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Chemical evidence of polynuclear intermediates in a ligand redistribution equilibrium between dinuclear rhodium complexes. X-ray structure of $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$ (bzta = benzothiazole-2-thiolate)

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Abstract

The monosubstituted dinuclear complex $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$ (**3**) has been isolated from the reaction of the tetracarbonyl complex $[\{Rh(\mu\text{-bzta})(CO)_2\}_2]$ (**1**) with triphenylphosphine. The crystal structural analysis of **3** has confirmed this complex to be dinuclear. The two metal centres exhibit distorted square-planar coordination and are bridged by two bzta ligands in a *cis,cis* and head-to-tail arrangement. The added PPh_3 group has been located *trans* to a S atom of the bridging ligand. In solution, complex **3** is in dynamic equilibrium with **1** and the disubstituted complex $[\{Rh(\mu\text{-bzta})(CO)(PPh_3)\}_2]$ (**2**) as a result of a reorganization process. Scrambling experiments carried out with related 6-methylbenzothiazole-2-thiolate complexes suggest that polynuclear intermediates are responsible for the ligand-redistribution equilibrium. Addition of further triphenylphosphine to the equilibrium mixture gives **2** quantitatively. Complex **2** reacts with triphenylphosphine to give the mononuclear complex *trans*-$[Rh(bzta)(CO)(PPh_3)_2]$ (**8**) in high yield, as a result of a bridge-splitting reaction.

1. Introduction

Substitution reactions in metal carbonyl complexes are a convenient approach to the synthesis of many organometallic derivatives [1]. Some of these carbonyl derivatives have played an important role as homogeneous catalysts, especially those containing phosphine ligands [2]. Kinetic, stereochemical and theoretical studies [3] have been carried out on the mechanistic pathways for ligand-substitution processes in metal complexes. These studies for mononuclear d^8 square-planar complexes have established that the substitution reactions proceed *via* an associative (S_N2) mechanism, through a pentacoordinate trigonal-pyramidal intermediate [4]. Substitution reactions in dinuclear doubly bridged d^8 complexes have been less studied but Kalck and co-workers [5] have pointed out that they follow a similar path. Nevertheless, the substitution cannot be a simple process in these systems since unexpected compounds, some of higher nuclearity, are isolated occasionally, suggesting new reaction pathways [6].

Although a large number of rhodium and iridium dinuclear disubstituted carbonyl complexes $[\{M(\mu\text{-}X)(CO)(PR_3)\}_2]$ have been prepared [7], the monosubstituted carbonyls $[M_2(\mu\text{-}X)_2(CO)_3(PR_3)]$ have received less attention. These complexes undergo disproportionation and are in equilibrium with the non- and di-substituted complexes, as Poilblanc and co-workers observed in thiolate-iridium chemistry [8]. In fact, we have reported that the tetracarbonyl complex $[\{Rh(\mu\text{-pyS})(CO)_2\}_2]$ crystallizes from solutions of $[Rh_2(\mu\text{-pyS})_2(CO)_3(PPh_3)]$ (pyS = pyridine-2-thiolate) at low temperature [9].

We report here the preparation and full structural characterization of a monosubstituted complex isolated from the equilibrium of replacement of carbonyl groups by triphenylphosphine in the complex $[\{Rh(\mu\text{-bzta})(CO)_2\}_2]$ (bzta = benzothiazole-2-thiolate). Several scrambling experiments with related 6-methylbenzothiazole-2-thiolate (Me-bzta) rhodium complexes have been studied in order to gain chemical information on the phenomenon of reorganization of ligands observed in solution.

2. Results and discussion

2.1. Synthesis and characterization of $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$ (3)

In a previous paper [9], we described the synthesis of the tetracarbonyl complex $[\{Rh(\mu\text{-bzta})(CO)_2\}_2]$ (**1**),

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which is formed by carbonylation of the dinuclear diolefin complex [{Rh(μ-bzta)(cod)}$_2$] (cod = 1,5-cyclooctadiene). Complex **1** undergoes a carbonyl-substitution reaction with two equivalents of triphenylphosphine to give quantitatively the disubstituted dinuclear complex [{Rh(μ-bzta)(CO)(PPh$_3$)}$_2$] (**2**), which exists in solution as the single head-to-tail isomer with the phosphine ligands *trans*. We have found now that the replacement of carbonyl groups can be carried out stepwise. In this way, addition of only one equivalent of triphenylphosphine to a dichloromethane solution of complex **1** leads to the isolation of dark-red crystals of the monosubstituted dinuclear complex [Rh$_2$(μ-bzta)$_2$(CO)$_3$(PPh$_3$)] (**3**) in low yield. Nevertheless, when monitoring the reaction by ^{31}P{^{1}H} NMR spectroscopy, a mixture of the disubstituted complex **2** [δ = 42.2, d, ^1J(Rh–P) = 162 Hz] and the monosubstituted **3** [δ = 40.6, d, ^1J(Rh–P) = 160] is observed. Complex **3** is isolated from this mixture due to its reduced solubility at low temperature.

The dinuclear formulation of **3** is in accordance with microanalytical data and IR spectroscopy, which shows three strong ν(CO) absorptions at 2065, 1997 and 1995 cm^{-1} in the solid state. There are several possible structures for **3**. Carbonyl substitution could take place *trans* either to the sulphur atom or to the nitrogen. In addition, two different relative dispositions of the bridging ligands are possible since the tetracarbonyl precursor of **3** exists in solution as the head-to-tail and the head-to-head isomers [9]. In order to confirm the monosubstitution process and to elucidate the structural features, a determination of the crystal and molecular structure of **3** was undertaken.

Figure 1 shows a perspective view of [Rh$_2$(μ-bzta)$_2$(CO)$_3$(PPh$_3$)] molecule (**3**). Significant bond distances and angles are collected in Table 1. The complex is formed by two different square-planar metallic centres bridged by two benzothiazole-2-thiolates which are coordinated through the nitrogen and the exocyclic S atoms. These two bridging ligands have a relative *cis,cis* disposition in the metal coordination spheres and are symmetrically bonded in a head-to-tail arrangement. The metals complete their coordination spheres with a triphenylphosphine and a carbonyl [Rh(1)] or two carbonyl groups [Rh(2)].

