Thermochimica Acta, 132 (1988) 217–227
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SPECTROSCOPIC AND THERMAL STUDIES ON DIRHODIUM TETRA-ACETATE ADDUCTS WITH THIOCARBONYL DONORS

G. FARAGLIA and L. VOLPONI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Universita',
via Loredan 4, 35100-Padova (Italy)

S. SITRAN

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova (Italy)

(Received 4 January 1988)

ABSTRACT

The complexes $[Rh_2(O_2CMe)_4(L)_2]$, in which L = DETC ($EtOSCNEt_2$), ETC (EtOSCNHEt), MTC (EtOSCNHMe) and TC ($EtOSCNH_2$), have been prepared and characterized by elemental analyses and electronic, IR and NMR (^1H and ^{13}C) spectra. The thermal behaviour of these complexes and of the DMTC ($EtOSCNMe_2$), TBA ($PhSCNH_2$) and TAA (MeSCNHPh) analogues is discussed. On heating the DETC and DMTC adducts the axial molecules are released completely yielding $[Rh_2(O_2CMe)_4]$ as degradation intermediate. Conversely, partial ligand release is observed for the complexes with thiocarbonyl donors bearing NH or NH_2 groups, probably as a result of side reaction with the rhodium tetra-acetate cage.

INTRODUCTION

Dinuclear rhodium(II) tetracarboxylates form axial adducts with a wide variety of neutral ligands [1–3]. As regards sulphur donors, 1 : 2 complexes with thioethers [4–7], dialkyl sulphoxides [5–12], thioureas and thioamides [13], have been reported, in which the axial Rh–S bond is generally weak. In fact Rh–S distances in $[Rh_2(O_2CMe)_4(DMSO)_2]$ (2.451(1) Å [12]), and in the analogous complexes with C_4H_8S (2.517(1) Å [12]) and $(PhCH_2)_2S$ (2.561(5) Å [9]), are significantly longer than those observed in rhodium(III) adducts. As an example, the complex *mer*-$[Rh(EtOSCNH_2)_3Cl_3] \cdot Me_2CO$, which contains the O-ethylthiocarbamate molecules in two different environments, shows an Rh–S distance of 2.332(3) Å for the ligand molecule *trans* to chlorine and an Rh–S distance of 2.376(3) Å for the two ligand molecules *trans* to one another [14]. In a previous paper we reported the crystal structures of $[Rh_2(O_2CMe)_4(DMTF)_2]$ (DMTF = *N,N*-dimethylthioformamide) and $[Rh_2(O_2CMe)_4(DMTC)_2]$ (DMTC = *N,N*-dimethyl O-

0040-6031/88/$03.50

ethylthiocarbamate) [15]. In the two compounds the dirhodium(II) tetraacetato moieties were equivalent, whereas the Rh–S distance in the green DMTC adduct (mean 2.624 Å) was significantly longer than the corresponding distance in the violet DMTF complex (2.546(1) Å). Moreover, the colour of the rhodium(II) adducts with sulphur donors seemed to depend on the Rh–S bond strength. In fact, the low energy absorption of the electronic spectra, at 497 nm for the orange DMSO complex [10] was observed at 550 nm and 637 nm in the DMTF and DMTC complexes, respectively. The fact that DMTC is a weaker donor than thioamides towards rhodium(II) acetate could depend on the electronegative ethoxo group bound to the thiocarbonyl carbon. It was therefore worthwhile to extend the study to thiocarbamic esters bearing different substituents at the nitrogen atom.

In this paper, we report the preparation of rhodium(II) acetate complexes with the thiocarbamic esters, MTC (EtOSCNHMe), ETC (EtOSCNHEt), TC ($EtOSCNH_2$) and DETC ($EtOSCNEt_2$), and their characterization by spectroscopic (IR, ^1H and ^{13}C NMR) and thermal analysis data.

