Trioxorhenium(VII) Alkoxides, Di-isopropylamides, Carboxylates and Related Compounds †

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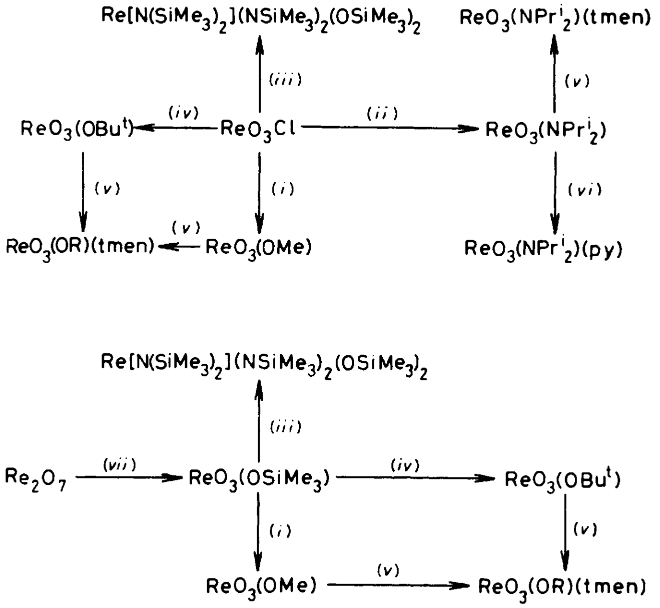
A number of trioxorhenium(VII) compounds of the type ReO_3X (X = NPr^i_2, OMe, OBu^t, or O_2CR; R = Me, CF_3, Bu^t, or Ph) have been prepared from ReO_3Cl, $ReO_3(OSiMe_3)$, and Re_2O_7. The compounds form adducts with tetrahydrofuran, pyridine (py), 2-hydroxypyridine, and *NNN'N'*-tetramethylethylenediamine (tmen); examples are $ReO_3(OMe)(tmen)$ and $ReO_3(O_2CMe)(py)$. For the carboxylates, the RCO_2 group may be unidentate or chelate depending upon the nature of the additional ligand. The acetatotrioxo-complex undergoes an exchange reaction with benzoic acid to give the corresponding benzoate. A five-co-ordinate rhenium(VII) complex with trimethylsilyl-amide, -imide, and -oxide groups, $Re[N(SiMe_3)_2](NSiMe_3)_2(OSiMe_3)_2$, is also described. I.r. and n.m.r. (^1H, ^{13}C) data are given.

During studies on the synthesis of rhenium alkoxo- and dialkylamido-compounds, it was found that tetrachloro-oxorhenium(VI) was a useful starting material for the preparation of new and known compounds.[1] The substitution chemistry of d^1 and d^0 rhenium oxohalides is still relatively poorly studied. In view of the facility of Re_2O_7 in the presence of alkylating agents to catalyse metathesis reactions [2] of unsaturated hydrocarbons, ethers, and carboxylic esters, there is interest in d^0 rhenium chemistry.[3] We now describe further studies on chlorotrioxorhenium (perrhenyl chloride).‡ Substitution reactions of other d^0 trioxorhenium compounds were found to provide, in some cases, routes to those compounds prepared from ReO_3Cl as well as carboxylate complexes not obtained from ReO_3Cl. The chemistry is summarized in the reaction Schemes 1 and 2; relevant n.m.r. data are in Table 1.

Results and Discussion

Trioxorhenium(VII) *Alkoxides and their Adducts*.—The interaction of ReO_3Cl with the silyl ethers Me_3SiOR (R = Me or Bu^t), in hydrocarbon solvents, allows the isolation of the corresponding trioxorhenium(VII) alkoxides of stoicheiometry $ReO_3(OR)$. Both compounds are characterised by spectroscopic data (see Experimental section and Table 1). The unstable t-butoxide, $ReO_3(OBu^t)$ first made § by interaction of Re_2O_7 with Bu^t_2O is very soluble in aliphatic and aromatic hydrocarbons, and has a single peak in the ^1H n.m.r. spectrum (δ −0.10); the molecular ion is observed in the mass spectrum (*m*/*e* = 308). The molecule is evidently monomeric with tetrahedral rhenium(VII) as in ReO_3Me.[4] The methoxide, however, is insoluble in hydrocarbons, slightly soluble in tetrahydrofuran and chlorinated hydrocarbons, is involatile and relatively high-melting and evidently polymeric, probably with bridging methoxo-groups. Both compounds are moisture sensitive and decompose over several days at ambient temperature to black unidentified deposits, in the solid state or in solution. The butoxide is less thermally stable than the methoxide but can be stored at −20 °C. Both compounds form adducts with *NNN'N'*-tetramethylethylenediamine (tmen) enabling the isolation of thermally stable (25 °C), moisture-sensitive white crystals. For the methoxide, the ^1H n.m.r. spectrum consists of two singlets at δ 4.56 and 2.64, the latter being slightly broadened (width at half-height, $\nu_{\frac{1}{2}}$ = 5.3 Hz) in the relative intensity ratio of 3 : 16 respectively. Thus it appears that the low-field peak is due to the methoxo-protons with the methylene and methyl protons of the tmen ligand resonating coincidentally. The ^{13}C-{^1H} spectrum, however, has three singlets (δ 65.16, 57.41, and 49.42) with relative intensities of approximately 1 : 2 : 4 which may be assigned to the methoxo, methylene, and tmen methyl carbons respectively. This is supported by coupling information in the 'gated' ^{13}C spectrum (see Table 1). In addition, the mass spectrum shows an intense parent ion (*m*/*e* = 266) corresponding to the loss of tmen from the molecular ion.