Both metal coordination spheres are slightly distorted from the idealized square-planar disposition, as shown by the *cis* or *trans* bond angles around the metals and by deviations from the calculated least-squares planes (max. values 0.278(1) Å for Rh(1) and 0.158(3) Å for Rh(2)); the bulky PPh$_3$ ligand provokes the larger distortion observed around the Rh(1) atom. These distorted coordination planes are staggered by an average of 38.5(1)° in order probably to minimize

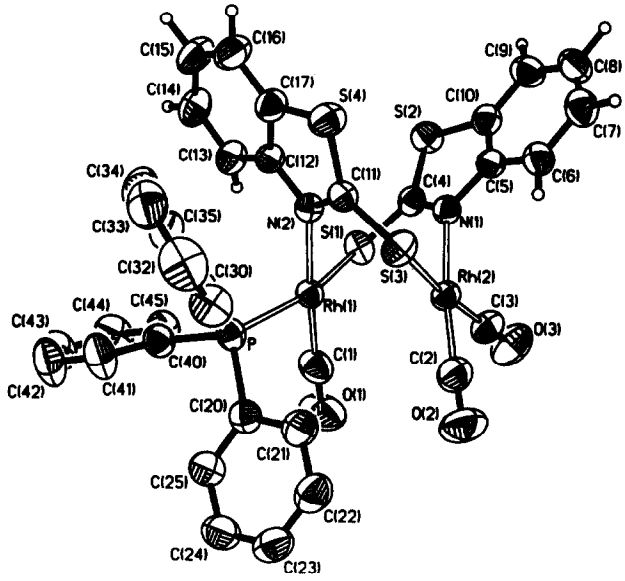


Fig. 1. Molecular representation of [Rh$_2$(μ-bzta)$_2$(CO)$_3$(PPh$_3$)] (**3**) showing the atom numbering scheme.

contacts between ligands on adjacent metal atoms. The metal coordination planes are not parallel, being tilted to each other by 30.3(1)°. This tilt is essentially the same as that observed in the related complexes [{Rh

TABLE 1. Selected bond distances (Å) and angles (°) for the complex [Rh$_2$(μ-bzta)$_2$(CO)$_3$(PPh$_3$)], **3**

Rh(1)···Rh(2)	3.0351(5)		
Rh(1)–S(1)	2.370(1)	Rh(2)–S(3)	2.376(1)
Rh(1)–N(2)	2.100(3)	Rh(2)–N(1)	2.107(2)
Rh(1)–C(1)	1.806(4)	Rh(2)–C(2)	1.843(3)
Rh(1)–P	2.287(1)	Rh(2)–C(3)	1.866(3)
C(4)–S(1)	1.706(3)	C(11)–S(3)	1.720(3)
C(4)–S(2)	1.740(3)	C(11)–S(4)	1.735(3)
C(10)–S(2)	1.737(3)	C(17)–S(4)	1.741(3)
C(4)–N(1)	1.318(4)	C(11)–N(2)	1.319(4)
C(5)–N(1)	1.400(4)	C(12)–N(2)	1.401(4)
C(1)–O(1)	1.155(6)	P–C(20)	1.823(4)
C(2)–O(2)	1.133(4)	P–C(30)	1.837(4)
C(3)–O(3)	1.139(5)	P–C(40)	1.838(3)
S(1)–Rh(1)–N(2)	89.4(1)	S(3)–Rh(2)–N(1)	90.7(1)
S(1)–Rh(1)–C(1)	91.0(1)	S(3)–Rh(2)–C(2)	90.9(1)
S(1)–Rh(1)–P	162.02(5)	S(3)–Rh(2)–C(3)	173.9(1)
N(2)–Rh(1)–C(1)	175.4(2)	N(1)–Rh(2)–C(2)	173.7(1)
N(2)–Rh(1)–P	91.8(1)	N(1)–Rh(2)–C(3)	88.3(1)
C(1)–Rh(1)–P	89.3(1)	C(2)–Rh(2)–C(3)	89.4(2)
Rh(1)–S(1)–C(4)	106.2(1)	Rh(2)–S(3)–C(11)	104.1(1)
S(1)–C(4)–S(2)	120.4(2)	S(3)–C(11)–S(4)	120.0(2)
S(1)–C(4)–N(1)	125.6(2)	S(3)–C(11)–N(2)	126.0(2)
S(2)–C(4)–N(1)	114.0(2)	S(4)–C(11)–N(2)	114.0(2)
Rh(2)–N(1)–C(4)	120.9(2)	Rh(1)–N(2)–C(11)	121.8(2)
Rh(2)–N(1)–C(5)	126.1(2)	Rh(1)–N(2)–C(12)	125.7(2)
C(4)–N(2)–C(5)	112.0(2)	C(11)–N(2)–C(12)	112.0(3)
Rh(1)–C(1)–O(1)	176.6(4)	Rh(2)–C(2)–O(2)	176.0(3)
		Rh(2)–C(3)–O(3)	179.5(3)

$(\mu\text{-}S_2NC_3H_4)(CO)(PR_3)\}_2]$ (R = Ph, 38.5° and R = Me, 30.0°) [10].

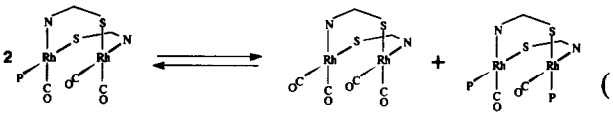
The intermetal distance (3.0351(5) Å) is clearly longer than those described for complexes with metal–metal bonds [7f]. However, the deviations of both metals from the mean plane passing through the coordinated atoms toward the other rhodium centre (0.311(1) and 0.108(1) Å) denote the existence of an attractive electronic intermetal interaction, as proposed in related complexes with similar intermetal separations [11].

