Interaction of Trirhenium(III) Cluster Alkyls with Carboxylic Acids, β-Diketones, and Diphenyltriazene †

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The interaction of the *triangulo*-trirhenium cluster alkyls, $Re_3Cl_3(CH_2SiMe_3)_6$ and Re_3Me_9, with carboxylic acids, β-diketones, and 1,3-diphenyltriazene leads to partial or complete loss of tetramethylsilane or methane from the end alkyl groups, respectively, and the formation of rhenium(III) complexes that may be either monomeric, *i.e. triangulo*-trirhenium, Re_3, or dimeric in which two such units are linked together by carboxylate bridges to give Re_6 species.

Examples of monomeric complexes are the benzoate, $Re_3Cl_3(CO_2Ph)_6$, β-diketonates, $Re_3Me_6(\beta\text{-dik})_3$, and the diphenyltriazenide, $Re_3Cl_3(CH_2SiMe_3)_3(PhN_3Ph)_3$.

The dimeric complexes are carboxylates such as $Re_6(\mu\text{-}Cl_6)(CH_2SiMe_3)_6(\mu\text{-}CO_2Me)_6$ and $Re_6(\mu\text{-}Me_6)Me_6(\mu\text{-}CO_2Me)_6$, in which the Cl or Me bridges between rhenium atoms in each Re_3 triangle are retained.

I.r. and ^1H n.m.r. spectra are reported and likely structures for the complexes suggested.

In this paper, which is the first of a series on the chemistry of the rhenium(III) *triangulo*-cluster alkyls, $Re_3Cl_3(CH_2SiMe_3)_6$ and Re_3Me_9,[1] we describe reactions with weak protonic acids, specifically carboxylic acids, β-diketones, and diphenyltriazene. In these reactions partial or complete loss of the terminal alkyl group, as $SiMe_4$ or CH_4, occurs with the formation of new types of rhenium complexes. With the exception of one β-diketonato-complex, none of the compounds has been obtained as crystals suitable for *X*-ray diffraction study. Spectroscopic data for the new compounds are collected in Table 1.

Interaction of μ-Trichloro-hexakis(trimethylsilylmethyl)-triangulo-*trirhenium*(III) *with Carboxylic Acids.*—(i) *Acetic acid.* The addition of acetic acid to a petroleum solution of $Re_3Cl_3(CH_2SiMe_3)_6$ at ambient temperatures yields a red precipitate. Analytical, molecular weight, and spectroscopic data for the compound indicate that it is $[ReCl(CH_2SiMe_3)(CO_2Me)]_6$ with the structure (A) shown in the diagram. Thus the i.r. spectrum shows, in addition to CH_2SiMe_3 absorptions, bands at 1 455 and 1 520 cm^{-1} typical for bridged carboxylato-groups and a band at 352 cm^{-1} which may be assigned to the Re–Cl stretch of the bridge chlorine of the Re_3Cl_3 triangular unit. The ^1H n.m.r. spectrum of the compound shows two singlets at $\delta = 1.26$ and 0.07 with relative intensities 3 : 11 respectively. The former peak may be assigned to CH_3CO_2 and the latter to CH_2SiMe_3 where the methyl and methylene peaks are coincident, as has been observed for other trimethylsilylmethyl complexes.[1]

On refluxing an acetic acid solution of $Re_3Cl_3(CH_2SiMe_3)_6$, a dark green compound is obtained. On the basis of analytical, molecular weight, and spectroscopic data this compound can be formulated as $[ReCl(CO_2Me)_2]_6$ with structure (B) as shown in the diagram. In addition to acetato-bands in the i.r. comparable to those of the first compound there are two bands at 1 720 and 1 627 cm^{-1} typical for unidentate carboxylato-groups. The ^1H n.m.r. spectrum in pyridine shows two singlets of equal intensity at $\delta = 1.24$ and 1.95 the former being assigned to the methyl of the bridging, the latter to the unidentate acetate.

(ii) *Trifluoroacetic acid.* The room-temperature reaction leads to a red, petroleum-soluble compound, $[ReCl(CH_2SiMe_3)(CO_2CF_3)]_6$, similar to the acetate. The reaction has been followed by n.m.r. spectroscopy where the liberation of one mole equivalent of tetramethylsilane per rhenium atom can be observed. The i.r. spectrum shows bands due to bidentate carboxylato-groups and, in addition, there is a ν(C–F) band at 1 204 cm^{-1}.

(iii) *Other carboxylic acids.* Acids such as picolinic, nicotinic, phenylacetic, malonic, benzoic, and adamantane-1-carboxylic react similarly. Although it was deemed unnecessary to characterize rigorously all these complexes the relevant spectroscopic data are in Table 1 and analytical data in Table 2.

With benzoic acid, however, both alkyl groups of each rhenium in $Re_3Cl_3(CH_2SiMe_3)_6$ can be successively replaced, but the linking of Re_3Cl_3 units by carboxylate bridges does not occur and instead the green complexes, $Re_3Cl_3(CH_2SiMe_3)_3(CO_2Ph)_3$ and $Re_3Cl_3(CO_2Ph)_6$ are obtained. In the mass spectrum of the former the molecular ion may be observed ($m/e = 1\,210$ a.m.u.). The pyridine-2-carboxylate (picolinate), a green solid, appears to be analogous to the benzoate, *i.e.* $Re_3Cl_3(CH_2SiMe_3)_3(CO_2C_5H_4N)_3$. The high frequency of the carbonyl absorption (1 670 and 1 600 cm^{-1}) suggests the co-ordination of the heterocyclic nitrogen leaving a unidentate carboxylato-group as shown in (C) in the diagram. For both the benzoate and the picolinate, steric factors may be responsible for the non-formation of bridges.