The ^1H n.m.r. spectrum of $ReO_3(OBu^t)(tmen)$ (in $CDCl_3$)



Scheme 1. Synthesis of rhenium alkoxide and dialkylamide complexes from ReO_3Cl (top) and $ReO_3(OSiMe_3)$ bottom (R = Me or Bu^t): (*i*) Me_3SiOMe; (*ii*) $NHPr^i_2$; (*iii*) $Li[N(SiMe_3)_2]$; (*iv*) Me_3SiOBu^t; (*v*) tmen; (*vi*) py; (*vii*) $(Me_3Si)_2O$

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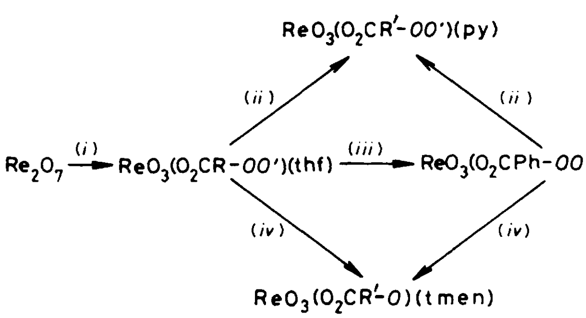
† *Non-S.I. unit employed:* mmHg = 133.3 Pa.

‡ CAUTION: The synthesis of ReO_3Cl by combustion of Re_3Cl_9 in oxygen,[1] although repeated several times, has resulted in an explosion, presumably due to formation of chlorine oxides. If this procedure is used adequate precautions should be taken. A safer procedure is that of C. J. Wolf, A. F. Clifford, and W. H. Johnson, *J. Am. Chem. Soc.*, 1957, **29**, 4257; another method is the interaction of Cl_2O and $ReCl_5$ (K. Dehnicke and W. Liese, *Chem. Ber.*, 1977, **110**, 3959).

§ See C. Ringel and G. Boden, *Z. Anorg. Allg. Chem.*, 1972, **393**, 65; these authors also briefly reported $ReO_3(OMe)(HCONMe_2)$ but no details were provided (*Z. Chem.*, 1967, **7**, 68).

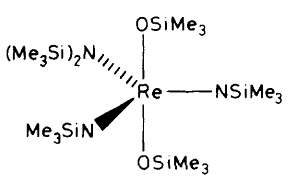


Scheme 2. Synthesis of trioxorhenium carboxylates and related compounds (R = Me, CF$_3$, or Bu^t; R' = Me, CF$_3$, Bu^t, or Ph): (*i*) (RCO)$_2$O in thf; (*ii*) py; (*iii*) PhCO$_2$H; (*iv*) tmen

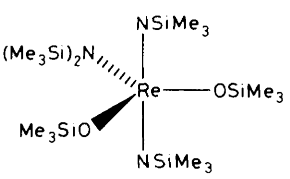
shows a near coincidence of the methyl and methylene tmen protons. A low-field peak (δ 1.53) appears as a shoulder on the adjacent more intense peak at δ 1.50 and these are assigned to the methylene and methyl tmen protons respectively; the high-field peak at δ 0.99 is assigned to the butoxo-protons. Again the ^{13}C-{^{1}H} n.m.r. spectrum has two singlets attributable to the tmen methylene (δ 57.10) and methyl carbons (δ 48.82, $v_{\frac{1}{2}}$ = 8 Hz) as well as the butoxo-methyl (δ 1.39) and unique (δ 31.95) carbons. The assignments were made on the basis of intensity ratios and the gated ^{13}C spectrum.

Methoxo- and butoxo-trioxorhenium(VII) could also be prepared by the interaction of the corresponding trimethylsilyl ether with trioxo(trimethylsiloxo)rhenium(VII) [$ReO_3(OSiMe_3)$, or trimethylsilylperrhenate [5]] in hydrocarbon solvents. Thus addition of the ether to hexane solutions of $ReO_3(OSiMe_3)$ gave a precipitate of $[ReO_3(OMe)]_n$ or a solution of $ReO_3(OBu^t)$, from which the tmen adducts could be prepared as before. The compounds were identical (i.r., ^{1}H and ^{13}C n.m.r., m.p.) to those prepared from ReO_3Cl. Apart from $ReO_3(OSiMe_3)$, the only other d^0 rhenium alkoxides or siloxides are the recently reported $Re(NBu^t)_3(OSiMe_3)$,[3a] $Re_2(NBu^t)_4(OSiMe_3)_4(OReO_3)$,[3a] $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$,[3b] and $Re(CCMe_3)(CHCMe_3)(OSiMe_3)_2$.[3b] Attempts to prepare the analogous phenoxide from ReO_3Cl or $ReO_3(OSiMe_3)$ with either $SiMe_3(OPh)$, NaOPh, or LiOPh failed.