EXPERIMENTAL

The precursor complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ was prepared by mild reaction of rhodium(III) chloride trihydrate (Ventron) in an acetic acid/absolute ethanol solution containing sodium acetate. The crude product was recrystallized from boiling methanol [16–18]. Thiocarbamic esters were prepared by reaction of $C_2H_5O{-}CS{-}SCH_2{-}COONa$ with ammonia, $MeNH_2$, $EtNH_2$ and Et_2NH in H_2O [19]. The oily products were extracted with diethylether and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield oils (except for TC, white crystals, melting point 38–40 °C) which were purified by in-vacuo distillation. The complexes $[Rh_2(O_2CMe)_4(DMTC)]$ and $[Rh_2(O_2CMe)_4(L)_2]$, where L = *N,N*-dimethyl O-ethylthiocarbamate (DMTC), thiobenzamide (TBA) and thioacetanilide (TAA), were prepared as reported in ref. 15.

Preparation of the complexes

$[Rh_2(O_2CMe)_4(DETC)_2]$

A benzene solution of DETC (0.6 mmol in 3 cm^3) was added to an ethanol solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ (0.12 mmol in 3 cm^3). The dark green solution was carefully filtered from a small undissolved residue and gradually evaporated in dinitrogen flux to a final volume of 1 cm^3. The dark green crystals were decanted and washed with n-pentane. The compound can be recrystallized from dichloromethane/n-pentane or benzene/n-pentane (yield, 85%). The experimental composition was: C, 34.54; H, 5.62; N, 3.61% (calculated for $C_{22}H_{42}N_2O_{10}Rh_2S_2$: C, 34.57; H, 5.54; N, 3.66%).

$[Rh_2(O_2CMe)_4(L)_2]$, *L = MTC, ETC and TC*

The violet compounds were obtained with quantitative yields by adding an ethanolic solution of the appropriate ligand (0.7 mmol in 2 cm^3) to a solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ in the same solvent (0.15 mmol in 5 cm^3) with vigorous stirring (30 min). A violet powder formed immediately, which was filtered, washed with small fractions of ethanol and dried in vacuo. Finally, the solid was washed with n-pentane. The MTC and ETC adducts are soluble in dichloromethane and chloroform and are slightly soluble in benzene to give violet solutions. They dissolve in acetone to form blue–green solutions, in which free ligand and rhodium(II) acetate are present. The experimental composition of $[Rh_2(O_2CMe)_4(MTC)_2]$ was: C, 28.29; H, 4.60; N, 4.07% (calculated for $C_{16}H_{30}N_2O_{10}Rh_2S_2$: C, 28.25; H, 4.54; N, 4.12%); $[Rh_2(O_2CMe_4(ETC)_2]$: C, 30.67; H, 5.02; N, 4.05% (calculated for $C_{18}H_{34}N_2O_{10}Rh_2S_2$: C, 30.52; H, 4.84; N, 3.95%); $[Rh_2(O_2CMe)_4(TC)_2]$: C, 26.02; H, 4.28; N, 4.23% (calculated for $C_{14}H_{26}N_2O_{10}Rh_2S_2$: C, 25.78; H, 4.02; N, 4.29%).

The MTC and ETC adducts can be recrystallized from dichloromethane/n-pentane.

Measurements

The IR spectra were recorded by using either a Perkin–Elmer 580B spectrophotometer (4000–400 cm^{-1}) or a Bruker FT IR instrument (450–100 cm^{-1}) as Nujol mulls between KBr and polyethylene discs. The ^1H and ^{13}C NMR spectra were obtained using a Jeol FX 90 Q spectrometer. The electronic spectra (Nujol mulls on paper) were measured using a Beckman DK 2A spectrophotometer. The TG, DTG and DTA curves either in dinitrogen or in air (flux rate, 250 cm^3 min^{-1}; heating rate, 5 °C min^{-1}) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material, neutral Al_2O_3).