Interaction of Carboxylic Acids with Nonamethyltrirhenium(III).—The addition of acetic acid to a suspension or solution of Re_3Me_9 at ambient temperatures causes effervescence due to evolution of methane and the formation of an orange solution from which an orange solid, $Re_6Me_{12}(CO_2Me)_6$, can be isolated. The compound is volatile and can be sublimed at 120 °C/10^{-3} Torr (although with considerable decomposition); it is best purified by recrystallisation. The mass spectrum does not show the molecular ion but shows peaks higher than required for the trimer as well as a peak corresponding to the trimeric unit $Re_3Me_6(MeCO_2)_3$ (at $m/e = 828$ a.m.u.). The decomposition pattern is similar to that of other

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† No reprints available.

triangulo-trirhenium species[1] showing successive loss of methyl groups. In the i.r. spectrum there are broad ν(C–O) absorptions at 1 533 and 1 440 cm^{-1}, indicating bridging or chelating acetato-groups, as well as ν(C–H) and δ(C–H) absorptions similar to those in Re_3Me_9. The ^1H n.m.r. spectrum shows three singlets of equal intensity at δ = 0.18, 1.45, and 2.36 consistent with two non-equivalent alkyl groups per acetato-ligand. Some similar weak peaks found in the initial preparations disappear on purification; they may be due to the existence of isomers. The structure of the acetate is doubtless of the type (D) shown in the diagram.

TABLE 1

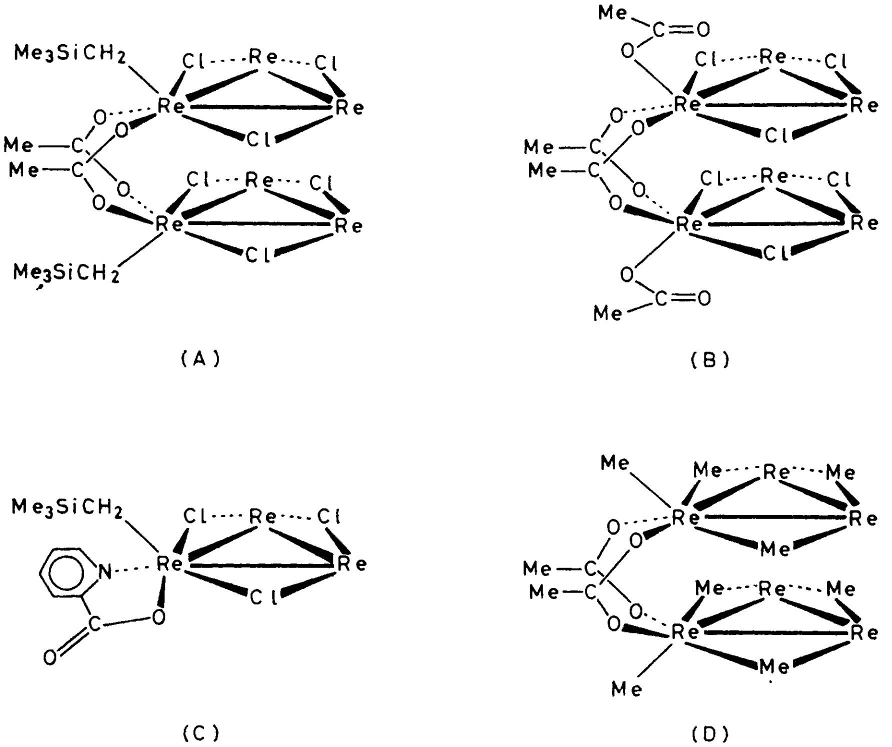
Spectroscopic data for rhenium(III) carboxylates, β-diketonates and triazenido-complexes

