Journal of Organometallic Chemistry, 344 (1988) 343–350
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The synthesis and dynamic behaviour of halogentricarbonylrhenium(I) complexes of some sterically hindered dithioethers

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(Received October 19th, 1987)

Abstract

The complexes *fac*-$[ReX(CO)_3(RSCH_2CH_2SBu^t)]$ (X = Cl, Br, I; R = ^tBu, Me) have been prepared by the reaction of $[ReX(CO)_5]$ with the appropriate dithioether in tetrahydrofuran. Sulphur inversion in these complexes has been studied by variable temperature ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. These methods showed that, for R = ^tBu, when sulphur inversion was slow on the NMR timescale only the *meso*-2 invertomer was present as a significant population in solution. Where R = Me, evidence for the presence of two invertomers, namely DL-2 and DL-3, was obtained from the low temperature NMR spectra. Some halogen and invertomer dependence of the NMR chemical shifts, most notably in the $^{13}C\{^1H\}$ NMR parameters, was observed.

Introduction

Since the first observations of pyramidal sulphur inversion in a transition metal complex [1], chalcogen inversion has been studied in a wide range of transition metal complexes, and many of the factors that influence the magnitude of the barrier to inversion are now well understood [2]. Until recently, however, one possible factor that had not been investigated quantitatively was the influence of attachment of bulky substituents to the inverting centre. During the course of a detailed survey of such effects in a wide range of complexes, we recently showed [3] that increasing the steric bulk of the alkyl group R in the series of complexes *cis*-$[W(CO)_4(RSCH_2CH_2SR)]$ (R = Me, Et, ^iPr, ^tBu) resulted in a marked decrease in the barrier to sulphur inversion. We have also undertaken detailed 1D and 2D NMR investigations of dynamic behaviour in the complexes *fac*-$[PtXMe_3L]$ (X = Cl, Br, I; L = $MeSCH_2CH_2SBu^t$, $MeSCH_2CH_2SEt$, $^tBuSCH_2CH_2SBu^t$). [4,5]. We now report similar studies on the isoelectronic and isostructural complexes *fac*-

[ReX(CO)$_3$(RSCH$_2$CH$_2$SBu^t)] (X = Cl, Br, I; R = ^{t}Bu, Me). Of particular interest were the relative populations of the various invertomers observable when inversion was slow on the NMR timescale. Chalcogen inversion in some rhenium(I) complexes has been described previously [6–8].

Experimental

All reactions were performed under dry nitrogen, but no precautions were taken to exclude air during subsequent work up. Tetrahydrofuran and hexane were dried over sodium diphenylketyl under nitrogen and freshly distilled prior to use. Dichloromethane was dried over calcium hydride under nitrogen and freshly distilled prior to use. The complexes [ReX(CO)$_5$] (X = Cl, Br, I) were prepared by literature procedures [9]. The ligand 2,2,7,7-tetramethyl-3,6-dithiaoctane was purchased from K and K Chemicals and used without further purification. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Bruker AM250 Fourier transform NMR spectrometer operating at 250.13 MHz (^{1}H) and 62.90 MHz (^{13}C). A standard variable temperature unit was used to control probe temperatures during the acquisition of variable temperature spectra. All spectra were recorded with solutions in CD$_2$Cl$_2$ (below ambient temperatures) or CDCl$_3$ (above ambient temperatures) with Me$_4$Si as internal standard. Infrared spectra were recorded in THF solution, using matched CaF$_2$ solution cells, on a Perkin–Elmer 398 spectrometer interfaced to a Perkin–Elmer 3600 Data Station. Elemental analyses were performed by Butterworth Laboratories Ltd., London.