Both bridging ligands exhibit a tough planarity, with atom deviations from the least-squares plane through the benzothiazole moieties less than 0.185(1) Å (S(1) atom). The dihedral angle between each ideal ligand plane is 56.30(5)°. If compared with the free base [12], the benzothiazole-2-thione undergoes a simultaneous elongation of the exocyclic C–S bond (from 1.662(4) to 1.706 or 1.720(3) Å) and a shortening of the C–N length (from 1.353(6) to 1.318(4) Å) upon coordination. These changes clearly indicate a partial reduction of the thione character compared with the free base probably associated with the electronic delocalization these bridging ligands usually cause [13]. Similar bond length changes have been observed in the heteronuclear $[(PPh_3)Pt(\mu\text{-bzta})_2RhCl(CO)]$ [C–S: 1.714(5) Å; N–C 1.306(6) Å] [14] and in the related 2-mercaptothiazolinate complexes $[Rh(\mu\text{-}S_2NC_3H_4)(CO)(PR_3)]_2$ (R = Ph or Me) [10] where the PR_3 groups are also *trans* to the bridging S atoms. Nevertheless, the exocyclic C–S bond distances observed in **3**, mean 1.711(3) Å, are at the lower end of the range found in related complexes [15] with the analogous pyridine-2-thiolate ligand, 1.72–1.86 Å, and indicate that the bzta ligand maintains a significant thione character after coordination. However, all the endocyclic C–S lengths (mean 1.738(2) Å) are significantly shorter than typical C–S single bonds, for instance 1.829(26) Å in alkanethiolates [16], showing the aromaticity of the bridging ligands, and suggesting somewhat less multiple-bond character for these endocyclic C–S bonds compared with the exocyclic ones.

Interestingly, no significant differences are detected in the molecular dimensions of the benzothiazole-2-thiolate group, as a consequence of the presence of different *trans* ligands (PPh_3 *vs.* CO), either in the Rh–S or Rh–N bonds, or in the internal C–S or C–N bond lengths. However, the different electronic densities on the two metal centres is indicated by the carbonyl ligands which are all linearly coordinated but showing shorter Rh–CO distances (and consequent longer C–O lengths) for the carbonyl group coordinated to Rh(1) (see Table 1), the metal atom with the greater electronic density.

Monosubstituted dinuclear carbonyl complexes in rhodium and iridium chemistry are scarce, in contrast to the disubstituted ones, and most of them have been spectroscopically characterized only in solution. For instance, the complexes $[Rh_2(\mu\text{-Cl})_2(CO)_3(PR_3)]$ [R = Me, NMe_2, Ph, or OMe] were detected in $[\{Rh(\mu\text{-Cl})(CO)_2\}_2]/PR_3$ systems, especially when a low PR_3/Rh ratio was used [17]. Likewise, spectroscopic evidence of $[Ir_2(\mu\text{-SBu}^t)_2(CO)_3(PMe_3)]$ was obtained in the reaction of PMe_3 with $[\{Ir(\mu\text{-SBu}^t)(CO)_2\}_2]$ [8]. There are very few examples of monosubstituted complexes isolated in the solid state and all of them have bidentate ligands as bridging ligands: the pyridine-2-thiolate (pyS) complex $[Rh_2(\mu\text{-pyS})_2(CO)_3(PPh_3)]$ [9] and the 2-pyridonate (Opy) complex $[Rh_2(\mu\text{-Opy})_2(CO)_3(PPh_3)]$ [18], intermediates in the synthesis of the corresponding disubstituted complexes; the carboxylate complex $[Rh_2(\mu\text{-OOCR})_2(CO)_3(PPh_3)]$ [R = Me or Et] [19] and the phenyl(1-phenyliminoethyl)amido-complex $[Rh_2\{\mu\text{-PhNC(Me)NPh}\}_2(CO)_3(PPh_3)]$ which interestingly does not undergo further carbonyl-substitution with extra phosphine [20]. Moreover, complex **3** is the only example characterized by an X-ray diffraction study.

Complex **3** displays a quite amazing behaviour in solution. When red crystals of **3** are dissolved in dichloromethane, a mixture of the substituted complexes **2** and **3** is formed immediately, as shown by $^{31}P\{^1H\}$ NMR spectroscopy. The IR spectrum in the carbonyl region indicates that the tetracarbonyl complex **1** is also present [ν(CO): 2085, 2065, 2023 and 1990 cm^{-1}]. Consequently, complex **3** rearranges in solution following the disproportionation process given in eqn. (1).



3 1 2 (1)

The temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum clearly indicates that complexes **1**, **2** and **3** are in dynamic equilibrium (the equilibrium is shifted to the formation of **3** as the temperature decreases). Equilibrium is also reached when equimolar amounts of complexes **1** and **2** are mixed together.

Several possible intermolecular paths can be outlined to explain this equilibrium. In particular the following processes are proposed:

(i) triphenylphosphine dissociation followed by intermolecular carbonyl interchange between dinuclear units and re-entry of the free triphenylphosphine;

(ii) dissociation of fragments $[RhL_2]^+[L_2 = (CO)_2$ or $(CO)(PPh_3)]$ and further recombination;

(iii) splitting of the bridges to give the mononuclear

fragments [Rh(bzta)L_2] [$L_2 = (CO)_2$ or $(CO)(PPh_3)$] followed by recombination;