Compound	^1H n.m.r. (δ) [a]	Assignment	i.r. [c] (ν/cm^{-1})						
			ν(C–O)		other vibrations				
Carboxylates									
$Re_6Cl_6(CH_2SiMe_3)_6(CH_3CO_2)_6$	1.26 (s, 3 H) 0.07 (s, 11 H)	O_2CCH_3 CH_2SiMe_3	1 520s,br 1 455s,br		1 337m,br 1 260s,sh 1 085s,br	1 020s,br 800s,br 759m,br	687s 614w		
$Re_6Cl_6(CH_3CO_2)_{12}$	1.24 (s, 3 H) 1.95 (s, 3 H)	O_2CCH_3 μ-O_2CCH_3	1 720w,br [d] 1 627m,br 1 520s,br 1 460s,br		2 940w 1 033m,br 764m,br	699s 670m			
$Re_6Cl_6(CH_2SiMe_3)_6(CF_3CO_2)_6$	0.15 (s) [b]	CH_2SiMe_3	1 692m,br [d] 1 648m,br 1 601m,br		2 970w 1 438w,br 1 262m,br	1 204s,br 1 170m,br 927w,br	850s,br 763w 742w,sh	693w	
$Re_3Cl_3(CH_2SiMe_3)_3(PhCO_2)_3$	7.01, 8.02 } (m, 5 H) [b] 0.42 (s, 11 H)	O_2CPh CH_2SiMe_3	1 611w,sh [e] 1 521s,br		3 080w,sh 2 961m,sh 2 904w	1 327w,sh 1 255s,sh 1 187m,sh	1 105w,br 1 078w,sh 1 035m,sh	880s,sh 850s,br 771w	729s,sh 730s,sh
$[Re_3Cl_3(PhCO_2)_6]_n$ [f]	7.51 8.05br (m)	{ O_2CPh { μ-O_2CPh	1 614m,sh 1 510s,sh 1 500s 1 470m		3 075w 1 190m,sh 1 157w	1 080m 1 036m,sh 1 011w	918w 863w 724s,br	710s,sh	
$Re_3Cl_3(CH_2SiMe_3)_3(C_5H_4N$-2-$CO_2)_3$	8.22br (m, 4 H) [b] 0.08 (s, 11 H)	$O_2CC_5H_4N$ CH_2SiMe_3	1 670s,br 1 600m		1 320m,br 1 288m 1 249m,br	1 150m,br 1 050m 1 017m	840s,br 755m 724m	709w 687m 641w	524w 442m
$[Re_3Cl_3(CH_2SiMe_3)_3(PhCH_2CO_2)_3]_n$	3.61 (s, 2 H) [b] 7.30 (s, 5 H) 0.03 (s, 11 H)	O_2CCH_2Ph O_2CCH_2Ph CH_2SiMe_3	1 505s,br [d]		3 020w 2 940w 1 244m	1 170m,br 1 027m,br 839s,br	710s,br 517w 477w	350w	
$[Re_3Cl_3(PhCH_2CO_2)_6]_n$	3.78br (s, 2 H) 7.50br (s, 5 H)	O_2CCH_2Ph O_2CCH_2Ph	1 640w 1 510s,br 1 490s		3 020w 720s,br 650m,br	520w			
$[Re_3Cl_3(CH_2SiMe_3)_3(C_5H_4N$-3-$CO_2)_3]_n$	8.30br (m, 4 H) 0.10 (s, 11 H)	$O_2CC_5H_4N$ CH_2SiMe_3	1 655m 1 588s,br		1 400s,br 1 320m 1 300m 1 250s	1 193m 1 020s,br 845s,br 745m	700m 640w		
$[Re_3Cl_3(CH_2SiMe_3)_3(C_{10}H_{15}CO_2)_3]_n$	1.75br (m, 15 H) 0.05 (s, 11 H)	$O_2CC_{10}H_{15}$ CH_2SiMe_3	1 615m,br [d] 1 500s,br		2 900s,br 1 400s,br 1 308s	1 250m 1 100s,br 973m	910m 845m 760s,br	678s 520s 440m	340m
$[Re_3Cl_3(CH_2SiMe_3)_3(HO_2CCH_2CO_2)_3]_n$			1 720s,br [d] 1 600s,br 1 530s,br		2 950m 1 400s,br 1 245s	1 160m 910m 838s	712m 678m 351m		
$Re_6Me_{12}(MeCO_2)_6$	1.45 (s, 3 H) 0.18 (s, 3 H) 2.36 (s, 3 H)	O_2CCH_3 CH_3 terminal CH_3 bridge	1 533s,br [d] 1 440s,br		2 950w,br 1 400m,br 1 344m	1 260m 940w 800w,br	687s,br 530w		
$Re_6Me_{12}(PhCH_2CO_2)_6$	7.69, 7.26 } (s, 5 H) 3.39 (s, 2 H) 2.32 (s, 2H) 0.05 (s, 3 H)	Ph–CH_2–CO^2 Ph–CH_2–CO_2 CH_3 terminal CH_3 bridge	1 530s,br [d] 1 490s		3 020w 2 960w 1 400s,br	1 220w 755w 710s,br	528m 470m 390m		
β-Diketonates			ν(C $\underline{\cdots}$ C)	ν(C $\underline{\cdots}$ O)					
$Re_3Me_6(CH_3COCHCOCH_3)_3$	5.15 (m, 1 H) 1.9 (m, 3 H) 1.7 (m, 3 H) 0.6 (m, 3 H) −0.2 (m, 3 H)	C–H ligand CH_3 ligand CH_3 ligand CH_3 bridge CH_3 terminal	1 580s	1 520s 1 510s 1 420w	3 020w 2 940w 1 360s 1 275s 1 190w 1 025s	932w 780m 730w 670w 540m 420m			
$Re_3Me_6(C_4H_3SCOCHCOCF_3)_3$	7.25 (m, 3 H) 6.7 (m) 5.9 (s, 1 H) 0.8 (m, 3 H) −0.3 (s, 3 H)	} C_4H_3S CH ligand CH_3 bridge CH_3 terminal	1 600s 1 580s	1 540m 1 510w	1 410m 1 360m, 1 310s 1 250m 1 230m	1 200m 1 160m 1 145m 1 080w 1 065m	1 020w 940m 860m 790m 720m	690m 650m	
$Re_3Me_6(PhCOCHCOCH_3)_3$	7.9br, 7.45br } (2s, 5H) 6.1 (s, 1 H) 2.15 (s, 3 H) 1.2 (s, 3 H) 0.1 (s, 3 H)	} C_6H_5 C–H ligand CH_3 ligand CH_3 bridge CH_3 terminal	1 590m	1 540m 1 510m 1 465s	1 305m 1 280m 1 200w 1 180w	1 025w 995w 960m 845m	760s 720s 680m		
$Re_6Me_{12}(CF_3COCHCOCH_3)_6$	5.5 (s, 1 H) 1.8 (s, 3 H) 0.8 (s, 3 H) −0.1 (s, 3 H)	C–H ligand CH_3 ligand CH_3 bridge CH_3 terminal	1 620s 1 600s	1 525w	1 290s 1 220m 1 195m	1 155m,br 1 133m 860w	785w 730m 537m		
$Re_3Cl_3(CH_2SiMe_3)_5(C_4H_3SCOCHCOCF_3)$	7.70, 7.25 } (2m, 3 H) 6.60 (s, 1 H) 0.10, 0.05 } (2s, 55 H)	} C_4H_3S C–H ligand } CH_2SiMe_3	1 585vs 1 570vs	1 540s 1 510w	3 100w 1 500w 1 405m 1 353s 1 345s 1 308m 1 290s	1 260m,sh 1 250s 1 242s 1 230m 1 195s 1 148s 1 080w	1 065m 1 030w 1 020w 1 000w 955m 930m 840s	790m 750m 722s 678m 650m 620m 585w	517w 490w 445w
$Re_3Cl_3(CH_2SiMe_3)_3(CF_3COCHCOCH_3)_3$	6.0 (1 H) 2.5 (3 H) 0.1 (11 H)	C–H ligand CH_3 ligand CH_2SiMe_3	1 610vs 1 575w	1 540w,sh 1 525w	1 364m 1 297s 1 245m 1 225m 1 198m	1 156m 1 138m 1 030w,br 955w 915w	860m,sh 845vs 830s,sh 788w 750w	730m 680w 585m 420m	
Diaryltriazenide			ν(–N=N–)						
$Re_3Cl_3(CH_2SiMe_3)_3(PhN_3Ph)_3$	6.88br (m, 10 H) 0.08br (s, 11 H)	PhN_3Ph CH_2SiMe_3	1 589 1 278		3 050w,br 2 940w,br 1 480s	1 243m 1 022m 920m,br	834s, br 754s 687s		