(*Di-isopropylamido*)*trioxorhenium*(VII) *and* [*Bis*(*trimethylsilyl*)*amido*]*bis*(*trimethylsiloxo*)*bis*(*trimethylsilylimido*)*rhenium*(VII).—Treatment of ReO_3Cl with di-isopropylamine in hydrocarbons resulted in the formation of (di-isopropylamido)trioxorhenium(VII), $ReO_3(NPr^i_2)$, and di-isopropylamine hydrochloride. The pale yellow, moisture-sensitive, crystalline material was very soluble in aliphatic, aromatic, and chlorinated hydrocarbons and in ethers. The compound is low-melting (*ca.* 30 °C) and volatile but is thermally unstable, decomposing ($t_{\frac{1}{2}}$ *ca.* 1 d, 20 °C) both in the solid state and in solution, precluding reliable molecular weight and analytical data. The compound was characterised spectroscopically and by the formation of stable adducts with pyridine and tmen. The i.r. spectrum of $ReO_3(NPr^i_2)$ has two bands in the region expected for Re=O vibrations (989 and 950 cm^{-1}) consistent with an all *cis* ReO_3 unit;[4] however the low-frequency band is broadened, presumably by coincidence with another ligand vibration, and may obscure more complex multiplicity. The ^{1}H n.m.r. spectrum has a septet (δ 3.50) and a doublet (δ 0.83) in the required intensity ratio (1 : 6) for these to be assigned to the methyl (high-field resonance) and unique protons of equivalent isopropyl groups. The assignment is supported by the identical coupling constant (J_{H-H} = 6.6 Hz). The ^{13}C-{^{1}H} n.m.r. spectrum has two singlets (δ 59.04 and 22.05). The low-field peak is split into a doublet (J_{C-H} = 139 Hz) in the gated ^{13}C spectrum and is assigned to the *N*-bonded carbon; the high-field peak (quartet, J_{C-H} = 127 Hz) is due to the methyl carbons.



(1b)



(1a)

The addition of pyridine or tmen to solutions of $ReO_3(NPr^i_2)$ enables the ready isolation of the thermally stable, crystalline adducts. Both complexes appear to contain five-co-ordinate rhenium(VII). The orange tmen complex is formulated as $[ReO_3(NPr^i_2)]_2(tmen)$ on the basis of analytical and spectroscopic data. The ^{1}H n.m.r. spectrum has two peaks due to the isopropyl protons (unique proton, δ 3.70, septet, J_{H-H} = 6.5 Hz, relative intensity 4; methyl protons, δ 0.92, doublet, J_{H-H} = 6.5 Hz, relative intensity 24) and two peaks due to the tmen ligand protons (methylene protons, δ 2.54, singlet, relative intensity 4; methyl protons, δ 2.12, singlet, relative intensity 12). The ^{13}C-{^{1}H} n.m.r. is consistent and the resonances are assigned on the basis of the gated ^{13}C spectrum. The spectra do not change significantly upon cooling (−80 °C) or warming (+60 °C). The mass spectrum has a parent ion for the species $ReO_3(NPr^i_2)^+$ (*m*/*e* = 335) with the rhenium isotope pattern. Thus, as both nitrogen atoms in the tmen ligand appear equivalent by spectroscopy the compound evidently has a tmen bridge with $ReO_3(NPr^i_2)$ groups bound to the nitrogen atoms. No definitive structural information can be deduced from the i.r. spectrum, although there are bands in the Re=O region.

The orange-red pyridine (py) adduct has a ^{1}H n.m.r. spectrum consistent with the stoicheiometry $ReO_3(NPr^i_2)(py)$. The pyridine protons give a complex resonance between δ 8.58 and 6.42 (outermost lines) and the isopropyl groups two peaks (unique proton, δ 3.80, septet, J_{H-H} = 6.6 Hz; methyl protons, δ 0.97, doublet, J_{H-H} = 6.6 Hz). The ^{13}C-{^{1}H} n.m.r. spectrum may be assigned on the basis of the gated ^{13}C spectrum (see Table 1). As for the tmen complex, the mass spectrum exhibits a parent ion [*m*/*e* = 335, $ReO_3(NPr^i_2)^+$] due to loss of pyridine from the molecular ion.

Treatment of ReO_3Cl with dimethylamine at low temperatures gave pale yellow solutions similar to those containing $ReO_3(NPr^i_2)$, but the colour is discharged and dark intractable precipitates formed on warming. Addition of pyridine or tmen gave coloured solutions similar to those from $ReO_3(NPr^i_2)$, but again decomposition occurs on warming and dialkylamidorhenium species were not identified. However, the reaction of ReO_3Cl with $Li[N(SiMe_3)_2]$ in diethyl ether produced an intense red solution from which a red, air-stable, crystalline material was isolated. Analytical and spectroscopic data indicate this to be $Re^{VII}[N(SiMe_3)_2](NSiMe_3)_2(OSiMe_3)_2$. The highest ion in the mass spectrum (*m*/*e* 684) has the rhenium isotope pattern and corresponds to the loss of one methyl unit from the molecular ion. The ^{1}H n.m.r. spectrum consists of three equally intense singlets, as does the ^{13}C-{^{1}H} spectrum due to the three non-equivalent $SiMe_3$ sets; the spectrum is unchanged at −90 °C. The i.r. spectrum is consistent with the presence of $SiMe_3$ groups and shows the absence of a terminal Re=O vibration, but a definitive assignment of Re–O, Re–N, or Re=N vibrations is not possible. However, as each $SiMe_3$ set of oxo- and imido-groups is equivalent according to n.m.r. spectra the solution stereochemistry must conform to one of two

Table 1. Hydrogen-1, $^{13}\mathrm{C}$-{$^1\mathrm{H}$}, and gated $^{13}\mathrm{C}$ data of the new rhenium compounds [a]