RESULTS AND DISCUSSION

The green compound $[Rh_2(O_2CMe)_4(DETC)_2]$ was obtained by slow evaporation of a benzene/ethanol solution containing $[Rh_2(O_2CMe)_4(MeOH)_2]$ and DETC in the molar ratio 1 : 5. Conversely, the analogous complexes with thiocarbamic esters, bearing one or two hydrogen atoms bound to nitrogen, separated as violet powders when the appropriate ligand was added to an ethanol solution of the methanol precursor (molar ratio, 4 : 1). Attempts to isolate 1 : 1 adducts by reaction of thiocarbamic esters (MTC or ETC) and $[Rh_2(O_2CMe)_4(MeOH)_2]$ (in ethanol; molar ratio, 1 : 1) failed. In both cases the 1 : 2 complexes separated immediately, the residual ethanolic solution containing the unreacted half of rhodium(II) acetate.

TABLE 1

IR (cm^{-1}) and electronic (nm) spectral data

Compound	3500–3100 cm^{-1}	1650–1500 cm^{-1} [a]	400–300 cm^{-1}	λ_{max}(nm) [b]
$[Rh_2(O_2CMe)_4(DETC)_2]$		1596s, 1523s	381ms, 330m	630, 400sh
$[Rh_2(O_2CMe)_4(MTC)_2]$	3280mbr [c], 3155w	1590s, 1572s	378ms, 333m	560, 450sh
$[Rh_2(O_2CMe)_4(ETC)_2]$	3270m	1595s, 1549s	381ms, 334m	555, 470sh
$[Rh_2(O_2CMe)_4(TC)_2]_2$	3475sbr, 3390m, 3188m	1632s, 1590s	379ms, 333w	558, 450sh

[a] Free ligand absorptions: DETC, 1505 cm^{-1}; MTC, 1535 cm^{-1}; ETC, 1524 cm^{-1}; TC, 1610 cm^{-1}. [b] Solid samples in Nujol. [c] m = Medium, w = weak, s = strong, sh = shoulder, br = broad.

The low energy absorption (Table 1) in the electronic spectrum of $[Rh_2(O_2CMe)_4(DETC)_2]$ (λ_{max}, 630 nm) is very close to that of $[Rh_2(O_2CMe)_4(DMTC)_2]$ (λ_{max}, 637 nm [15]), whereas the corresponding absorption maxima of the complexes with thiocarbamic esters containing NH and NH_2 groups are observed in the 550–560 nm range, as for the DMTF and DMTA adducts (λ_{max}, 550 nm and 565 nm, respectively [15]). If the position of the visible absorption can be correlated to the Rh–S distance, the Rh–S bond strength in the thioamide and thiocarbamic ester 1 : 2 adducts should follow the order DETC ≈ DMTC < DMTA < MTC ≈ ETC ≈ TC ≈ DMTF < TAA < TBA.

The IR spectra of the complexes (Table 1) present a strong absorption at ca. 1590 cm^{-1}, due to asymmetric stretching of the acetato CO_2 group, and two medium absorptions at ca. 380 cm^{-1} and 333 cm^{-1}, assigned to the asymmetric and symmetric Rh–O bond stretching, respectively. As regards the thiocarbamato moieties, the ν(CN) trend is in accordance with coordination through the thiocarbonyl sulphur atom. Such an absorption is observed at 1505 cm^{-1} in free DETC and shifts to higher energy in the corresponding complex (1523 cm^{-1}) owing to the enhanced C–N double bond strength. The related $\Delta\nu$ (18 cm^{-1}) is smaller than that observed for palladium(II) and platinum(II) DETC adducts (ca. 45 cm^{-1}, [20]) and suggests a weak Rh–S bond, as in the analogous DMTC complex ($\Delta\nu = 22$ cm^{-1}). The strong absorptions at 1535 cm^{-1} (free MTC) and at 1524 cm^{-1} (free ETC) are assigned as mainly ν(CN) with a small δ(NH) contribution [21], in accordance with analogous thioamides. The energy shift in $[Rh_2(O_2CMe)_4(MTC)_2]$ is larger than in the ETC complex (37 cm^{-1} and 25 cm^{-1}, respectively). The NH bond stretching frequencies are observed beyond 3000 cm^{-1}, and the TC absorption at 1632 cm^{-1} is of bending of the NH_2 group [22]. In the 300–100 cm^{-1} region the complexes show weak unassigned bands (cm^{-1}; DETC, 296vw, 158w, 141sh; ETC, 258vw, 247vvw,