Preparation of 2,2-dimethyl-3,6-dithiaoctane

Sodium metal (3.5 g, 0.15 mol) was dissolved in methanol (250 cm^3) under nitrogen, and 2-methyl-2-propanethiol (13.7 g, 0.15 mol) was then added quickly to the resulting solution of NaOMe. The mixture was stirred at room temperature for 1 h and 2-chloroethylmethyl sulphide (16.8 g, 0.15 mol) was then added dropwise during 30 min. The mixture was stirred at room temperature for 16 h, and then reduced in volume to ca. 50 cm^3 by rotary evaporation. The solution was filtered, and the product isolated by distillation at reduced pressure, the fraction boiling at 58–60 °C (0.1 mmHg) being collected. The yield of 2,2-dimethyl-3,6-dithiaoctane was 18.0 g (72.0%). ^{1}H NMR data (CDCl$_3$ solution); δ 1.37 (s, 9H), 2.18 (s, 3H, CH_3S–), 2.76 (s, 4H, –SCH_2CH_2S–).

Preparation of complexes

Complexes **1**–**6** (Table 1) were prepared by the reaction of [ReX(CO)$_5$] (X = Cl, Br, I) with the appropriate ligand in dry tetrahydrofuran under reflux, the reaction time being dependent on the nature of X. The following example is typical of the method.

[ReBr(CO)$_5$] (0.22 g, 0.54 mmol) and 2,2,7,7-tetramethyl-3,6-dithiaoctane (0.2 cm^3) were heated in dry THF (25 cm^3) under nitrogen for 3 h under reflux. The solvent was removed at reduced pressure, and the residual white solid was washed with hexane (10 cm^3) to remove the surplus ligand. Recrystallisation from dichloromethane/hexane afforded colourless crystals of *fac*-[ReBr(CO)$_3$(^{t}BuSCH$_2$CH$_2$SBu^t)] (0.22 g, yield 68.5%).

Yields, analytical data and solution infrared data for these complexes are listed in Table 1.

Results and discussion

Single-site sulphur inversion in complexes of this type would proceed according to the pathway shown in Fig. 1. For complexes **1**–**3**, this involves interconversion of two *meso* invertomers and a pair of isochronous DL invertomers, whereas for **4**–**6** interconversion between four distinct DL invertomers would arise. Previous studies [6–8,10–12] have established that whilst inversion in trimethylplatinum(IV) halide and tricarbonylrhenium(I) halide complexes of dichalcogenoethers is closely analogous, the axial carbonyl ligands present in the $\mathrm{Re^I}$ complexes are far less sterically demanding than the axial methyl ligands of the $\mathrm{Pt^{IV}}$ complexes. This is reflected in larger relative populations of invertomers in which the alkylthio groups are *trans* to the axial halide ligand than are observed for analogous $\mathrm{Pt^{IV}}$ complexes. Further, in previously studied $\mathrm{Re^I}$ complexes of this type containing symmetrical dichalcogenoethers [6–8], a general increase in the relative population of the *meso*-2 invertomer at the expense of the other two invertomers was seen to result from increasing the steric bulk of the halide ligand. In the light of this tendency, we have recorded variable temperature ^{1}H and ^{13}C {^{1}H} NMR spectra for complexes **1**–**3** in order to investigate how the bulkier $(CH_3)_3C$ group would influence these trends. It was also hoped to obtain information concerning the energetics of the inversion process from these studies. The ^{1}H and ^{13}C {^{1}H} NMR parameters obtained from these studies are listed in Tables 2 and 3 respectively.

The spectra obtained at 20 °C were fully consistent with the rapid interconversion of invertomers via single-site sulphur inversion. On cooling to −90 °C, the only significant change in both the ^{1}H and ^{13}C {^{1}H} NMR spectra was that the AA′BB′