Compound	$^1\mathrm{H}$	Assignment	$^{13}\mathrm{C}$-{$^1\mathrm{H}$}	Assignment	$^{13}\mathrm{C}$, $J_{\mathrm{C-H}}$
$\mathrm{ReO_3(OBu^t)}$ [b]	−0.10, s	$\mathrm{C(CH_3)_3}$	−0.20	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	q, 120
			29.12	$\mathit{C}\mathrm{(CH_3)_3}$	s
$\mathrm{ReO_3(OBu^t)(tmen)}$	1.53, s, (4)	$\mathrm{(CH_3)_2N(C}\mathit{H}_2\mathrm{)_2N(CH_3)_2}$	57.10	$\mathrm{N(CH_2)_2N}$	t, 136
	1.50, s, (12)	$\mathrm{(C}\mathit{H}_3\mathrm{)_2N(CH_2)_2N(C}\mathit{H}_3\mathrm{)_2}$	48.82	$\mathrm{(CH_3)_2N}$	q, 136
	0.99, s, (9)	$\mathrm{C(CH_3)_3}$	31.95	$\mathit{C}\mathrm{(CH_3)_3}$	s
			1.39	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	q, 118
$\mathrm{ReO_3(OBu^t)(tmen)}$ [b]	2.34, s, (12)	$\mathrm{(C}\mathit{H}_3\mathrm{)_2N(CH_2)_2N(C}\mathit{H}_3\mathrm{)_2}$	57.49	$\mathrm{N(CH_2)_2N}$	t, 136
	1.99, s, (4)	$\mathrm{(CH_3)_2N(C}\mathit{H}_2\mathrm{)_2N(CH_3)_2}$	48.87	$\mathrm{(CH_3)_2N}$	q, 136
			$(\nu_{1/2} = 8\ \mathrm{Hz})$		
	0.39, s, (9)	$\mathrm{C(CH_3)_3}$	30.10	$\mathit{C}\mathrm{(CH_3)_3}$	s
			1.80	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	q, 118
$\mathrm{ReO_3(OMe)}$	3.74, s	$\mathrm{OCH_3}$			
$\mathrm{ReO_3(OMe)(tmen)}$	4.56, s, (3)	$\mathrm{OCH_3}$	65.16	$\mathrm{OCH_3}$	
	2.64, s, (16)	$\mathrm{(C}\mathit{H}_3\mathrm{)_2N(C}\mathit{H}_2\mathrm{)_2N(C}\mathit{H}_3\mathrm{)_2}$	57.41	$\mathrm{N(CH_2)_2N}$	
			49.42	$\mathrm{N(CH_3)_2}$	
$\mathrm{ReO_3(NPr_2^i)}$	3.50, septet, $J_{\mathrm{H-H}} = 6.6$, (1)	$\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$	59.04	$\mathit{C}\mathrm{H(CH_3)_2}$	d, 139
	0.83, d, $J_{\mathrm{H-H}} = 6.6$, (6)	$\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$	22.05	$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$	q, 127
$\mathrm{[ReO_3(NPr^i_2)]_2(tmen)}$ [b]	3.70, septet, $J_{\mathrm{H-H}} = 6.5$, (4)	$\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$	59.16	$\mathit{C}\mathrm{H(CH_3)_2}$	d, 139
	2.54, s, (4)	$\mathrm{(CH_3)_2N(C}\mathit{H}_2\mathrm{)_2N(CH_3)_2}$	55.07	$\mathrm{N(CH_2)_2N}$	t, 135
	2.12, s, (12)	$\mathrm{(C}\mathit{H}_3\mathrm{)_2N(CH_2)_2N(C}\mathit{H}_3\mathrm{)_2}$	45.27	$\mathrm{(CH_3)_2N}$	q, 137
	0.92, d, $J_{\mathrm{H-H}} = 6.5$, (24)	$\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$	21.59	$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$	q, 130
$\mathrm{ReO_3(NPr^i_2)(py)}$ [b]	8.50, m		148.71		
	6.85, m (5)	$\mathrm{C_5H_5N}$	136.54	$\mathrm{C_5H_5N}$	
	6.53, m		123.97		
	3.80, septet, $J_{\mathrm{H-H}} = 6.6$, (2)	$\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$	59.05	$\mathit{C}\mathrm{H(CH_3)_2}$	d, 137
	0.97, d, $J_{\mathrm{H-H}} = 6.6$, (12)	$\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$	21.43	$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$	q, 137
$\mathrm{Re[N(SiMe_3)_2](NSiMe_3)_2}$-$\mathrm{(OSiMe_3)_2}$ [b]	0.55, s, (9)		6.91		
	0.36, s, (9)	$\mathrm{(CH_3)_3Si}$	5.39	$\mathrm{(CH_3)_3Si}$	
	0.26, s, (9)		2.40		
$\mathrm{ReO_3(O_2CMe)(thf)}$	4.01, m, (4)	$\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}}$	191.00	$\mathrm{CH_3}\mathit{C}\mathrm{O_2}$	s
	2.14, s, (3)	$\mathrm{CH_3CO_2}$	72.89	$\overline{\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2O}}$	t, 151
	1.93, m, (4)	$\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}}$	25.48	$\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2O}}$	t, 136
			21.50	$\mathit{C}\mathrm{H_3CO_2}$	q, 131
$\mathrm{ReO_3(O_2CCF_3)(thf)}$	4.00, m, (4)	$\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}}$	161.6,	$\mathrm{F_3C}\mathit{C}\mathrm{O_2}$	q, $J_{\mathrm{C-F}} = 44$
	1.91, m, (4)	$\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}}$	115.5, q ($J_{\mathrm{C-F}} =$ 288 Hz)	$\mathrm{F_3}\mathit{C}\mathrm{CO_2}$	q, $J_{\mathrm{C-F}} = 288$
			71.52	$\overline{\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2O}}$	
			25.53	$\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2O}}$	
$\mathrm{ReO_3(O_2CCMe_3)(thf)}$	4.02, m, (4)	$\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}}$	198.39	$\mathrm{(CH_3)_3C}\mathit{C}\mathrm{O_2}$	s
	1.97, m, (4)	$\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}}$	73.03	$\overline{\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2O}}$	t, 151
	1.20, s, (9)	$\mathrm{(CH_3)_3CCO_2}$	39.80	$\mathrm{(CH_3)_3}\mathit{C}\mathrm{CO_2}$	s
			26.01	$\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2O}}$	t, 135
			25.40	$\mathrm{(}\mathit{C}\mathrm{H_3)_3CCO_2}$	q, 128
$\mathrm{ReO_3(O_2CPh)(thf)}$	7.73, m, (5)	$\mathrm{C_6H_5CO_2}$	182.57	$\mathrm{C_6H_5}\mathit{C}\mathrm{O_2}$	
	4.02, m, (4)	$\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}}$	135.77		
	1.87, m, (4)	$\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}}$	130.35	$\mathit{C}_6\mathrm{H_5CO_2}$	
			128.88		
			127.31		
			72.93	$\overline{\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2O}}$	
			25.38	$\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2O}}$	
$\mathrm{ReO_3(O_2CMe)(py)}$	8.49, m		188.6	$\mathrm{CH_3}\mathit{C}\mathrm{O_2}$	
	7.75, m (5)	$\mathrm{C_5H_5N}$	149.76		
	7.31, m		138.19	$\mathrm{C_5H_5N}$	
	1.80, s, (3)	$\mathrm{CH_3CO_2}$	124.54		
			21.57	$\mathit{C}\mathrm{H_3CO_2}$	
$\mathrm{ReO_3(O_2CCF_3)(py)}$	8.51, m		163.0	$\mathrm{CF_3}\mathit{C}\mathrm{O_2}$	q, $J_{\mathrm{C-F}} = 42$
	7.80, m (5)	$\mathrm{C_5H_5N}$	150.02		
	7.36, m		139.20	$\mathrm{C_5H_5N}$	
			124.93		
			116.0	$\mathit{C}\mathrm{F_3CO_2}$	q, $J_{\mathrm{C-F}} = 288$