TABLE 2

Thermal data of the complexes (in dinitrogen)

Compound	Decomposition interval (°C)	TG weight loss (%)		DTA peak temperature (°C) [a]
		Experimental	Calculated	
$[Rh_2(O_2CMe)_4(MeOH)_2]$	70–120	12.3	12.7 (2MeOH)	115(d)
	220–300	46.8	46.7 (4Ac)	285(d)
$[Rh_2(O_2CMe)_4(DMTC)_2]$	65–200	37.8	37.6 (2DMTC)	78(m), 150(d), 185(d)
	240–310	32.7	33.3 (4Ac)	285(d)
$[Rh_2(O_2CMe)_4(DMTC)]$	130–200	23.8	23.2 (DMTC)	195(d)
	240–300	40.9	41.1 (4Ac)	282(d)
$[Rh_2(O_2CMe)_4(DETC)_2]$	110–190	41.8	42.2 (2DETC)	160(d), 183(d)
	250–300	31.4	30.9 (4Ac)	271(d)
$[Rh_2(O_2CMe)_4(MTC)_2]$	140–170	22.0	17.5 (MTC)	170(d)
	170–500	34.6	52.5 (MTC + 4Ac)	(210,240,270)(d)
$[Rh_2(O_2CMe)_4(ETC)_2]$	140–180	22.2	18.8 (ETC)	155(d)
	180–500	39.6	52.1 (ETC + 4Ac)	220(d)
$[Rh_2(O_2CMe)_4(TC)_2]$	110–200	31.6	32.2 (TC)	180sh(d), 200(d)
	200–500	28.5	36.2 (4Ac)	280(d)
$[Rh_2(O_2CMe)_4(TBA)_2]$	135–210	39.0	38.3 (2TBA)	160sh(d), 175(d)
	210–550	28.6	33.0 (4Ac)	285(d)
$[Rh_2(O_2CMe)_4(TAA)_2]$	110–220	19.7	20.3 (TAA)	125(d), 177(d), 203(d)
	220–550	38.4	52.0 (TAA + 4Ac)	270(d)

[a] (d), Decomposition endotherm; (m), melting endotherm; sh = shoulder.

149vvw; TC, 253vw, 240sh, 150vw, 98vvw). The Rh–Rh absorptions are absent, owing to the symmetry of the complex molecules [23].

The thermal analysis data are summarized in Table 2. The degradation of $[Rh_2(O_2CMe)_4(MeOH)_2]$ takes place in two steps, the first concerning the release of both methanol molecules to form $[Rh_2(O_2CMe)_4]$ as an intermediate. When the sample is flushed with dinitrogen for a long time (ca. 15 h) before heating, cage breakdown (220–300 °C) causes an endothermic decomposition peak at 285 °C and the final product is rhodium. The thermograms of samples prefluxed with dinitrogen for a shorter period (ca. 2 h) differ above 200 °C. In this case $[Rh_2(O_2CMe)_4]$ degradation shows two exothermic peaks (272 and 295 °C), probably due to partial reaction with the residual air in the combustion chamber. The decomposition product at ca. 300 °C is essentially rhodium. Successively an exothermic process is observed (ca. 480 °C) and the related weight increase is in accordance with formation of Rh_2O_3. As reported for $[Rh_2(O_2CMe)_4(H_2O)_2]$ [24] and for analogous adducts with dimethyl sulphoxide and pyridine [25], in air flux, cage breakdown is a strongly exothermic process (DTA peak, 280 °C) and