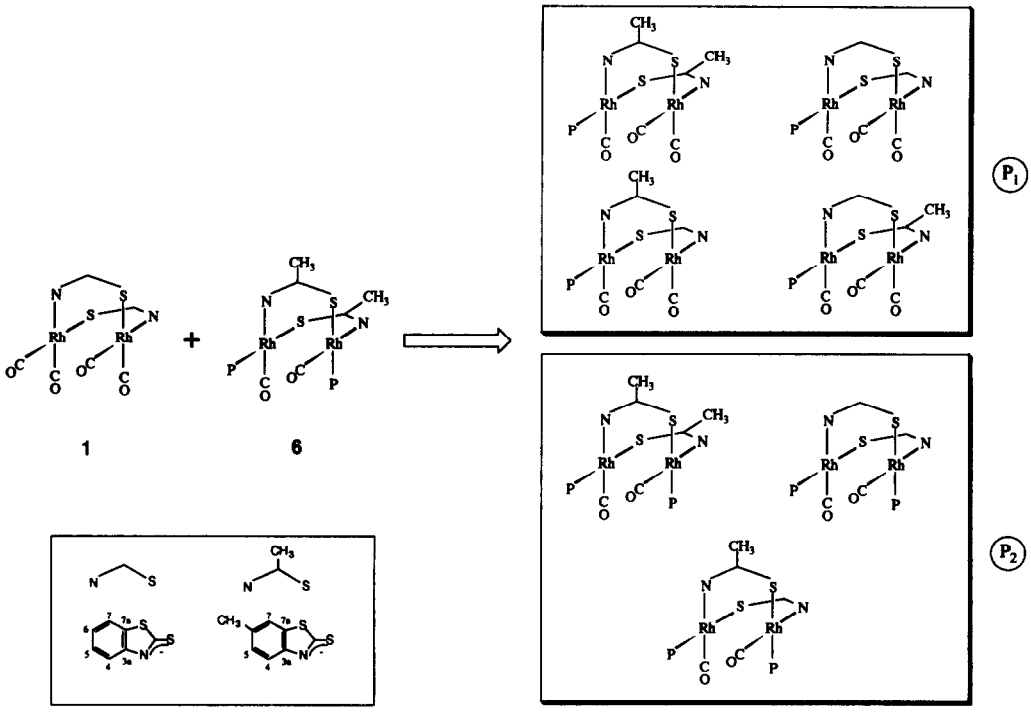
(iv) interaction between two dinuclear units through a polynuclear intermediate where interchange of bridging ligands takes place.

In order to gain some information on the redistribution process, scrambling experiments were undertaken. Dinuclear complexes with the related ligand 6-methylbenzothiazole-2-thiolate (Me-bzta) were prepared for this purpose.

2.2. *Synthesis and characterization of 6-methylbenzothiazole-2-thiolate dinuclear complexes*

The complex [{Rh(μ-Me-bzta)(cod)}$_2$] (**4**) can be prepared as described for the related complex with unsubstituted bzta [9]. Alternatively, the protonation of the methoxy bridging ligands in the complex [{Rh(μ-OMe)(cod)}$_2$] by 6-methylbenzothiazole-2-thiol gives **4** in high yield. A single isomer is formed, as shown by the aromatic region of its ^{1}H NMR spectrum. However, time-averaged signals are observed at room temperature for the olefinic protons. 1,5-Cyclooctadiene in complex **4** is easily displaced in solution by carbon monoxide at atmospheric pressure to give a deep purple solution of the tetracarbonyl complex [{Rh(μ-Me-bzta)(CO)$_2$}$_2$] (**5**) [ν(CO): 2088, 2065 and 2021 cm^{-1}]. Alternatively, complex **5** can be more conveniently prepared in high yield by protonation of acetylacetonate in the compound [Rh(acac)(CO)$_2$] with 6-methylbenzothiazole-2-thiol. It is noteworthy that this complex exists in solution as a mixture of the head-to-tail and head-to-head isomers in relative proportions 7:1 (as determined by ^{1}H NMR spectroscopy).

Addition of two equivalents of triphenylphosphine to dichloromethane solutions of complex **5** immediately causes decarbonylation to give the disubstituted complex [{Rh(μ-Me-bzta)(CO)(PPh$_3$)}$_2$] (**6**). Its ^{31}P{^{1}H} NMR spectrum clearly shows the presence of a single isomer [δ = 42.1, d, ^1J(Rh–P) = 162 Hz] having equivalent phosphines. The spectroscopic data of complexes **4–6** resemble closely those of the corresponding complexes with unsubstituted bzta. For example, the shift to lowfield of the resonance due to an H^4 proton indicates a bridging co-ordination of the ligand such as we have observed in di- and tri-nuclear complexes of the related benzothiazole-2-thiolate ligand [21]. Molecular weight determinations in chloroform solutions support the dinuclear formulation for these complexes. As found for the bzta complexes, addition of one equivalent of triphenylphosphine to the tetracarbonyl complex **5** produces an equilibrium between **5**, **6** and the complex [Rh$_2$(μ-Me-bzta)$_2$(CO)$_3$(PPh$_3$)] (**7**) [δ = 40.5, d, ^1J(Rh–P) = 160 Hz] as detected by IR and ^{31}P{^{1}H} NMR spectroscopy. The equilibrium constant



Scheme 1. Distribution of triphenylphosphine containing products found in the reaction between complexes **1** and **6**. (P_1 denotes monosubstituted complexes and P_2 disubstituted complexes.)

(defined as $K = [7]^2/[5][6]$), determined by integration of the methyl resonances in the ^1H NMR spectrum ($\delta = 2.29$ and 2.22 for complex **7** in CD_2Cl_2), is 14.90 at 296 K. The equilibrium is reached so fast that kinetic studies are not possible. However, our attempts to isolate analytical pure samples of the monosubstituted complex **7** were unsuccessful.

2.3. Scrambling experiments

Since the Me-bzta complexes **5**–**7** have similar spectroscopic and chemical properties to their bzta counterparts, it is inferred that an equilibrium between the tetracarbonyl (unsubstituted or P_0), monosubstituted (P_1) and disubstituted (P_2) carbonyl complexes (Scheme 1) should be formed if the appropriate dinuclear units having different bridging ligands were mixed in solution, *i.e.* complexes **1** and **6** or complexes **2** and **5**. In this case, there is a possibility of formation of mixed-ligand bridged complexes and valuable information on the reorganization mechanism might be derived from this chemical test experiment.