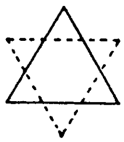
[a] In chloroform or [^{2}H]chloroform. [b] In benzene or [$^2H_6$]benzene. [c] Nujol. [d] KBr disc. [e] Also in carbon disulphide. [f] n Is always 1 or 2.

In refluxing acetic acid, Re_3Me_9 gave black intractable solids containing no acetato-ligands (i.r.).

The reaction of Re_3Me_9 with solutions of phenylacetic acid gives an orange powder which appears to be analogous to the acetate. The i.r. shows ν(C–O) bands at 1 530 and 1 490 cm^{-1} and the ^1H n.m.r. spectrum has peaks at $\delta = 7.69$ and 7.26 (C_6H_5) and 3.39 (CH_2) attributable to the phenylacetato-ligand and at $\delta = 2.32$, 0.05 due to the bridging and terminal methyls respectively, the bridging alkyls appearing at a lower chemical shift as in Re_3Me_9.[1] On this basis the peak at $\delta = 1.45$ in the spectrum of the acetato-complex may be assigned to the acetato-hydrogen atoms.



Proposed structures for rhenium cluster carboxylates. In these and other diagrams the ligands around only two rhenium atoms are shown for clarity. Although the planar, metal–metal bonded Re_3 triangular units with their bridging Cl or Me groups are shown eclipsed they may in fact be staggered, *i.e.*



(A) $Re_6Cl_6(CH_2SiMe_3)_6(CO_2Me)_6$, (B) $Re_6Cl_6(CO_2Me)_{12}$, (C) $Re_3Cl_3(CH_2SiMe_3)_3(C_5H_4NCO_2)_3$, and (D) $Re_6Me_{12}(CO_2Me)_6$

Attempts to synthesise similar carboxylates using trifluoroacetic acid and butyric acid gave mixtures of products which could not be separated.

Reactions of Rhenium Alkyls with β*-Diketones* (HL).—(i) $Re_3Cl_3(CH_2SiMe)_6$. The reactions of this alkyl with β-diketones in petroleum or tetrahydrofuran yields green or brown solutions, depending upon the reaction conditions. The reaction of $Re_3Cl_3(CH_2SiMe_3)_6$ with only a slight excess of 1,1,1-trifluoro-4-thenoylbutane-2,4-dione gives a green product identified as $Re_3Cl_3(CH_2SiMe_3)_5L$ on the basis of analytical, spectroscopic, and molecular-weight data. The reaction of $Re_3Cl_3(CH_2SiMe_3)_6$ with a large excess of trifluoropentane-2,4-dione or hexafluoropentane-2,4-dione gives green solutions which turn brown upon continued stirring or reflux but only the trifluoropentane-2,4-dionato complex, $Re_3Cl_3(CH_2SiMe_3)_3L_3$, has been completely characterised. No attempt was made to synthesise compounds of the form $Re_3Cl_3R_4L_2$ although there is no reason to believe they could not be obtained. The mass spectrum of the thenoyltrifluoro-diketonate complex shows the molecular ion (*m*/*e* = 1 320 a.m.u.), and successive loss of $-CH_2SiMe_3$, $-CF_3$, and thenoyl groups. The mass spectrum of the trifluoro-diketonate complex shows loss of three CH_2SiMe_3 groups but the molecular ion was not observed.