Table 1 (*continued*)

Compound	^1H	Assignment	^{13}C-{^1H}	Assignment	^{13}C, J_{C-H}
$ReO_3(O_2CCMe_3)(py)$	8.56, m (5)	C_5H_5N	196.00	$(CH_3)_3C\mathit{C}O_2$	
	7.96, m		150.57	C_5H_5N	
	7.49, m		140.20		
			125.34		
	0.86, s, (9)	$(CH_3)_3CCO_2$			
			39.44	$(CH_3)_3\mathit{C}CO_2$	
			25.70	$(\mathit{C}H_3)_3CCO_2$	
$ReO_3(O_2CPh)(py)$	8.68, m	$C_5\mathit{H}_5N$, $C_6\mathit{H}_5CO_2$	184.50	$C_6H_5\mathit{C}O_2$	
	7.88, m		150.42	C_5H_5N, $\mathit{C}_6H_5CO_2$	
	7.44, m		140.17		
			135.31		
			130.07		
			128.60		
			127.84		
			125.49		
$ReO_3(O_2CMe)(tmen)$	3.04, s, (6)	$(CH_3)N$	174.1	$CH_3\mathit{C}O_2$	s
	2.89, q, (4), 9.1 [c]	$N(CH_2)_2N$	58.02	$N(CH_2)_2N$	t, 141
	2.67, s, (6)	$(CH_3)N$	51.93	$(CH_3)N$	q, 142
	2.16, s, (3)	CH_3CO_2	50.73		
			24.39	$\mathit{C}H_3CO_2$	q, 128
$ReO_3(O_2CCF_3)(tmen)$	3.16, s, (6)	$(CH_3)N$	158.17	$\mathit{C}F_3CO_2$	q, $J_{C-F} = 38.4$
	2.99, q, (4), 5.58 [c]	$N(CH_2)_2N$	115.94	$CF_3\mathit{C}O_2$	q, $J_{C-F} = 290.0$
	2.71, s, (6)	$(CH_3)N$	58.28	$N(CH_2)_2N$	t, 141
			53.16	$(CH_3)N$	q, 139
			51.13	$(CH_3)N$	q, 139
$ReO_3(O_2CCMe_3)(tmen)$	2.91, s, (6)	$(CH_3)N$	180.05	$(CH_3)_3C\mathit{C}O_2$	s
	2.81, s, (4)	$N(CH_2)_2N$	57.52	$N(CH_2)_2N$	t, 149
	2.57, s, (6)	$(CH_3)N$	51.78	$(CH_3)N$	q, 140
			50.27	$(CH_3)N$	q, 140
	1.03, s, (9)	$(CH_3)_3CCO_2$	40.78	$(CH_3)_3\mathit{C}CO_2$	s
			27.84	$(\mathit{C}H_3)_3CCO_2$	q, 127
$ReO_3(O_2CCMe_3)(tmen)$ [d]	3.07, s, (6)	$(CH_3)N$			
	2.91, q, (4), 6.7 [c]	$N(CH_2)_2N$			
	2.73, s, (6)	$(CH_3)N$			
$ReO_3(O_2CPh)(tmen)$	7.67, m, (5)	$C_6H_5CO_2$	168.76	$C_6H_5\mathit{C}O_2$	s
			134.37	$\mathit{C}_6H_5CO_2$	s
	3.13, s, (6)	$(CH_3)N$	131.71		d, 159
	3.06, q, (4), 9.8 [c]	$N(CH_2)_2N$	129.55		d, 162
			128.42		d, 163
	2.75, s, (6)	$(CH_3)N$	58.29	$N(CH_3)_2N$	t, 140
			52.34	$(CH_3)N$	q, 140
			50.91	$(CH_3)N$	q, 140
$ReO_3(O_2CMe)(NC_5H_4OH)$	11.58, s, (1)	$C_5H_4NO\mathit{H}$	174.94	$CH_3\mathit{C}O_2$	
	7.87, m, (2)	$C_5\mathit{H}_4NOH$	155.53	C_5H_4NOH	
	7.05, d, (1)		145.86		
	6.82, t, (1)		123.21		
	2.09, s, (3)	CH_3CO_2	22.16	$\mathit{C}H_3CO_2$	