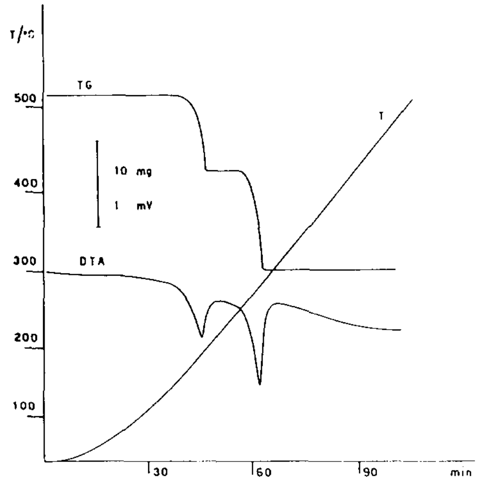


Fig. 1. Thermograms of [$Rh_2(O_2CMe)_4$(DMTC)] (36.58 mg; dinitrogen preflux, 15 h).

the final product at ca. 500 °C is Rh_2O_3. The importance of a prolonged flushing of the furnace with dinitrogen before heating is clearly shown in the thermograms of the DMTC and DETC adducts (Figs. 1–3), which release completely the axial ligand molecules before cage breakdown. Whereas [$Rh_2(O_2CMe)_4(DETC)_2$] evolves both DETC molecules in a single step, two very close steps are observed in the thermograms of [$Rh_2(O_2CMe)_4(DMTC)_2$], the second coinciding with the decomposition process in [$Rh_2(O_2CMe)_4$(DMTC)]. The thermal data support the scarce tendency of DETC to form the 1 : 1 adduct with rhodium tetra-acetate. When [$Rh_2(O_2CMe)_4(DMTC)_2$] is heated at ca. 80 °C under reduced pressure, the main

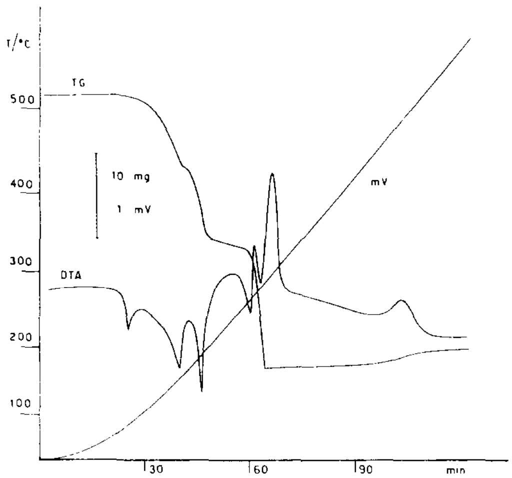


Fig. 2. Thermograms of [$Rh_2(O_2CMe)_4(DMTC)_2$] (44.93 mg; dinitrogen preflux, 2 h).

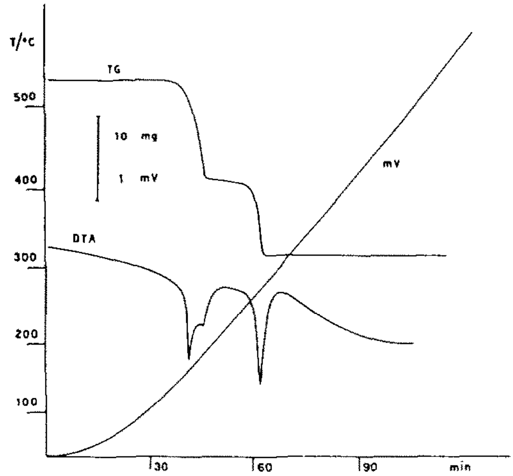


Fig. 3. Thermograms of $[Rh_2(O_2CMe)_4(DETC)_2]$ (28.12 mg; dinitrogen preflux, 15 h).

product is the 1 : 1 adduct. Under the same conditions $[Rh_2(O_2CMe)_4$-$(DETC)_2]$ yields essentially $[Rh_2(O_2CMe)_4]$ containing traces of the corresponding 1 : 1 complex (ν(CN) at ca. 1560 cm^{-1}).