(ii) Re_3Me_9. The addition of β-diketones to tetrahydrofuran solutions of Re_3Me_9, produces red solutions from which complexes of the form, $Re_3Me_6L_3$ and presumably of structure (E) and also $Re_6Me_{12}L_6$ can be obtained. The mass spectra of these complexes are similar to those of the analogous acetato-species showing ions generally 28 mass units below that expected for the

TABLE 2

Analytical data * for rhenium(III) carboxylates, β-diketonates, and diaryltriazenido-complexes

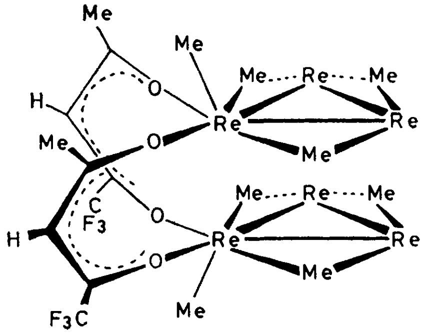
		M.p.[d]	Found (%)					Required (%)				
Carboxylates	Colour	(θ_c/°C)	C	H	Cl	Other	M[a]	C	H	Cl	Other	M
$Re_6Cl_6(CH_2SiMe_3)_6(CH_3CO_2)_6$	Red-brown	>360	18.7	4.5	10.5		2 011[b]	19.5	3.8	9.4		2 211
$Re_6Cl_6(CH_3CO_2)_{12}$	Green	>360	14.3	1.7	10.4	Si 0.0	2 200[b]	14.1	1.8	10.4	Si 0.0	2 043
$Re_6Cl_6(CH_2SiMe_3)_6(CF_3CO_2)_6$	Red	140 d †	17.3	2.5	9.0	F 12.2	2 400[c]	17.1	2.6	8.3	F 13.5	2 520
$Re_3Cl_3(CH_2SiMe_3)_3(PhCO_2)_3$	Green	150 d	31.4	3.9			1 172	30.6	3.7			1 201
$Re_3Cl_3(PhCO_2)_6$	Dark green	320 d	35.7	2.2	7.7			36.2	2.2	7.7		
$Re_3Cl_3(CH_2SiMe_3)_3(C_5H_4N\text{-}2\text{-}CO_2)_3$	Green	>200 d	29.5	4.1	7.1	N 3.0		27.9	3.5	8.1	N 3.2	
$[Re_3Cl_3(CH_2SiMe_3)_3(PhCH_2CO_2)_3]_n$ [e]	Brown	157—160	33.5	3.3	7.8			32.4	4.0	8.0		
$[Re_3Cl_3(PhCH_2CO_2)_6]_n$	Green	>220 d	38.1	2.8	7.4			38.9	2.8	7.2		
$[Re_3Cl_3(CH_2SiMe_3)_3(C_5H_4N\text{-}3\text{-}CO_2)_3]_n$	Brown	>360	29.6	3.9	7.3	N 3.6		27.9	3.5	8.1	N 3.3	
$[Re_3Cl_3(CH_2SiMe_3)_3(C_{10}H_{15}CO_2)_3]_n$	Red-brown	>360	37.6	5.4	6.8			36.8	5.5	7.2		
$[Re_3Cl_3(CH_2SiMe_3)_3(HO_2CCH_2CO_2)_3]_n$	Red-brown	170 d	17.5	2.3	7.5			20.4	3.4	8.5		
$Re_6Me_{12}(CH_3CO_2)_6$	Orange	110 d	17.5	3.4		O 10.3	1 550[c]	17.4	3.3		O 11.6	1 656
$Re_6Me_{12}(PhCH_2CO_2)_6$	Brown	130 d	35.5	3.8		O 9.2		34.1	3.7		O 9.1	
β-Diketonates												
$Re_3Me_6(CH_3COCHCOCH_3)_3$	Red	170	25.9	4.2		O 9.9	935	26.7	4.1		O 10.2	945
$Re_3Me_6(C_4H_3SCOCHCOCF_3)_3$	Red	100	26.7	2.1		F 12.1 S 7.9	1 040	27.5	2.3		F 13.0 S 7.3	1 311
$Re_3Me_6(PhCOCHCOCH_3)_3$	Red-brown	Tar	36.6	3.4				38.2	3.9			
$Re_6Me_{12}(CF_3COCHCOCH_3)_6$	Red	>150 d	20.8	2.4		F 16.6	2 182	22.7	2.7		F 15.5	2 238
$Re_3Cl_3(CH_2SiMe_3)_5(C_4H_3SCOCHCOCF_3)$	Green	Sub. 120 °C/ 5 × 10^{-2} Torr	24.8	4.3	8.1		1 265	25.4	4.5	8.4		1 322
$Re_3Cl_3(CH_2SiMe_3)_3(CF_3COCHCOCH_3)_3$	Dark brown	Sub. 120 °C/ 5 × 10^{-2} Torr	24.3	3.9	8.3			23.4	3.2	8.7		
Diaryltriazenide												
$Re_3Cl_3(CH_2SiMe_3)_3(PhN_3Ph)_3$	Brown	>120 d	38.6	4.5	6.3	N 6.3	1 425[c]	37.8	4.2	6.9	N 8.1	1 515

[a] Osmometrically in dichloromethane. [b] Osmometrically in chloroform. [c] Cryoscopically in benzene. [d] Many compounds decompose over a large range of temperature. [e] n Is always 1 or 2.