[a] All chemical shifts (δ) are in p.p.m., referenced to $SiMe_4$. Coupling constants are in Hz. All spectra were recorded in $CDCl_3$ unless otherwise indicated. [b] in C_6D_6. [c] The separation between the outer lines of the AA′BB′ quartet of the tmen CH_2 groups is given after the relative intensity. [d] In CD_2Cl_2.

possible isomers, assuming trigonal-bipyramidal geometry, as in (1a) and (1b). We prefer the arrangement involving *cis* multiple rhenium–nitrogen bonds for which there is a precedent.[3b]

Rhenium imido-compounds have long been known;[6] other compounds containing aryl,[7,*] alkyl,[3a,3b,†] and trimethylsilylimido-groups [3a] are known. Rhenium amido-compounds are rare; there are two poorly characterised compounds, $[ReO(NH_2)_4]_n$[8] and $Re_3Cl_6(NH_2)_3\cdot3NH_3$,[9] $Re(CO)_2(NHCOR)(PPh_3)$,[10] and the compounds $Re(NHPh)(CO)_2(PR_3)_3$[7] and $ReO[N(SiMe_3)_2]_3$.[1] The present complex, $ReO_3(NPr^i_2)$, appears to be the first authentic dialkylamido-compound of rhenium(VII). No new compounds have been isolated from the interactions of $ReO_3(NPr^i_2)$ and $Re[N(SiMe_3)_2](NSiMe_3)_2(OSiMe_3)_2$ with H_2, CO, or CO_2 at 10 atm (*ca.* 10^6 Pa) pressure.

Trioxorhenium(VII) *Carboxylates and their Adducts.*—Treatment of dirhenium heptaoxide with carboxylic anhydrides in tetrahydrofuran (thf) allows the isolation of the corresponding carboxylatotrioxorhenium(VII) thf solvates, $ReO_3(O_2CR)(thf)$ (R = Me, CF_3, or CMe_3), as colourless, moisture-sensitive crystals. As the compounds were thermally unstable ($t_{\frac{1}{2}}$ *ca.* 7 d, 20 °C) reproducible analytical data were not obtained. In all cases bands in the i.r. spectra were consistent with chelating carboxylate groups [ν_{sym}(O–C–O): R = CH_3, 1 480; R = CF_3, 1 470; R = CMe_3, 1 485 cm^{-1}]

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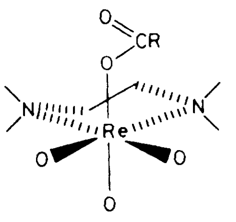
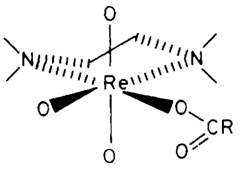
[*] Examples are: $ReMe_3(NPh)(PMe_3)_2$ (K. W. Chiu, W. K. Wong, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *Polyhedron*, 1982, **1**, 31); $ReX_3(NR')(PR_3)_2$ (X = halogen, R = alkyl, R′ = aryl) (J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc. A*, 1970, 2239 and refs. therein); $[Re(NPh)(Et_2NCS_2)_2]_2O$ (J. F. Rowbottom and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 826); $ReCl_3(NR')(CO)(PPh_3)$ (R′ = aryl) (G. La Monica and S. Cenini, *Inorg. Chim. Acta*, 1978, **29**, 183).

[†] $[Re(NMe)(NH_2Me)_4Cl]^{2+}$: R. S. Shandles and R. K. Murmann, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1869.



(2a)



(2b)

and Re=O vibrations, hence the compounds contain six-co-ordinate rhenium. We are unable to differentiate between possible *mer* and *fac* isomers owing to the presence of bands due to thf in the spectra. For $ReO_3(O_2CCF_3)(thf)$, there is a single resonance in the ^{19}F n.m.r. spectrum (δ 2.0). The ^1H and ^{13}C spectra of each of the compounds show similar features and so only the spectra of the acetate, $ReO_3(O_2CMe)(thf)$, will be discussed. The ^1H spectrum has two complex resonances of at least seven lines (δ 4.01, separation of outer lines 13.3 Hz, relative intensity 4) and five lines (δ 1.93, separation of outer lines 13.5 Hz, relative intensity 4) due to the thf protons and a singlet (δ 2.14, relative intensity 3) due to the acetate protons. The gated ^{13}C n.m.r. spectrum has four peaks due to thf carbons (δ 72.89, triplet, J_{C-H} = 151 Hz; δ 25.48, triplet, J_{C-H} = 136 Hz), the acetate methyl (δ 21.5, quartet, J_{C-H} = 131 Hz), and carboxylate (δ 191.0, singlet) carbons. The mass spectra have parent ions due to $ReO_3(O_2CR)^+$ ($R = Me$, $m/e = 294$: $R = CF_3$, $m/e = 348$) or due to loss of one methyl unit from this ion ($R = CMe_3$, $m/e = 321$). Treatment of solutions of the thf adducts with tmen or pyridine (L) gave colourless, crystalline thermally stable (20 °C) adducts, $ReO_3(O_2CR)L$.