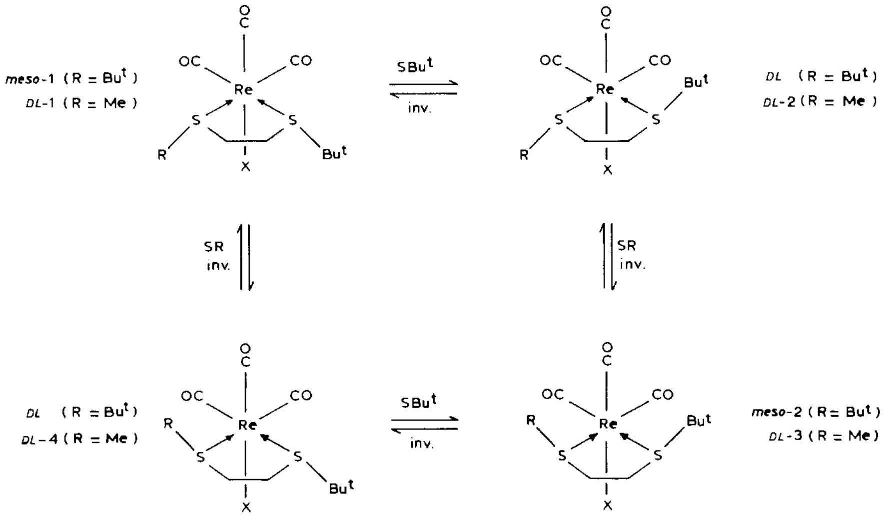

Fig. 1. Interconversion of invertomers via single-site sulphur inversion in the complexes *fac*-$[\mathrm{ReX(CO)_3(RSCH_2CH_2SBu^t)}]$ (X = Cl, Br, I; R = Me, ^{t}Bu).

Table 1

Syntheses, infrared and analytical data, and melting points for the complexes *fac*-$[ReX(CO)_3(^tBuSCH_2CH_2SR)]$ (X = Cl, Br, I; R = ^{t}Bu, Me)

Complex	Reaction time (h)	Yield [a] (%)	ν(CO) [b] (cm^{-1})	Analyses (Found (calc) (%)) C	Analyses (Found (calc) (%)) H	M.p. [c] (°C)
fac-$[ReCl(CO)_3(^tBuSCH_2CH_2SBu^t)]$ (**1**)	2	76.0	2031s 1940vs 1894s	30.6 (30.5)	4.3 (4.3)	131–132
fac-$[ReBr(CO)_3(^tBuSCH_2CH_2SBu^t)]$ (**2**)	3	68.5	2027s 1942vs 1895s	28.3 (28.1)	4.0 (4.0)	159–160
fac-$[ReI(CO)_3(^tBuSCH_2CH_2SBu^t)]$ (**3**)	65	73.0	2030s 1945vs 1898s	25.7 (25.9)	3.7 (3.7)	171–172
fac-$[ReCl(CO)_3(MeSCH_2CH_2SBu^t)]$ (**4**)	3	85.0	2031s 1940vs 1899s	25.6 (25.4)	3.4 (3.4)	150–152
fac-$[ReBr(CO)_3(MeSCH_2CH_2SBu^t)]$ (**5**)	10	65.0	2031s 1945vs 1903s	23.2 (23.4)	2.9 (3.1)	120–121
fac-$[ReI(CO)_3(MeSCH_2CH_2SBu^t)]$ (**6**)	60	57.1	2033s 1943vs 1901s	21.3 (21.4)	2.8 (2.9)	143–144

[a] Yields are quoted relative to $[ReX(CO)_5]$. [b] Recorded in THF solution. [c] Uncorrected.

Table 2
^{1}H NMR parameters for complexes **1–6**

Complex	T (° C)	δ (ppm)		
		CH_3S–	$(CH_3)_3$CS–	-SCH_2CH_2S–
1[a]	20		1.53(s)	2.85–3.20(m)
2[a]	20		1.52(s)	2.90–3.16(m)
3[a]	20		1.50(s)	2.96–3.18(m)
4[b]	−20	2.65(s)[c]	1.54(s)[c]	
		2.66(s)[d]	1.60(s)[d]	–
	60	2.62(s)	1.54(s)	
5[b]	−20	2.71(s)[c]	1.52(s)[c]	
		2.68(s)[d]	1.58(s)[d]	–
	60	2.62(s)	1.54(s)	
6[b]	−20	2.79(s)[c]	1.50(s)[c]	
		2.71(s)[d]	1.55(s)[d]	
	60	2.71(s)	1.52(s)	