Consequently, equimolar amounts of complexes **1** and **6** were dissolved in $CDCl_3$ in an NMR tube. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows an apparently complex mixture of species in solution which can be successfully analysed at −50°C (Fig. 2) by inspection of the chemical shifts of the resonances observed as doublets. Four well-spaced resonances centred at approximately δ 41 ppm were assigned to P_1-type complexes and the three close ones around δ 42 ppm to P_2-type complexes. These results are interpreted in terms of a scrambling process of bridging ligands between dinuclear complexes to give mixed-ligand bridged complexes as shown in Scheme 1. This reorganization is statistical since the relative intensities of the signals assigned to the P_1 complexes are equal and those for the P_2 complexes are in a ratio 1:2:1, the complex with mixed-bridging ligands having double the probability of the other two. In this reorganization the tetracarbonyl complexes (P_0) are also involved as deduced from the large number of methyl resonances in the ^1H NMR spectrum of the mixture.

The lack of retention of the bridges in the dinuclear frameworks allow us to exclude (i) and (ii) as possible pathways for the reorganization process which complexes **3** and **7** undergo since for them the bridging-ligands system should be retained. However, paths (iii) and (iv) cannot be ruled out because of the bridging ligand scrambling process. In any case, pathway (iii) involves dissociation of the dinuclear units into mononuclear fragments, which is not consistent with the high thermal stability towards fragmentation observed for the related Rh-bzta dinuclear complexes. This behaviour contrasts with the results recently reported by Jensen *et al.* on the reversible fragmentation of the complex upon heating $[Pd_2(\mu\text{-pyS})_2Cl_2(PMe_3)_2]$ in solution [15]. In contrast, no scrambling of bridging ligands is observed in equimolar mixtures of the tetracarbonyl complexes **1** and **5** and of the disubstituted **2** and **6**, which remain unchanged for long periods. The lack of reaction between these complexes excludes a fast equilibrium between di- and mono-nuclear complexes since recombination of the latter would give a mixture containing the corresponding mixed-bridged complex.

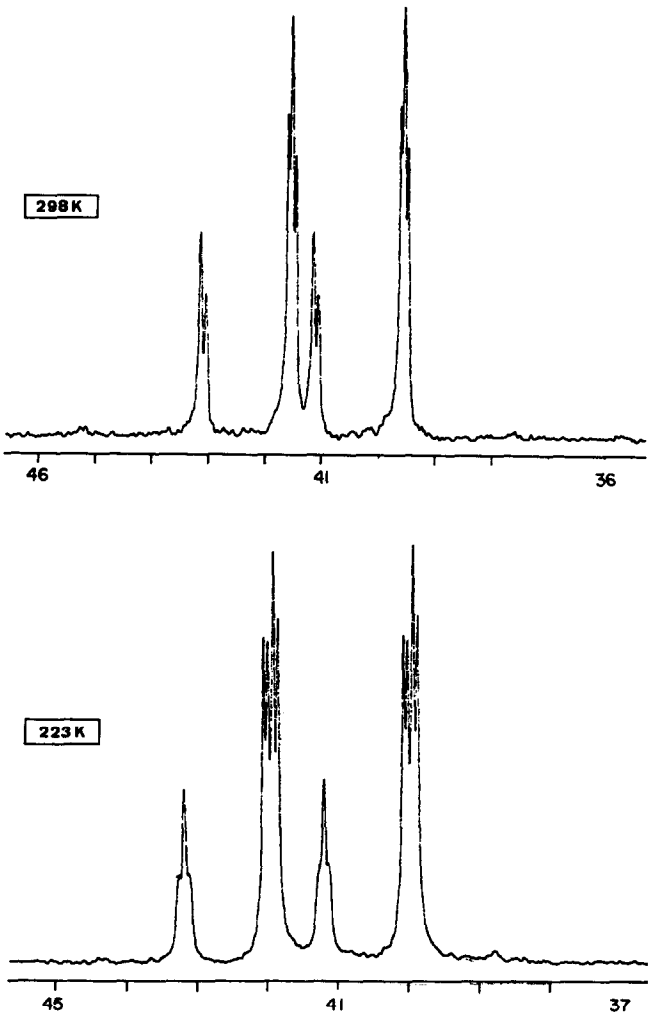


Fig. 2. $^{31}P\{^1H\}$ NMR spectra of an equimolar mixture of complexes **1** and **6** in $CDCl_3$ at different temperatures.

Furthermore, addition of Me-bztaH to complex **2** in molar ratio 1:1 gives a mixture of the three complexes of type P_2 (Scheme 1) in the same proportions as in the reaction between complexes **1** and **6**. This suggests that the redistribution reactions should start via attack of a bridging ligand on another dinuclear complex through one of its donor atoms. This can be either the nitrogen

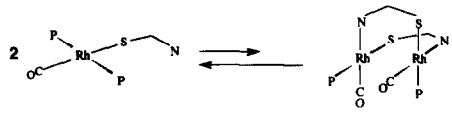
atom, arising from a rupture of the Rh–N bond due to a change of the coordination μ-N,S to μ-S of the bridging ligand, or the coordinated sulfur atom, which still has a lone pair of electrons. Both may occur together. In fact, changes in coordination μ-N,S to μ-S have been observed in dinuclear pyridine-2-thiolate complexes of rhodium. In addition, this ligand, as well as the related benzothiazole-2-thiolate, have the ability to bridge up to three metal atoms through the N and S donor atoms [21].

Thus an associative mechanism through polynuclear intermediates probably involving four metal centres should be operative (pathway (iv)). Tetranuclear intermediates have been proposed for the exchange of allyl-palladium groups in thiocyano- and halogen-bridged dimers [22], in the disproportionation of a halogen-bridged palladium–platinum heterobimetallic complex [23] and in the isomerization of Schiff-base nickel(II) complexes [24].

