH₂CH(CH₃)₂], 3.67 [t, $J_{\text{H-H}}$ = 7.2 Hz NCH₂CH₂CH(CH₃)₂] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 15.88 (PCH₂CH₂CH₃), 17.85 (PCH₂CH₂CH₃), 22.28, 22.58 [NCH₂CH₂CH(CH₃)₂], 25.20 (d, $J_{\text{P-C}}$ = 28.0 Hz, PCH₂CH₂CH₃), 26.1, 26.4 [NCH₂CH₂CH(CH₃)₂], 36.2, 38.9 [NCH₂CH₂CH(CH₃)₂], 43.9, 49.7 [NCH₂CH₂CH(CH₃)₂] ppm.

[PtCl(diphenyl-2-pyridylphosphane)(HR₂C₂N₂S₂ κ-S,S-Pt)] (HR₂C₂N₂S₂ = *N,N'*-diisoamylidithiooxamidate) (12): This yellow compound was obtained according to the procedure described for **9** by using [Pt(diphenyl-2-pyridylphosphane)Cl₂]₂ (264.6 mg, 0.25 mmol) in place of [Rh(1,5-cyclooctadiene)Cl]₂. Yield: 320.0 mg (85%). C₂₉H₃₇ClN₃PPtS₂ (753.26): calcd. H 4.95, C 46.24, N 5.58, S 8.51; found H 4.90, C 46.20, N 5.60, S 8.60. ^1H NMR (CDCl_3 , 27 °C): δ = 0.92, 0.93 [2d, *J* = 7.2 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.596–1.691 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 3.71, 3.28 [2t, *J* = 7.0 Hz, 4 H, NCH₂CH₂CH(CH₃)₂] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 22.30, 21.92 [NCH₂CH₂CH(CH₃)₂], 25.8, 26.4 [NCH₂CH₂CH(CH₃)₂], 35.8, 38.4 [NCH₂CH₂CH(CH₃)₂], 43.0, 48.9 [NCH₂CH₂CH(CH₃)₂], 124.9–150.5 (ArC, PyC) ppm.

[Rh(phpy)₂{μ-(isoamyl)₂C₂N₂S₂}Rh(1,5-cyclooctadiene) κ-N,N'-Rh^{III} κ-S,S-Rh^I] (13): This orange compound was prepared by procedures (a) and (b). (a) **5** (134.2 mg, 0.2 mmol) was dissolved in chloroform (40 mL). To the solution were added [(1,5-cyclooctadiene)RhCl]₂ (49.3 mg, 0.1 mmol) and methanol (10 mL). The reaction mixture was heated at reflux for 2 h, concentrated to 10 mL and purified by chromatography [alumina column, chloroform/petroleum ether (4:1, v/v) as eluent]. The solid pure product was obtained by the addition of petroleum ether (40/60) to a concentrated portion (about 10 mL) of the eluate. Yield: 72 mg (41%). C₄₂H₅₀N₄Rh₂S₂ (880.82): calcd. H 5.72, C 57.27, N 6.36, S 7.28; found H 5.75, C 57.50, N 6.35, S 7.20. (b) **9** (94.1 mg, 0.2 mmol) was dissolved in chloroform (40 mL). To the solution were added [Rh(phpy)Cl]₂ (89.3 mg, 0.1 mmol) and methanol (10 mL). The reaction mixture was treated as above. Yield: 93 mg (53%). Found H 5.80, C 57.40, N 6.35, S 7.30. ^1H NMR (CDCl_3 , 27 °C): δ = 0.40, 0.44 [2d, *J* = 6.46 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.56 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 2.00 (m, 4 H, CH₂-cod), 2.45 (m, 4 H, CH₂-cod), 3.51 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 4.88 (m, 4 H, CH-cod), 6.11 (d, *J* = 7.5 Hz, 2 H, H^{6'}), 6.75 (t, *J* = 7.5 Hz, 2 H, H^{5'}), 6.88 (t, *J* = 7.5 Hz, 2 H, H^{4'}), 7.18 (t, *J* = 6.0 Hz, 1 H, H⁵), 7.19 (t, *J* = 6.0 Hz, 1 H, H⁵), 7.55 (d, *J* = 8.0 Hz, 2 H, H^{3'}), 7.84 (m, 2 H, H⁴), 7.84 (m, 2 H, H³), 8.16 (d, *J* = 5.7 Hz, 2 H, H⁶) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 21.91, 22.13 [NCH₂CH₂CH(CH₃)₂], 26.40 [NCH₂CH₂CH(CH₃)₂], 31.10, 31.34 (CH₂-cod), 34.92 [NCH₂CH₂CH(CH₃)₂], 53.54 [NCH₂CH₂CH(CH₃)₂], 80.99, 81.09 ($J_{\text{Rh-C}}$ = 8.32 Hz, CH-cod), 118.00 (C³), 122.20 (C⁴), 122.47 (C⁵), 123.37 (C^{3'}), 129.51 (C^{5'}), 132.20 (C^{6'}), 136.83 (C⁴), 143.33 (C^{2'}), 150.50 (C⁶), 165.67 (C²), 170.93 (d, $J_{\text{Rh-C}}$ = 31.9 Hz, C^{1'}) ppm.