The complexes with ligands containing NH groups present a quite different thermal behaviour. The first endothermic step in the $[Rh_2(O_2CMe_4)$-$(MTC)_2]$ thermograms (170 °C, Fig. 4) is probably related to the release of about one MTC molecule, followed by massive decomposition. The total weight loss up to 700 °C is less than expected for rhodium or Rh_2O_3 as final product (Table 2). The ETC and TAA adducts show a similar decomposition pattern, suggesting side reactions before total evolution of the axial ligand

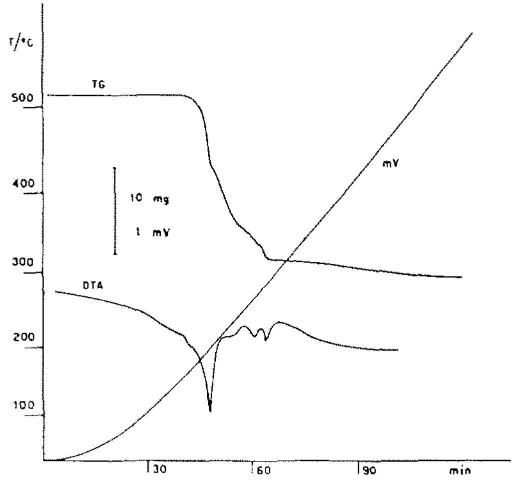


Fig. 4. Thermograms of $[Rh_2(O_2CMe)_4(MTC)_2]$ (37.23 mg; dinitrogen preflux, 2 h).

TABLE 3

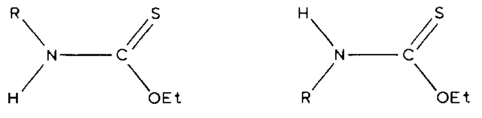
^{1}H NMR data ($CDCl_3$, ppm, T ca. 25 °C)

Compound		$O\text{-}\mathbf{CH_2}\text{-}CH_3$	$O\text{-}CH_2\text{-}\mathbf{CH_3}$	αN	βN	NH	O_2CCH_3
$[Rh_2(O_2CMe)_4(DETC)_2]$		4.85	1.31	4.09, 3.54	1.28, 1.21		1.84
DETC		4.50	1.34	3.83, 3.48	1.32, 1.28		
$[Rh_2(O_2CMe)_4(MTC)_2]$		4.95	1.54	2.90 [a]		8.65	1.89
MTC	s [b]	4.50	1.30	3.08 [c]		9.6	
	w	4.56	1.37	2.87 [c]		7.1	
$[Rh_2(O_2CMe)_4(ETC)_2]$		4.96	1.53	3.38 [d]	1.08	8.37	1.88
ETC	s [e]	4.39	1.23	3.50 [f]	1.15	6.28	
	w	4.47	1.29	3.24 [f]	1.07	7.02	

[a] $J = 4.8$ Hz. [b] The stronger signals belong to the isomer present at 65%. [c] $J = 5.3$ Hz. [d] $J = 5.2$ Hz. [e] The stronger signals belong to the isomer present at 60%. [f] $J = 5.8$ Hz.

molecules. At temperatures of the order of 120 °C, $[Rh_2(O_2CMe)_4]$ reacts with acetamide to form cages in which the acetato groups are partially or totally replaced by acetamidato groups [25–28]. Moreover, analogous species containing benzamidato [29] and *N*-phenylacetamidato [30,31] moieties have been isolated. Such a reaction, with consequent evolution of acetic acid, could occur in the adducts with ligands containing either NH or NH_2 groups, notwithstanding the first degradation step for the TC and TBA complexes is consistent with the release of two ligand molecules (Table 2).