2.4. Bridge-splitting reactions

The complexes $[\{Rh(\mu\text{-bzta})(CO)(PPh_3)\}_2]$ (**2**) and $[\{Rh(\mu\text{-Me-bzta})(CO)(PPh_3)\}_2]$ (**6**) undergo a bridge-splitting reaction with triphenylphosphine to give the mononuclear rhodium complexes $[Rh(bzta)(CO)(PPh_3)_2]$ (**8**) and $[Rh(Me\text{-bzta})(CO)(PPh_3)_2]$ (**9**). *trans* Geometry is assigned on the basis of the equivalence of the phosphines in the $^{31}P\{^1H\}$ NMR spectra ($\delta = 34.3$, d, $^1J(Rh\text{–}P) = 134$ Hz, **8**; $\delta = 34.4$, d, $^1J(Rh\text{–}P) = 134$ Hz, **9**) but coordination of bzta through either N or S is unclear since both coordination modes are known [25]. However, reaction with strong acids provides a chemical proof of the thiolate coordination mode rather than through the nitrogen atom. Thus, protonation of **8** with $HBF_4 \cdot OEt_2$ in dichloromethane at room temperature occurs rapidly and yields the cationic complex $[Rh(bzta\text{-}H)(CO)(PPh_3)_2][BF_4]$ (**10**) as a single isomer. The ν(NH) band at 3190 cm^{-1} and the broad resonance at 12.84 ppm for the NH proton in the IR and ^1H NMR spectra of **10** are indicative of the protonation of the nitrogen atom on the coordinated bzta. In the same way, the ν(CO) stretching frequency of **10** (1995 cm^{-1}), slightly higher than that of **8** (1982 cm^{-1}), indicates a small reduction in the electronic density on the rhodium atom upon protonation of the bzta. Splitting of the ν(BF) band for the tetrafluoroborate anion is observed as a consequence of the reduction of its symmetry, probably due to F···H interactions with the NH subunit.

The $^{31}P\{^1H\}$ NMR spectrum of analytically pure samples of the mononuclear complex **8** shows an equilibrium with the corresponding dinuclear complex **2** (eqn. (2)) which is largely shifted in favour of the mononuclear complex. A similar equilibrium is also found between complexes **9** and **6**. Interestingly neither free triphenylphosphine nor triphenylphosphine oxide is detected by NMR spectroscopy.



(2)

8 **2**

Similar equilibria are involved in the synthesis of carbonyl–phosphine dinuclear complexes $[\{M(\mu\text{-}X)(CO)(PPh_3)\}_2]$ by substitution of chloride of the mononuclear complexes $[MCl(CO)(PPh_3)_2]$ by bi(monodentate) anionic ligands (X^-) [M = Rh, $X^- = S_2NC_3H_4$ [10]; M = Ir, $X^- = PPh_2$ [26]; M = Ir, X^- = pyrazolate (pz) [27]]. When the substitution of the chloride is not followed by triphenylphosphine dissociation, the corresponding mononuclear complexes $[MX(CO)(PPh_3)_2]$ are obtained [M = Ir, $X^- = 3,5\text{-}Me_2pz$; $3,5\text{-}Me_2\text{-}4\text{-}NO_2\text{-}pz$ [28]]. The reaction of $[RhCl(CO)(PPh_3)_2]$ with Libzta gave the mononuclear complex **8** in high yield according to (eqn. (2)).

3. Experimental details

3.1. General

All the reactions were carried out by Schlenk techniques under dinitrogen. Solvents were dried by standard methods and distilled under dinitrogen immediately prior to use.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 and 80.984 MHz respectively. Chemical shifts are reported relative to tetramethylsilane and phosphoric acid as external references. The proton numbering is shown in Scheme 1. IR spectra were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl windows. Elemental analyses were performed with a Perkin-Elmer 240-B microanalyser. Molecular weights were determined with a Knauer osmometer using chloroform solutions.

The starting materials $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ [29] and $[Rh(acac)(CO)_2]$ [30] were prepared according to reported methods. $[\{Rh(\mu\text{-bzta})(CO)_2\}_2]$ (**1**) and $[\{Rh(\mu\text{-bzta})(CO)(PPh_3)\}_2]$ (**2**) were prepared from $[\{Rh(\mu\text{-bzta})(cod)\}_2]$ according to the published procedure [9]. $HBF_4 \cdot OEt_2$ (54% solution in diethyl ether) was purchased from Merck.

3.2. Synthesis of $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$ (3)

A solution of triphenylphosphine (26.2 mg, 0.1 mmol) in dichloromethane (3 ml) was slowly added to a stirred dichloromethane solution (10 ml) of $[\{Rh(\mu\text{-bzta})(CO)_2\}_2]$ (65 mg, 0.1 mmol). After 20 min, the mixture

was dark-red and was concentrated under vacuum to *ca.* 2 ml. Red crystals of the complex were grown by slow diffusion of 1:1 mixture of diethyl ether–hexane (15 ml) into the solution and cooling at −15°C for 15 d. The crystals were isolated by filtration, washed with cold hexane and dried under vacuum (18 mg, 20%). IR (cm^{-1}, Nujol) 2065, 1997, 1995 [ν(CO)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): 40.6 (d, $^1J(Rh-P) = 160$ Hz, PPh_3). Anal. Found: C, 47.92; H, 3.02; N, 3.22. $C_{35}H_{23}N_2O_3PRh_2S_4$ Calcd.: C, 47.52; H, 2.62; N, 3.16.

3.3. Synthesis of [{Rh(μ-Me-bzta)(cod)}$_2$] (4)

Solid 6-methylbenzothiazole-2-thiol (112 mg, 0.62 mmol) was added to a solution of [{Rh(μ-OMe)(cod)}$_2$] (150 mg, 0.31 mmol) in dichloromethane (15 ml) to give an orange-red solution after 15 min. Evaporation of the solution to 2 ml and slow addition of methanol gave the complex as an orange-yellow microcrystalline solid, which was filtered, washed with methanol and vacuum dried (225 mg, 92%). ^1H NMR ($CDCl_3$, 20°C): 8.60 (d, 2H, H^4), 7.19 (dd, 2H, H^5), 6.95 (d, 2H, H^7), 4.36 (m, 8H, =CH, cod), 2.60 (m, 8H, $>CH_2$, cod), 2.35 (s, 6H, CH_3), 1.94 (m, 8H, $>CH_2$, cod). Anal. Found: C, 49.10; H, 5.02; N, 3.27. $C_{32}H_{36}N_2Rh_2S_4$ Calcd.: C, 49.10; H, 4.63; N, 3.27. Mol. Weight. Found: 770, calcd.: 782.