[Rh(phpy)₂{μ-(isoamyl)₂C₂N₂S₂}Pd(η³-allyl) κ-N,N'-Rh κ-S,S-Pd] (14): This orange compound was prepared by procedures (a) and (b). (a) This product was obtained from **5** (134.2 mg, 0.2 mmol) and [(η³-allyl)PdCl]₂ (36.6 mg, 0.1 mmol) according to procedure (a) above. Yield: 65 mg (40%). C₃₇H₄₃N₄PdRhS₂ (817.20): calcd. (817.22): H 5.30, C 54.38, N 6.86, S 7.85; found H 5.35, C 54.45, N 6.90, S 7.80. (b) This product was obtained from **10** (81.4 mg, 0.2 mmol) and [Rh(2-phpy)Cl]₂ (89.3 mg, 0.1 mmol) according to procedure (b) above. Yield: 80 mg (49%). Found H 5.25, C 54.50, N 6.80, S 7.80. ^1H NMR (CDCl_3 , 27 °C): δ = 0.43, 0.47 [2d, *J* = 6.6 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 1.06 [m, 2 H, NCH₂CH₂CH(CH₃)₂], 1.25 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 2.91 (d, 2 H, CH₂-allyl), 3.60 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 3.95 (d, 2 H, CH₂-allyl), 5.27 (m, 1 H, CH-allyl), 6.16 (d, *J* = 7.5 Hz, 2 H, H^{6'}), 6.78 (t, *J* = 7.5 Hz, 2 H, H^{5'}), 6.89 (t, *J* = 7.5 Hz, 2 H, H^{4'}), 7.15 (m, 2 H, H⁵), 7.57 (d, *J* = 8.0 Hz, 2 H, H^{3'}), 7.85 (m, 2 H, H⁴), 7.85 (m, 2 H, H³), 8.15 (d, *J* = 5.5 Hz, 1 H, H⁶), 8.19 (d, *J* = 5.7 Hz, 1 H, H⁶) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 21.86, 21.99 [NCH₂CH₂CH(CH₃)₂], 26.42 [NCH₂CH₂CH(CH₃)₂], 34.60 [NCH₂CH₂CH(CH₃)₂], 54.11 [NCH₂CH₂CH(CH₃)₂], 60.28 (CH₂-allyl), 112.75 (CH-allyl), 118.58 (C³), 122.12 (C^{4'}), 122.30 (C⁵), 123.37 (C^{3'}), 129.42 (C^{5'}), 132.19 (C^{6'}), 136.82 (C⁴), 143.24 (C^{2'}), 150.15 (C⁶), 165.63 (C²), 170.98 (2d, $J_{\text{Rh-C}}$ = 31.64 Hz, C^{1'}) ppm.