[a] Spectra were essentially invariant with temperature except as noted in the text. The methylene region exhibited an AA′BB′ multiplet at this temperature. [b] Spectra were invariant between −90 and 0 ° C, except for changes brought about by the temperature dependence of the chemical shifts. Parameters are quoted at −20 ° C, as the most satisfactory resolution of signals was obtained at this temperature. The methylene regions of the spectra for these complexes were complex at all temperatures and was not analysed. Relative invertomer populations were: **4**: DL-2 (55.3%), DL-3 (44.7%); **5**: DL-2 (45.6%), DL-3 (54.5%); **6**: DL-2 (34.7%), DL-3 (65.3%). [c] DL-2 invertomer. [d] DL-3 invertomer.

multiplet for the methylene protons in the ^{1}H NMR spectra at 20 ° C changed to a broad singlet (or possibly ill-refined multiplet). Additionally, the carbonyl region of the ^{13}C {^{1}H} NMR spectra at −90 ° C exhibited two signals in the intensity ratio 2/1. Two explanations of these observations are possible; either (i) the ground state (slow inversion) spectra could not be obtained even at −90 ° C; or (ii) only one of the *meso* invertomers exhibited a measurable solution population at −90 ° C. We strongly favour the latter explanation, since the former rationalisation would imply abnormally low inversion barriers for complexes **1–3**, well below 40 kJ mol^{-1}. In view of the trends in invertomer populations previously observed for Re$^{\mathrm{I}}$ complexes of this type [6–8], we believe that the invertomer observed at −90 ° C can be identified as the *meso*-2 isomer, in which both thioalkyl groups are directed away from the sterically demanding axial halide ligand. These results contrast markedly with those obtained for the analogous complexes *fac*-[PtXMe$_3$(^{t}BuSCH$_2$CH$_2$SBu^t)] (X = Cl, Br, I) [5], where all three invertomers were observed in solution at the slow inversion limit, with the *DL* invertomer predominating. It is therefore clear that for compounds **1–3** axial halide ligand–alkylthio group non-bonded interactions have by far the greatest influence on relative invertomer populations.

Similar studies have been undertaken with complexes **4–6**, and the data so obtained are listed in Tables 2 and 3. Here, four non-isochronous invertomers are possible (Fig. 1) when all sulphur inversion is slow on the NMR timescale. However, at −90 ° C measurable populations were observed for only two invertomers in both the ^{1}H and ^{13}C {^{1}H} NMR spectra. This is, perhaps, unsurprising in view of the results obtained for **1–3**, and the two sets of signals have accordingly been assigned to the DL-2 and DL-3 invertomers, in which the t-butyl group is directed away from the axial halide ligand. The relative populations of the two invertomers were notably

Table 3

Proton-decoupled ^{13}C NMR parameters for complexes **1**–**6** at low temperature (slow inversion)

Complex	T (° C)	Invertomer	δ (ppm)					
			$\mathit{C}\mathrm{H_3S}$–	$\mathrm{(}\mathit{C}\mathrm{H_3)_3CS}$–	$\mathrm{(CH_3)_3}\mathit{C}\mathrm{S}$–	$\mathrm{(CH_3)_3CS}\mathit{C}\mathrm{H_2}$–	$\mathrm{CH_3S}\mathit{C}\mathrm{H_2}$–	CO
1	−90	*meso*-2		29.89	51.60	32.73		191.79 [a] 192.37 [b]
2	−90	*meso*-2		29.82	52.01	32.88		191.38 [a] 191.85 [b]
3	−90	*meso*-2		29.91	52.84	33.34		191.09 [a] 191.37 [b]
4	−60	DL-2	17.57	29.83	51.57	30.81	36.10	190.17, 191.23
		DL-3	22.87	29.94	51.55	29.66	35.74	192.02, 192.46 192.91 [c,d]
5	−60	DL-2	19.08	29.71	52.08	30.82	36.69	189.21, 190.48
		DL-3	28.83	29.82	52.06	29.99	36.17	191.30, 191.79 192.26 [c]
6	−60	DL-2	22.77	29.55	52.78	30.84	38.12	188.06, 189.65
		DL-3	25.46	29.65	52.63	30.47	37.04	190.57, 191.05, 191.56 [c]

[a] Axial. [b] Equatorial. [c] No attempt to assign signals to specific invertomers was made. [d] At −90 ° C.