The spectroscopic properties of the carboxylate ligands in the pyridine adducts $ReO_3(O_2CR)(py)$ ($R = Me$, CF_3, CMe_3, or Ph) are similar to those in the thf compounds, indicating replacement of thf by py and the presence of chelating carboxylate groups. Of interest are the ^{13}C n.m.r. chemical shifts of the carboxylate carbons (RCO_2, R = Me, δ 188.6; R = CF_3, δ 163.0; R = CMe_3, δ 196.0). The ^1H n.m.r. spectrum (25 °C) of $ReO_3(O_2CMe)(py)$ with excess pyridine added (*ca.* 10 mol %) is essentially identical to that of $ReO_3(O_2CMe)(py)$. On cooling, separate resonances for free and co-ordinated pyridine are observed as shown by the low-field multiplet (δ 8.57, 25 °C) appearing as a superimposition of two such multiplets at −20 °C (coalescence *ca.* −15 °C) with a separation of 2.2 Hz between their midpoints. Hence pyridine is labile, exchanging rapidly at 25 °C in solution. The tmen complexes, however, have unidentate RCO_2 groups according to the i.r. bands [ν(C=O): R = Me, 1 658; R = CF_3, 1 730; R = CMe_3, 1 668 cm^{-1}]. The ^1H n.m.r. spectrum of the acetate has three singlets [δ 3.04 (relative intensity 6), 2.67 (6), and 2.16 (3)] and a second-order AA′BB′ quartet [δ 2.89, relative intensity 4, separation between outer lines, 9.1 Hz] with intensity between the more intense inner lines. On the basis of intensity and by comparison with the spectrum of the trifluoroacetate, we assign the high-field singlet to the acetate protons. The ^{13}C n.m.r. spectrum has two resonances assigned to non-equivalent pairs of tmen methyl carbons (δ 51.93, quartet, J_{C-H} = 142 Hz; 50.73, quartet, J_{C-H} = 142 Hz), one equally intense resonance for the tmen methylene carbons (δ 58.02, triplet J_{C-H} = 141 Hz) as well as acetate methyl (δ 24.39, quartet, J_{C-H} = 128 Hz) and carboxylate carbons (δ 174.1, singlet). The nature of these spectra is similar for the analogous trifluoroacetate, pivalate, and benzoate compounds (see below) and are consistent with a *fac* configuration of oxo-ligands as shown in (2a) where the tmen ligand is undergoing rapid λδ ring inversion. Low-temperature ^{13}C n.m.r. studies did not resolve the static spectrum, however, as low solubility precluded measurements below the low coalescence temperatures involved (acetate −97, pivalate *ca.* −95 °C). High-temperature ^1H n.m.r. indicated that ligand dissociation occurs as the tmen methyl protons coalesce to a single peak (105 °C for the acetate). The n.m.r. behaviour is consistent with well studied λδ ring-inversion processes in similar octahedral complexes.* For the stereochemistry to be *mer* as in (2b), an accidental n.m.r. coincidence of non-equivalent methylene carbons must be invoked, unless the complex is rapidly fluxional on the n.m.r. time-scale over the temperature range studied. We prefer the *fac* assignment.

Carboxylate Exchange.—Although $ReO_3(O_2CPh)(thf)$ could be prepared in a manner similar to that for the acetate it was more conveniently obtained from the acetate by exchange in diethyl ether. The compound appears to be somewhat more thermally stable than analogous alkyl carboxylates but cannot be stored indefinitely at ambient temperature. It was characterised spectroscopically and by the formation of thermally stable adducts with pyridine and tmen. The ^1H n.m.r. has two complex resonances (at least five lines each) attributable to thf protons [δ 4.02, relative intensity 4, separation of outer peaks 13.4 Hz; δ 1.87, relative intensity 4, separation of outer peaks 13.2 Hz] and a complex resonance due to the phenyl protons in two areas [δ 7.32—7.79 and 7.96—8.14, total intensity 5]. In the $^{13}C-\{^1H\}$ n.m.r. spectrum, resonances due to the carboxylate carbon (δ 182.6) as well as phenyl and thf carbons are seen. The i.r. spectrum has bands attributable to aromatic ring vibrations [ν(C ⋯ C) = 1 600 cm^{-1}] and symmetric (CO_2) stretches (1 508 cm^{-1}); bands due to ν(Re=O) cannot be unequivocally assigned due to the complex nature of the fingerprint region. The spectra are consistent with a chelating carboxylate group. The mass spectrum has a weak parent ion due to the species ReO_3Ph^+ ($m/e = 312$), evidently formed by decarboxylation of the benzoate, as well as other intense ions ($PhCO_2H^+$, Ph^+, $C_4H_4O^+$) in the fragmentation pattern. Similar features are observed in the mass spectra of the tmen and py adducts both of which were characterised by analysis and spectra. The pyridine adduct is analogous to the thf complex [i.r.: ν(C ⋯ C) = 1 601 and 1 610, ν_{sym}(O–C–O) = 1 507 cm^{-1}]. The ^1H n.m.r. indicates coincident pyridine and phenyl proton resonances (δ 7.20—8.74). The tmen complex has unidentate carboxylate ligands as expected [i.r.: ν(C=O) = 1 662 cm^{-1}]. The ^1H n.m.r. spectrum (similar to that of the acetate above) has the AA′BB′ quartet (methylene protons, δ 3.06, separation of highest field line from centre, 4.9 Hz) as a shoulder on the lower field singlet of the two (δ 3.13 and 2.75) assigned to the methyl protons. Resonances due to the carboxylate carbon (δ 168.8) phenyl, tmen methyl, and methylene carbons are observed.