[Rh(phpy)₂{μ-(isoamyl)₂C₂N₂S₂}PdCl(tri-*n*-propylphosphane) κ-N,N'-Rh κ-S,S-Pd] (15): This compound was prepared by procedures (a) and (b). (a) **5** (0.2 mmol, 134.2 mg) was dissolved in chloroform (50 mL). To the solution were added [PdClIP(*n*-propyl)₃]₂ (60.4 mg, 0.1 mmol) and methanol (10 mL). The reaction mixture was heated at reflux for 6 h, concentrated to 10 mL and purified by chromatography [alumina column, chloroform/petroleum ether (4:1, v/v) as eluent]. The orange solid was obtained by addition of petroleum ether (40/60) to a concentrated portion (about 10 mL) of the eluate. Yield: 97.2 mg (50%). C₄₃H₅₉ClN₄PPdRhS₂ (971.82): calcd. (971.84): H 6.12, C 53.14, N 5.77, S 6.60; found H 6.20, C 53.50, N 5.55, S 6.50. (b) This product was obtained from **11** (112.3 mg, 0.2 mmol) and [Rh(phpy)Cl]₂ (89.3 mg, 0.1 mmol) according to procedure (b) described for **13**. Yield: 118.0 mg (61%). Found H 6.15, C 53.60, N 5.60, S 6.45. ^1H NMR (CDCl_3 , 27 °C): δ = 0.37 0.40 0.43, 0.45 [4d, *J* = 6.6 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 0.88 [m, 9 H, P(CH₂CH₂CH₃)₃], 1.01 [m, 6 H, P(CH₂CH₂CH₃)₃], 1.19 [m, 2 H, NCH₂CH₂CH(CH₃)₂], 1.19 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 1.58 [m, 6 H, P(CH₂CH₂CH₃)₃], 3.43 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 6.10, 6.12 (d, *J* = 6.1 Hz, 2 H, H^{6'}), 6.76 (t, *J* = 6.1 Hz, 2 H, H^{5'}), 6.87 (t, *J* = 6.1 Hz, 2 H, H^{4'}), 7.20 (m, 2 H, H⁵), 7.54 (d, *J* = 8.0 Hz, 2 H, H^{3'}), 7.83 (m, 2 H, H⁴), 7.83 (m, 2 H, H³), 8.12 (m, 2 H, H⁶) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 27 °C): δ = 21.95, 22.65 [NCH₂CH₂CH(CH₃)₂], 26.38, 26.49 [NCH₂CH₂CH(CH₃)₂], 26.76, 26.87 [P(CH₂CH₂CH₃)₃], 34.71, 34.89 [NCH₂CH₂CH(CH₃)₂], 35.90 [P(CH₂CH₂CH₃)₃], 51.90 [P(CH₂CH₂CH₃)₃], 52.28, 52.78 [NCH₂CH₂CH(CH₃)₂], 118.73 (C³), 122.37 (C^{4'}), 122.60 (C⁵), 123.52 (C^{3'}), 129.56 (C^{5'}), 132.21 (C^{6'}), 137.11 (C⁴), 143.29 (C^{2'}), 150.14 (C⁶), 165.57 (C²), 170.20, 170.45 (2d, $J_{\text{Rh-C}}$ = 31.6 Hz, C^{1'}) ppm.

(Rh(phpy)₂{μ-(isoamyl)₂C₂N₂S₂}PtCl(diphenyl-2-pyridylphosphane) κ-N,N'-Rh κ-S,S-Pt] (16): This compound was obtained as an orange solid according to procedure (b) described for **13** starting from **12** (150.6 mg, 0.2 mmol) and [Rh(phpy)Cl]₂ (89.3 mg, 0.1 mmol). Yield: 116.5 mg (50%). C₅₁H₅₂ClN₅PPtRhS₂ (1163.54): H 4.50, C 52.65, N 6.02, S 5.51; found H 4.55, C 52.70, N 6.10, S 5.60. ^1H NMR (CDCl_3 , 27 °C): δ = 0.29 0.30 0.38, 0.42 [4d, *J* = 6.60 Hz, 12 H, NCH₂CH₂CH(CH₃)₂], 0.66–1.32 [m, 6 H, NCH₂CH₂CH(CH₃)₂], 3.06, 3.50 [m, 4 H, NCH₂CH₂CH(CH₃)₂], 6.06 (d, *J* = 7.70 Hz, 2 H, H^{6'}), 6.73, 6.75 (2t, *J* = 7.7 Hz, 2 H,

H^{5'}), 6.84, 6.87 (2t, $J = 7.7$ Hz, 2 H, H^{4'}), 7.0–7.86 (m), 8.04 (d, $J = 5.5$ Hz, 2 H, H⁴), 8.13 (d, $J = 5.50$ Hz, 2 H, H⁶), 8.54 (t, $J = 7.2$ Hz, 2 H, H⁶), 8.70 (d, $J = 6.6$ Hz, 2 H, H⁶) ppm. ¹³C{¹H} NMR (CDCl₃, 27 °C): $\delta = 21.87, 22.00, 22.10$ [NCH₂CH₂CH(CH₃)₂], 26.40 [NCH₂CH₂CH(CH₃)₂], 34.57, 34.67 [NCH₂CH₂CH(CH₃)₂], 52.51, 53.12 [NCH₂CH₂CH(CH₃)₂], 122.5–136.0, 118.70 (C³), 122.36 (C⁴), 122.45 (C⁵), 123.43, 123.52 (C^{3'}), 129.51, 129.60 (C^{5'}), 132.16 (C^{6'}), 137.08 (C⁴), 143.22 (C^{2'}), 149.75, 149.93 (C⁶-PyP) 150.20, 150.34 (C⁶), 165.46, 165.54 (C²), 170.17, 170.41 (2d, $J_{\text{Rh-C}} = 30.5$ Hz, C^{1'}) ppm.

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