The ^{1}H NMR spectra of the complexes (Table 3) show the acetato proton signal at ca. 1.85 ppm. Owing to the barrier to rotation about the C–N bond, of the order of 70 kJ mol^{-1} [32], the free thiocarbamate molecules are planar. In particular, the DETC spectrum contains two equally intense quartets for the non-equivalent methylene groups bound to nitrogen. The presence of two signals for each proton group indicates that MTC and ETC are, at ca. 25 °C, a mixture of the *syn* and *anti* isomers, whose relative amount can be estimated from the relative intensities of either NR or NH resonances. On coordination a downfield shift of the OEt proton resonances is observed. The spectra of the MTC and ETC adducts show only one series of proton signals, suggesting that the ligand is bound in one of the isomeric moieties, as in the complexes $[Pt(EtOSCNHPr^n)_3Cl]Cl$ and *trans*-$[Pt(ETC)_2I_2]$, which were found to contain the *anti* isomer by crystal



syn *anti*

Formula 1

TABLE 4

^{13}C NMR data ($CDCl_3$, ppm, *T* ca. 25 °C)

Compound		O-$\mathbf{CH_2}$-CH_3	O-CH_2-$\mathbf{CH_3}$	αN	βN	C=S	$O_2\mathbf{C}$-CH_3	O_2C-$\mathbf{CH_3}$
$[Rh_2(O_2CMe)_4(DMTC)_2]$		69.0	14.5	43.2, 38.3		188.0	191.5	23.8
DMTC		67.1	14.1	42.2, 37.4		188.1		
$[Rh_2(O_2CMe)_4(DETC)_2]$		68.4	14.2	48.0, 43.5	13.1, 12.3	187.0	191.2	23.5
DETC		66.4	14.0	47.2, 42.9	12.9, 11.6	187.0		
$[Rh_2(O_2CMe)_4(MTC)_2]$		68.2	14.5	29.5		190.7	192.7	24.0
MTC	s [a]	65.5	13.5 [b]	28.7		190.4		
	w	66.8	13.5 [b]	30.9		189.1		
$[Rh_2(O_2CMe)_4(ETC)_2]$		68.1	14.5	37.9	13.8	189.8	192.7	23.9
ETC	s [a]	65.7	13.6 [b]	39.9	13.6 [b]	190.0		
	w	67.3	13.6 [b]	37.8	13.1	189.3		

[a] Signals belonging to the major isomer. [b] Superimposed signals.

structure data [33,34]. Such a trend is also observed in the ^{13}C NMR spectra (Table 4), which, in addition, show the acetato CO_2 and CH_3 resonances at ca. 192 ppm and 24 ppm, respectively. The OEt methylene resonances are ca. 2 ppm downfield with respect to free ligands, whereas the thiocarbonyl carbon signals are nearly unchanged, as expected for weak metal–sulphur bonds. Conversely, *trans*-$[Pt(DMTC)_2Br_2]$ and *trans*-$[Pt(DETC)_2X_2]$ ($X =$ Cl and Br), in which strong Pt–S bonds are present, showed an upfield shift of the C=S carbon resonance of ca. 2 ppm [20].

ACKNOWLEDGEMENT

The authors thank Mrs Franca Marzola for far-IR spectra registration.