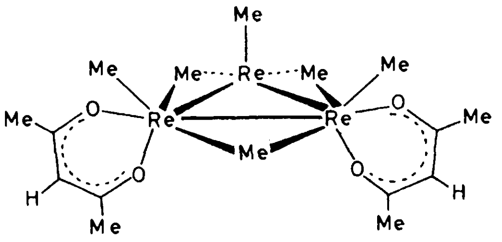
* Poor analytical data for some of the compounds may be attributed to non-crystallinity or intractibility in non-reactive solvents, presenting difficulties in purification.

† d = decomposes.

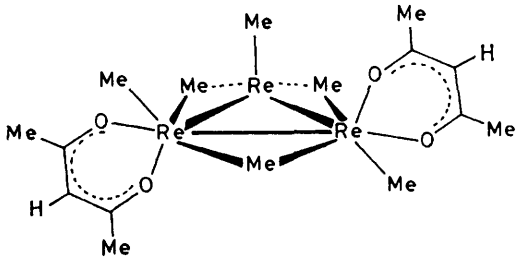
molecular ion for the trimeric species (possibly due to the loss of ethene) and peaks higher than those for a trimeric unit in the trifluoropentanedionato-complex, which is believed to be a hexamer. In none of these cases is the molecular ion observed. The i.r. spectra show the usual bands for chelating β-diketonato-ligands. The $\nu(\text{C}\overset{\cdots}{=}\text{C})$ absorption at *ca.* 1 600 cm^{-1} is split, presumably due to low symmetry. The $\nu(\text{C}\overset{\cdots}{=}\text{O})$ bands always



(E)



(F)



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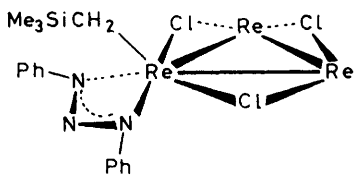

(H)

appear in the 1 510—1 540 cm^{-1} region as expected. The usual ligand-substituent effects are seen, *e.g.* a shift in the $\nu(\text{C}\overset{\cdots}{-}\text{C})$ absorption to higher frequencies in the trifluoropentanedionato-complex. The ring deformation was found at *ca.* 680 cm^{-1} except in the trifluoropentanedionato-compound. The ^{1}H n.m.r. spectra exhibit no unusual features. They do, however, indicate that the products are invariably mixtures of *cis*- and *trans*-isomers, *e.g.* (F) and (G). Three signals centred at δ 5.15 can be ascribed to the C–H ligand absorption in the pentanedionato-complex. The complexes with unsymmetrical ligands show broad ligand absorptions attributable to their being mixtures of the six possible isomers. The peak due to the bridging methyl group at *ca.* 1 p.p.m. is usually broad whereas the terminal methyl groups give a sharp singlet at *ca.* δ −0.2. Attempts to separate the isomers chromatographically and by fractional crystallisation were not successful.

*Interaction of μ-Trichloro-hexakis(trimethylsilylmethyl)-*triangulo-*trirhenium*(III) *with 1,3-Diphenyltriazene.*—When $Re_3Cl_3(CH_2SiMe_3)_6$ is refluxed in toluene with $(PhN)_2N$ brown solutions are obtained from which a brown powder can be isolated. On the basis of analytical and molecular-weight data the complex may be assigned the stoicheiometry $Re_3Cl_3(CH_2SiMe_3)_3(PhN_3Ph)_3$. The i.r. spectrum has bands at 1 589 and 1 278 cm^{-1}; the absence of a band at 1 190—1 210 cm^{-1} indicates the ligand is bidentate.

The ^{1}H n.m.r. spectrum has a multiplet at $\delta = 7.17$ (C_6H_5) and a broad singlet at $\delta = 0.45$ (CH_2SiMe_3). The relative areas are approximately 1 : 1 (expected 10 : 11 respectively). The structure (H) seems likely.

EXPERIMENTAL

Microanalyses were by the Imperial College, Butterworth Microanalytical Consultancy Limited and Pascher, Bonn, Laboratories. Instruments. I.r. spectra were recorded on Perkin-Elmer 325 and 457 spectrometers calibrated with polystyrene and n.m.r. spectra on Perkin-Elmer R12A (60 MHz) and Varian Associates XL-100-12 (F.T. mode with noise proton decoupling) machines. Molecular weights were determined either cryoscopically or osmometrically using a Perkin-Elmer–Hitachi osmometer.