3.4. Synthesis of [{Rh(μ-Me-bzta)(CO)$_2$}$_2$] (5)

Solid 6-methylbenzothiazole-2-thiol (140 mg, 0.77 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (200 mg, 0.77 mmol) to a mixture (1:1) of dichloromethane-methanol (15 ml). After 5 min deep-purple crystals separated. The crystallization was completed by concentration under vacuum (*ca.* 5 ml) and further addition of methanol (10 ml). The complex was collected by filtration, washed with methanol and dried under vacuum (237 mg, 90%). IR (cm^{-1}, CH_2Cl_2) 2088, 2065, 2021 [ν(CO)]. ^1H NMR ($CDCl_3$, 20°C): 8.20 (d, 2H, H^4), 7.19 (dd, 2H, H^5), 7.14 (d, 2H, H^7), 2.39 (s, 6H, CH_3) [major isomer]; 7.39 (d, H^4), 7.26 (d, H^7), 7.12 (dd, H^5), 2.18 (s, CH_3) [minor isomer]. Anal. Found: C, 35.33; H, 1.83; N, 3.96. $C_{20}H_{12}N_2O_4Rh_2S_4$ Calcd.: C, 35.41; H, 1.78; N, 4.12. Mol. Weight. Found: 696, calcd.: 678.

3.5. Synthesis of [{Rh(μ-Me-bzta)(CO)(PPh$_3$)}$_2$] (6)

Carbon monoxide was bubbled through a solution of **4** (100 mg, 0.12 mmol) in dichloromethane (10 ml) for 20 min to give a dark-red solution of **5**. A solution of triphenylphosphine (67 mg, 0.24 mmol) in dichloromethane (5 ml) was then added to give an orange solution and evolution of carbon monoxide. Evaporation of this solution to 2 ml and slow addition of hexane (10 ml) gave the complex as orange microcrystals, which were separated by filtration, washed with hexane, and vacuum dried (135 mg, 92%). IR (cm^{-1}, CH_2Cl_2) 1984 [ν(CO)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): 42.1 (d, $^1J(Rh-P) = 162$ Hz, PPh_3). ^1H NMR ($CDCl_3$, 20°C): 8.09 (d, 2H, H^4), 7.74 (m, 12H, PPh_3), 7.22 (m, 18H, PPh_3), 6.89 (dd, 2H, H^5), 6.70 (d, 2H, H^7), 2.22 (s, 6H, CH_3). Anal. Found: C, 56.91; H, 3.82; N, 2.27. $C_{54}H_{42}N_2O_2P_2Rh_2S_4$ Calcd.: C, 56.54; H, 3.69; N, 2.44. Mol. Weight. Found: 1132, calcd.: 1147.

3.6. Synthesis of [Rh(bzta)(CO)(PPh$_3$)$_2$] (8)

3.6.1. Method A

To a solution of the complex **2** (100 mg, 0.09 mmol) in dichloromethane (10 ml), solid triphenylphosphine (46 mg, 0.18 mmol) was added. The solution immediately turned yellow. Concentration of the solution to 2 ml and slow addition of hexane (10 ml) gave the complex as a yellow solid which was filtered, washed with hexane and dried under vacuum (117 mg, 80%). IR (cm^{-1}, CH_2Cl_2) 1982 [ν(CO)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): 34.3 (d, $^1J(Rh-P) = 134$ Hz, PPh_3). Anal. Found: C, 64.48; H, 4.39; N, 1.74. $C_{44}H_{34}NOP_2RhS_2$ Calcd.: C, 64.31; H, 4.17; N, 1.70.

3.6.2. Method B

Solid [RhCl(CO)(PPh$_3$)$_2$] (200 mg, 0.29 mmol) was added to a solution of lithium benzothiazole-2-thiolate [prepared by reaction of *n*-butyllithium (0.18 ml, 1.64 mol l^{-1} in hexane, 0.29 mmol) with 2-mercaptobenzothiazole (48.41 mg, 0.29 mmol)] in tetrahydrofuran (10 ml). An orange solution formed immediately and it was stirred for 30 min. Evaporation under vacuum to 2 ml and slow addition of methanol gave the complex as a yellow microcrystalline solid which was filtered, washed with methanol and vacuum dried (223 mg, 94%).

3.7. Synthesis of [Rh(Me-bzta)(CO)(PPh$_3$)$_2$] (9)

Solid triphenylphosphine (60 mg, 0.22 mmol) was added to a solution of the complex **6** (80 mg, 0.069 mmol) in dichloromethane (10 ml). Work-up as above gave the complex as a yellow microcrystalline solid which was separated by filtration, washed with methanol and vacuum dried (84 mg, 72%). IR (cm^{-1}, CH_2Cl_2) 1977 [ν(CO)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): 34.4 (d, $^1J(Rh-P) = 134$ Hz, PPh_3). Anal. Found: C, 64.48; H, 4.25; N, 1.52. $C_{45}H_{36}NOP_2RhS_2$ Calcd.: C, 64.67; H, 4.34; N, 1.67.

3.8. Synthesis of [Rh(bzta-H)(CO)(PPh$_3$)$_2$][BF$_4$] (10)

$HBF_4 \cdot OEt_2$ (50 μl, 0.36 mmol) was added to a stirred solution of the complex **8** (100 mg, 0.12 mmol) in a dichloromethane-diethyl ether (1:5) mixture (10

ml). A pale-yellow solid was immediately formed. The precipitation was completed by reduction of the volume to 2 ml and addition of diethyl ether (10 ml). The complex was filtered, washed with diethyl ether and vacuum dried (100 mg, 90%). IR (cm^{-1}, CH_2Cl_2) 1955 [ν(CO)]. ^1H NMR (d^6-acetone, 20°C): 12.84 (broad, 1 H, NH, bzta), 7.75 (m, 12H, PPh_3), 7.60 (m, 1H, bzta), 7.54 (m, 18H, PPh_3), 7.36 (m, 1H, bzta), 7.11 (m, 2H, bzta). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): 30.2 (d, ^1J(Rh–P) = 122 Hz, PPh_3). Anal. Found: C, 57.99; H, 4.34; N, 1.54. $C_{44}H_{35}BF_4NOP_2RhS_2$ Calcd.: C, 58.16; H, 3.88; N, 1.54.