REFERENCES

1 T.R. Felthouse, Prog. Inorg. Chem., 29 (1982) 73.
2 E.R. Boyar and S.D. Robinson, Coord. Chem. Rev., 50 (1983) 109.
3 I.B. Baranovskii, Russ. J. Inorg. Chem., 27 (1982) 769.
4 R.J.H. Clark, A.I. Hempleman, H.M. Dawes, M.B. Hursthouse and C.D. Flint, J. Chem. Soc. Dalton Trans., (1985) 1775.
5 J. Kitchens and J.L. Bear, J. Inorg. Nucl. Chem., 31 (1969) 2415.
6 J. Kitchens and J.L. Bear, J. Inorg. Nucl. Chem., 32 (1970) 49.
7 F.A. Cotton and T.R. Felthouse, Inorg. Chem., 19 (1980) 323.
8 T.A. Mal'kova and V.N. Shafranskii, Russ. J. Gen. Chem., 47 (1977) 2365.
9 R.A. Howard, A.M. Wynne, J.L. Bear and W.W. Wendlandt, J. Inorg. Nucl. Chem., 38 (1976) 1015.
10 G.Ya. Mazo, I.B. Baranovskii and R.N. Shchelokov, Russ. J. Inorg. Chem., 24 (1979) 1855.
11 J. Telser and R.S. Drago, Inorg. Chem., 23 (1984) 2599.
12 F.A. Cotton and T.R. Felthouse, Inorg. Chem., 19 (1980) 2347.
13 T.A. Mal'kova and T.N. Shafranskii, Russ. J. Phys. Chem., 49 (1975) 1653.
14 E. Forsellini, U. Casellato, G. Faraglia, L. Volponi and R. Graziani, Transition Met. Chem., 9 (1984) 419.
15 G. Faraglia, R. Graziani, L. Volponi and U. Casellato, Inorg. Chim. Acta, in press.
16 S.A. Johnson, H.R. Hunt and H.N. Neuman, Inorg. Chem., 2 (1963) 960.
17 G.A. Rempel, P. Legzdins and G. Wilkinson, Inorg. Synth., 13 (1972) 90.
18 A.P. Ketteringam and C. Oldham, J. Chem. Soc. Dalton Trans., (1973) 1067.
19 G. Faraglia, L. Sindellari and B. Zarli, Inorg. Chim. Acta, 48 (1981) 247.
20 G. Faraglia, F. Barbaro and L. Sindellari, Transition Met. Chem., 13 (1988).
21 G. Faraglia, L. Sindellari, B. Zarli and I. Agnoletti, Inorg. Chim. Acta, 58 (1982) 13.
22 G. Faraglia, L. Sindellari, L. Chiavegato and S. Sitran, Inorg. Chim. Acta, 76 (1983) L103.
23 R.J.H. Clark, A.J. Hempleman and C.D. Flint, J. Am. Chem. Soc., 108 (1986) 518; and references therein.
24 H. Schafer, C. Brendel, H. Rabenech and E. Schibilla, Z. Anorg. Allg. Chem., 518 (1984) 168, and references therein.

25 I.B. Baranovskii and R.E. Sevast'yanova, Russ. J. Inorg. Chem., 29 (1984) 1786.
26 M.J. Chavan, X.Q. Lin, M.Q. Ahsan, I. Bernal, J.L. Bear and K.M. Kadish, Inorg. Chem., 25 (1986) 1281.
27 M.J. Chavan, M.Q. Ahsan, R.S. Lifsey, J.L. Bear and K.M. Kadish, Inorg. Chem., 25 (1986) 3218.
28 M.Q. Ahsan, I. Bernal and J.L. Bear, Inorg. Chem., 25 (1986) 260.
29 A.R. Chakravartj, F.A. Cotton, D.A. Tocher and J.H. Tocher, Inorg. Chim. Acta, 101 (1985) 185.
30 J.L. Bear, T.P. Zhu, T. Malinski, A.M. Dennis and K.M. Kadish, Inorg. Chem., 23 (1984) 674.
31 R.S. Lifsey, X.Q. Lin, M.J. Chavan, M.Q. Ahsan, K.M. Kadish and J.L. Bear, Inorg. Chem., 26 (1987) 830.
32 A.E. Lemire and J.C. Thompson, Can. J. Chem., 48 (1970) 824.
33 R. Bardi, A.M. Piazzesi, A. Del Pra, M. Celeste, G. Faraglia and L. Trincia, Inorg. Chim. Acta, 102 (1985) 45.
34 R. Bardi, A.M. Piazzesi, A. Del Pra and L. Trincia, Acta Crystallogr., C43 (1987) 1281.