All syntheses and manipulations were carried out under oxygen-free nitrogen or argon. Tetrahydrofuran, diethyl ether, light petroleum (b.p. 40—60 °C), toluene, and benzene were dried by refluxing over sodium–benzophenone under nitrogen, and were distilled immediately prior to use. The light petroleum used had b.p. 40—60 °C unless otherwise stated. Higher-boiling light petroleums were dried over sodium. Acetonitrile and dichloromethane were dried by refluxing over calcium hydride under nitrogen and were distilled immediately before use. When necessary, solvents were degassed by freeze-pumping, or by nitrogen purge. Trirhenium nonachloride was prepared from rhenium (99.9%) *via* rhenium pentachloride, and was aged in air to the more reactive hydrated chloride (Re_3Cl_9, *ca.* $6H_2O$); $Re_3Cl_3(CH_2SiMe_3)_6$ and Re_3Me_9 were prepared as before.[1]

*μ-Hexakisacetato-bis[μ-trichloro-tris(trimethylsilylmethyl)-*triangulo-*trirhenium*(III)].—To $Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) in light petroleum (10 ml) was added, with vigorous stirring, glacial acetic acid (0.5 ml, 8 mmol). The resulting green solution was warmed gently until the solution had become red and a red–brown precipitate formed. The precipitate was decanted, washed with light petroleum (2 × 10 ml) and recrystallised from ethanol to yield a red–brown powder, soluble in polar organic solvents; yield 0.4 g [85% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

*μ-Hexakisacetato-bis[μ-trichloro-trisacetato-*triangulo-*trirhenium*(III)].—$Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) was dissolved in glacial acetic acid (20 ml) and refluxed for 2 h. The initial green solution turned red then green. The solution was cooled and light petroleum (20 ml) was added to give a green precipitate which was collected, washed with light petroleum (2 × 10 ml), and recrystallised from hot tetrahydrofuran to give a dark green powder, soluble in various polar organic solvents such as dichloromethane, chloroform, and tetrahydrofuran, *etc.*; yield 0.38 g [91% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

*μ-Hexachloro-μ-hexakistrifluoroacetato-bis[tris(trimethylsilylmethyl)-*triangulo-*trirhenium*(III)].—To $Re_3Cl_3(CH_2SiMe_3)_6$ (1 g, 0.08 mmol) in light petroleum (30 ml) was added trifluoroacetic acid (2 ml, 25 mmol) with stirring at −78 °C. The solution was allowed to warm to ambient temperature and was stirred for a further 2 h, after which the solvent and excess of acid were removed. The residue was recrystallised from methanol to give a red powder very soluble in hydrocarbons; yield 0.95 g [90% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

*Trisbenzoato-μ-trichloro-tris(trimethylsilylmethyl)-*triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (0.8 g, 0.7 mmol) dissolved in light petroleum (30 ml) was added benzoic acid (1 g, 11 mmol), and the resultant green solution was stirred for 2 h. After cooling to −78 °C and filtering, the solid was washed with cold light petroleum (2 × 10 ml) and recrystallised from hot light petroleum (b.p. 60—80 °C) or toluene to give a green powder which was very soluble in aromatic hydrocarbons; yield 0.7 g, [87% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

*Hexakisbenzoato-μ-trichloro-*triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (0.8 g, 0.7 mmol) in toluene (20 ml) was added benzoic acid (1 g, 11 mmol) and the green solution was refluxed for 20 h. The resultant green precipitate was collected, washed with light petroleum (3 × 10 ml) and extracted into dichloromethane (20 ml); the extract was filtered, concentrated (to *ca.* 5 ml), and cooled to −78 °C to yield a dark green powder soluble in polar organic solvents; yield 0.76 g [93% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

*μ-Trichloro-trisphenylacetatotris(trimethylsilylmethyl)-*triangulo-*trirhenium*(III) *and μ-Trichloro-hexakisphenylacetato-*triangulo-*trirhenium*(III).—Both compounds were obtained as for the benzoato-complexes. The mixed alkyl carboxylato-compound was recrystallised from hot tetrahydrofuran, and the second compound from hot toluene, to give red–brown and green powders respectively.

*μ-Trichloro-trispyridine-2-carboxylatotris(trimethylsilylmethyl)-*triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (1 g, 0.8 mmol) in tetrahydrofuran (20 ml) was added pyridine-2-carboxylic acid (0.65 g, 5.3 mmol). The resultant green solution was stirred for 5 h, the solvent removed under reduced pressure and the product extracted from an excess of carboxylic acid in toluene (2 × 10 ml). The solution was filtered, concentrated (to *ca.* 5 ml), and held at −78 °C overnight to yield an emerald green powder soluble in hydrocarbons; yield 0.89 g [87% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

μ-Trichloro-trispyridine-3-carboxylatotris(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (1 g, 0.8 mmol) in tetrahydrofuran (20 ml) was added pyridine-3-carboxylic acid (nicotinic acid 0.65 g, 5.3 mmol). The suspension was stirred for 12 h and then filtered to remove the unchanged carboxylic acid; the solution was then concentrated (to *ca.* 5 ml) and held at −78 °C overnight to give a red–brown powder, soluble in polar organic solvents, which was recrystallised from hot tetrahydrofuran; yield 0.90 g [90% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

Trisadamantanecarboxylato-μ-trichloro-tris(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) in light petroleum (20 ml) was added adamantanecarboxylic acid (0.67 g, 3.6 mmol) and the solution was stirred for 12 h. The brown precipitate was collected, washed with light petroleum (2 × 5 ml), and dissolved in dichloromethane (10 ml). The filtered solution was concentrated and cooled to −78 °C to give a brown powder, soluble in polar organic solvents and aromatic hydrocarbons; yield 0.46 g [86% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

μ-Trichloro-trismalonatotris(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (0.5 g, 0.4 mmol) in diethyl ether (20 ml) was added malonic acid (0.4 g, 3.6 mmol). The solution was stirred for 12 h after which the red precipitate was collected and washed with tetrahydrofuran (2 × 10 ml). The compound is soluble only in very polar solvents such as dimethyl sulphoxide and pyridine in which it decomposed; yield quantitative.