3.9. X-ray crystallographic study of $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$ (3)

3.9.1. Crystal data

$C_{35}H_{23}N_2O_3PRh_2S_4$, $M = 884.60$, triclinic, space group $P\bar{1}$, $a = 10.507(1)$, $b = 11.819(1)$, $c = 14.210(1)$ Å, $\alpha = 100.83(1)$, $\beta = 97.20(1)$, $\gamma = 90.70(1)°$, $V = 1718.4(3)$ Å^3, $Z = 2$, $D_c = 1.710$ Mg m^{-3}, $F(000) = 880$, λ(Mo Kα) = 0.71069 Å, $\mu = 12.62$ cm^{-1}, $T = 295$ K.

3.9.2. Data collection and processing

A Siemens AED-2 diffractometer with monochromated Mo Kα radiation was used. A dark-red prismatic block $0.266 \times 0.274 \times 0.304$ mm^3 was mounted on a glass fibre. 10303 intensities were registered to $2\theta_{max}$ 50° (ω–2θ scan technique). Averaging equivalents gave 5902 unique reflections, of which 5093 with $F \geq 6.0\ \sigma(F)$ were used for all calculations (program system SHELX76) [31]. Cell constants were refined from setting angles of 60 reflections in the range 2θ 20–34°. Three standard reflections were monitored every hour as a check on crystal and instrument stability. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied [32] (correct. fact. 0.829, 0.999).

3.9.3. Structure solution and refinement

The structure was solved by Patterson methods and extended by difference syntheses. Atoms were refined isotropically first, and in subsequent cycles with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were found in difference maps and included in the last cycles of refinement using a riding model and with a common thermal parameter. The final R value was 0.0255, with $R_w = 0.0285$. The weighting scheme was $w = k/\sigma^2(F) + gF^2$, with $k = 1.7206$ and $g = 0.000204$; 263 parameters; maximum $\Delta/\sigma < 0.030$, maximum $\Delta\rho$ 0.41 e Å^{-3}, close to the metal centre. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 33. Final atomic coordinates are given in Table 2.

TABLE 2. Atomic coordinates ($\times 10^4$; $\times 10^5$ for Rh atoms) and equivalent isotropic displacement coefficients (Å^2, $\times 10^4$) for the non-hydrogen atoms of the complex $[Rh_2(\mu\text{-bzta})_2(CO)_3(PPh_3)]$, 3

Atom	x	y	z	U_{eq} [a]
Rh(1)	71250(2)	2860(2)	32526(2)	377(1)
Rh(2)	44906(2)	32486(2)	22435(2)	415(1)
P	8398(1)	1489(1)	2535(1)	409(2)
S(1)	6386(1)	4390(1)	4359(1)	467(3)
S(2)	5741(1)	6786(1)	4123(1)	502(3)
S(3)	5793(1)	3303(1)	1000(1)	484(3)
S(4)	7910(1)	5020(1)	1001(1)	534(3)
N(1)	4959(2)	4998(2)	2832(2)	393(8)
N(2)	7707(2)	4062(2)	2460(2)	372(8)
O(1)	6051(3)	1145(3)	4239(3)	987(15)
O(2)	3487(3)	873(2)	1359(2)	866(12)
O(3)	2621(3)	3302(3)	3686(2)	796(12)
C(1)	6506(4)	1812(3)	3870(3)	596(15)
C(2)	3906(3)	1771(3)	1678(3)	571(13)
C(3)	3333(3)	3278(3)	3141(2)	526(11)
C(4)	5659(3)	5307(2)	3682(2)	408(9)
C(5)	4416(3)	5945(2)	2493(2)	412(10)
C(6)	3618(3)	5899(3)	1622(2)	486(11)
C(7)	3121(3)	6926(3)	1412(2)	574(12)
C(8)	3409(3)	7960(3)	2050(3)	602(14)
C(9)	4211(3)	8023(3)	2909(3)	570(12)
C(10)	4709(3)	6997(3)	3121(2)	461(10)
C(11)	7145(3)	4094(2)	1582(2)	398(9)
C(12)	8791(3)	4809(2)	2725(2)	394(9)
C(13)	9595(3)	4957(3)	3594(2)	493(11)
C(14)	10663(3)	5680(3)	3726(2)	589(13)
C(15)	10928(3)	6272(3)	3014(3)	670(14)
C(16)	10147(3)	6125(3)	2137(3)	621(13)
C(17)	9069(3)	5396(3)	2006(2)	474(9)
C(20)	7613(3)	72(3)	2086(2)	455(10)
C(21)	6542(3)	−20(3)	1388(2)	583(12)
C(22)	5931(4)	−1082(3)	999(3)	632(14)
C(23)	6339(4)	−2039(3)	1324(3)	629(14)
C(24)	7358(4)	−1961(3)	2058(3)	629(13)
C(25)	8012(3)	−910(3)	2428(2)	547(12)
C(30)	9199(3)	1789(3)	1526(2)	461(11)
C(31)	8865(4)	1237(3)	568(2)	617(13)
C(32)	9544(5)	1503(4)	−144(3)	783(17)
C(33)	10520(4)	2307(4)	69(3)	774(17)
C(34)	10849(4)	2867(4)	1006(3)	733(17)
C(35)	10199(3)	2607(3)	1723(3)	573(13)
C(40)	9779(3)	1238(3)	3392(2)	478(10)
C(41)	10771(4)	564(3)	3099(3)	714(15)
C(42)	11782(4)	362(4)	3763(3)	858(18)
C(43)	11828(4)	857(3)	4717(3)	755(16)
C(44)	10868(4)	1546(3)	5010(3)	721(15)
C(45)	9841(3)	1740(3)	4358(2)	563(11)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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