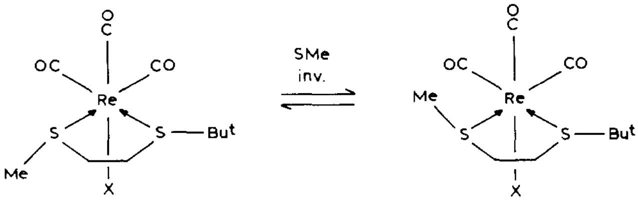

Fig. 2. The two intermediate invertomers that arise from fast SBu^t inversion and slow SMe inversion in complexes **4**–**6**.

halogen dependent, the DL-3 population increasing at the expense of that of the DL-2 invertomer with increasing halogen size. This again contrasts with results obtained for the trimethylplatinum(IV) halide complexes of the same ligand [5], for which all four invertomers were detected at the slow inversion limit and the DL-1 (X = Cl) or DL-4 (X = Br, I) invertomers predominated. These observations highlight the very different steric requirements of the axial methyl and axial carbonyl ligands in these isoelectronic and isostructural compounds; and further demonstrate the control of axial halide ligand–alkylthio group interactions over invertomer populations in these Re^I complexes.

The onset of rapid sulphur inversion at SBu^t, which we have shown to be the lower energy process for the analogous Pt^{IV} complexes [4,5], would not be detectable by NMR in these circumstances as this would create two further invertomers of the type shown in Fig. 2, featuring a pseudo-planar geometry at SBu^t. Indeed, no changes in the spectra were observed on warming solutions of **4**–**6** to around 0 °C, other than those derived from the marked temperature dependence of the chemical shifts. Above 0 °C, broadening and coalescence of signals in all regions of the spectra occurred, until at 60 °C averaged spectra consistent with rapid inversion at all sulphurs were observed. It was not possible to evaluate the barriers to SMe inversion by computer simulation of these variable temperature NMR spectra as a result of the small chemical shift differences between signals for the two invertomers in most regions of the spectra. Additionally, the strong temperature dependence of the chemical shifts of the signals precluded even an approximate reliable estimation of these inversion barriers from measurement of the coalescence temperatures. However, the temperature ranges over which the spectral changes occurred were similar to those recorded for analogous complexes of 2,5-dithiahexane [6] and suggested that the barriers to SMe inversion were of a similar magnitude in both series of complexes.

The ^{1}H NMR chemical shifts of **1**–**6** generally showed little halogen or invertomer dependence, although the thiomethyl signals of **4**–**6** showed a downfield shift on varying the halogen from Cl to Br to I, particularly for the DL-2 invertomer, where the thiomethyl group is directed towards the axial halide ligand. The ^{13}C {^{1}H} NMR chemical shifts were more markedly halogen dependent. All ligand carbon signals showed a downfield shift with increasing halogen size, particularly for the thiomethyl and methylene (adjacent to SMe) carbon signals of **4**–**6**. The largest variation for these latter signals was again observed for the DL-2 invertomer. The carbonyl resonances showed a small upfield shift with increasing halogen size, as expected from the relative electronegativities of the halogens [14]. Only five signals were observed in the low temperature $^{13}C\ \{^1H\}$ NMR spectra of **4–6**, presumably as a result of fortuitous chemical shift equivalences. The intensities of the signals did not readily suggest an assignment to specific invertomers, and no such assignment was therefore attempted. The chemical shifts of the carbonyl signals (in the range $\delta = 188–192$) were similar in magnitude to reported values for other *fac*-tricarbonylrhenium(I) complexes [15,16]. We were unable to detect carbonyl resonances at higher temperatures; it was suspected that this was due to broadening of these resonances by the quadrupolar rhenium nucleus but broadening as a result of a further fluxional process, such as carbonyl scrambling, for example, could not be discounted with certainty.

Acknowledgments

One of us (I.M.) wishes to thank the University of Exeter for the award of the Frank Southerden Scholarship.

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