μ-Hexakis-acetato-bis[μ-trimethyl-trimethyl-triangulo-*trirhenium*(III)].—To Re_3Me_9 (0.5 g, 0.7 mmol) in tetrahydrofuran (10 ml) was added glacial acetic acid (5 ml) with rigorous stirring. After 2 h, when all gas evolution had ceased and the solution was homogeneous, the solvent was removed under reduced pressure and the orange product extracted into dichloromethane; the extract was filtered, concentrated, and cooled to −78 °C to give an orange powder soluble in aromatic hydrocarbons and polar organic solvents; yield 0.45 g (70% based on Re_3Me_9).

μ-Hexakis-(phenylacetato)-bis[μ-trimethyl-trimethyl-triangulo-*trirhenium*(III)].—To Re_3Me_9 (0.5 g, 0.7 mmol) in tetrahydrouran (20 ml) was added phenylacetic acid (0.68 g, 5 mmol) as a solution in the same solvent (10 ml). The solution was stirred for 3 h when it was homogeneous and the solvent removed under reduced pressure. The brown solid was washed with light petroleum–toluene (1 : 1; 4 × 10 ml) to remove unchanged carboxylic acid, and was recrystallised from dichloromethane; yield 0.42 g (55% based on Re_3Me_9).

μ-Trichloro-tris(trimethylsilylmethyl)trisdiphenyltriazenido-triangulo-*trirhenium*(III).—To $Re_3Cl_3(CH_2SiMe_3)_6$ (1 g, 0.8 mmol) in toluene (30 ml) was added diphenyltriazene (0.5 g, 2.4 mmol). The solution was refluxed for 2 h, the solvent removed under reduced pressure and the brown residue washed with light petroleum (2 × 20 ml). The solid is very soluble in aromatic hydrocarbons and was recrystallised from toluene–light petroleum (4 : 1); yield 0.86 g (79%).

μ-Trimethyl-trimethyltris(pentane-2,4-dionato)-triangulo-*trirhenium*(III).—To Re_3Me_9 (0.6 g, 1 mmol) dissolved in tetrahydrofuran (15 ml) was added pentane-2,4-dione (1.2 g, 10 mmol) at ambient temperature. After the mixture had been stirred for 2 h, solvent was removed under reduced pressure and the product dried at 60 °C/10^{-2} Torr. The powder was dissolved in light petroleum (30 ml), filtered, concentrated (to 5 ml), and held at −78 °C overnight to give a red powder, yield 0.2 g (25% based on Re_3Me_9). The compound is soluble in light petroleum, and very soluble in aromatic hydrocarbons, diethyl ether, and dichloromethane, *etc.*

μ-Hexakis(1,1,1-trifluoropentane-2,4-dionato)-bis[μ-trimethyl-trimethyl-triangulo-*trirhenium*(III)] was prepared similarly; yield *ca.* 30%.

Trimethyl-μ-trimethyl-tris(1,1,1-trifluoro-4-thenoylbutane-2,4-dionato)-triangulo-*trirhenium*(III).—To Re_3Me_9 (0.6 g, 1 mmol) in tetrahydrofuran (15 ml) was added the ligand (0.77 g, 3.5 mmol); after the mixture had been stirred for *ca.* 2 h the solvent and then excess of ligand were removed under reduced pressure at 60 °C. The red residue was recrystallised from light petroleum; yield 0.5 g (45% based on Re_3Me_9).

μ-Trimethyl-trimethyltris(4-phenylbutane-2,4-dionato)-triangulo-*trirhenium*(III).—This reaction was carried out as above except that the ligand was purified before use by sublimation (60 °C/10^{-1} Torr) and the product was recrystallised from toluene–light petroleum (1 : 1); yield 0.57 g (60% based on Re_3Me_9).

μ-Trichloro-pentakis(trimethylsilylmethyl)(1,1,1-trifluoro-4-thenoylbutane-2,4-dionato)-triangulo-*trirhenium*(III).—$Re_3Cl_3(CH_2SiMe_3)_6$ (0.6 g, 0.5 mmol) was dissolved in light petroleum (15 ml) and the ligand (0.44 g, 2 mmol) was added. The solution was stirred for 1 h under reflux, solvent was removed under reduced pressure and excess of ligand was removed by sublimation (60 °C/10^{-2} Torr). The powder was extracted into light petroleum (20 ml), filtered, concentrated (to 4 ml), and held at −78 °C to give green crystals of the product; yield 0.44 g [55% based on $Re_3Cl_3(CH_2SiMe_3)_6$]. The product is very soluble in aliphatic and aromatic hydrocarbons.

μ-Trichloro-tris(1,1,1-trifluoropentane-2,4-dionato)-tris-(trimethylsilylmethyl)-triangulo-*trirhenium*(III).—This reaction was carried out as above except that the mixture of $Re_3Cl_3(CH_2SiMe_3)_6$ and ligand was refluxed in tetrahydrofuran for 12 h. The brown product was an oil which was purified by crystallisation from light petroleum at −78 °C; yield 0.41 g [35% based on $Re_3Cl_3(CH_2SiMe_3)_6$].

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