If, however, $ReO_3(O_2CMe)(thf)$ is treated with 2-hydroxypyridine (NC_5H_4OH) in ether or chlorohydrocarbon solvents, exchange is not observed and the adduct $ReO_3(O_2CMe)(NC_5H_4OH)$ can be isolated. The i.r. has bands for free hydroxy [ν(O–H) = 3 360 cm^{-1}] and unco-ordinated carbonyl groups [ν(C=O) = 1 645 cm^{-1}] as well as bands due to oxorhenium and ligand vibrations. Analytical data and n.m.r. spectra are consistent with the formulation; thus the hydroxyl proton appears at δ 11.58 and the acetate methyl protons at δ 2.09 in the ^1H n.m.r. There are also resonances due to the

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* For example in $Mo(CO)_4(tmen)$ coalescence occurs at −94 °C in the ^{13}C n.m.r. spectrum (C. J. Hawkins, R. M. Peachey, and C. L. Szoredi, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 881). For other examples, see C. J. Hawkins and J. A. Palmer, *Coord. Chem. Rev.*, 1982, **44**, 1.

Table 2. Analytical data for rhenium compounds

Compound	M.p. (θ_c/°C)	Analysis[a] (%)			
		C	H	N	O
$ReO_3(OBu^t)(tmen)$	142—143	27.6 (28.4)	5.7 (5.9)	6.5 (6.6)	15.6 (15.1)
$[ReO_3(OMe)]_n$	decomp.	4.5 (4.5)	1.0 (1.1)		23.3 (24.1)
$ReO_3(OMe)(tmen)$	114—116	21.6 (22.1)	4.5 (5.0)	7.5 (7.4)	16.3 (16.8)
$[ReO_3(NPr^i_2)]_2(tmen)$	72—73	27.6 (27.6)	5.6 (5.6)	6.8 (7.1)	12.5 (12.2)
$ReO_3(NPr^i_2)(py)$	79—80	31.7 (32.0)	4.7 (4.6)	6.5 (6.8)	11.7 (11.6)
$Re[N(SiMe_3)_2](NSiMe_3)_2(OSiMe_3)_2$	168—170	30.7 (30.9)	7.8 (7.7)	6.0 (6.0)	4.3 (4.6)
$ReO_3(O_2CMe)(py)$	113—114	22.7 (22.5)	2.2 (2.1)	3.8 (3.8)	21.1 (21.4)
$ReO_3(O_2CMe)(tmen)$	146—147	23.3 (23.5)	4.7 (4.7)	6.8 (6.9)	19.4 (19.6)
$ReO_3(O_2CCF_3)(py)$[b]	45—50 (decomp.)	19.8 (19.7)	1.2 (1.1)	3.3 (3.3)	18.6 (18.9)
$ReO_3(O_2CCF_3)(tmen)$[c]	167—169	20.8 (20.7)	3.5 (3.5)	6.0 (6.0)	17.4 (17.3)
$ReO_3(O_2CCMe_3)(py)$	175—176	28.7 (29.0)	3.4 (3.4)	3.3 (3.4)	19.5 (19.3)
$ReO_3(O_2CCMe_3)(tmen)$	138—139	29.5 (29.3)	5.6 (5.5)	6.2 (6.2)	17.5 (17.7)
$ReO_3(O_2CPh)(py)$	155—156	33.1 (33.2)	2.2 (2.3)	3.1 (3.2)	18.7 (18.4)
$ReO_3(O_2CPh)(tmen)$	149—150	33.3 (33.1)	4.50 (4.45)	6.02 (5.95)	16.7 (17.0)
$ReO_3(O_2CMe)(NC_5H_4OH)$	112—113	21.7 (21.6)	2.2 (2.1)	3.6 (3.6)	

[a] Calculated values are given in parentheses. [b] F, 13.1 (13.4%). [c] F, 11.9 (12.3%).

pyridine protons. The ^{13}C n.m.r. has a resonance assigned to the carboxylate carbon at δ 174.94 and others due to pyridine carbons and the acetato-methyl carbon (see Table 1). The data suggest the complex is similar to the analogous tmen compound with unidentate carboxylate and chelating 2-hydroxypyridine ligands. This observation is corroborated by the ^{13}C n.m.r. chemical shift of the carboxylate carbon. If the chemical shifts of the carboxylate carbons in the py or thf adducts are compared to those in the tmen (or the unique 2-hydroxypyridine) adducts, a consistent relative upfield shift in those complexes containing unidentate carboxylate groups (as shown by i.r.) is evident (see Table 1). This 'co-ordination chemical shift' effect is presumably due to the deshielding effect on the carboxylate carbon upon co-ordination of both carboxylate oxygen atoms.

The preparation of transition-metal oxo-carboxylates from a metal oxide and carboxylic anhydride is a well known[11] procedure. For rhenium there appear to be only two structurally characterised[12] oxo-carboxylates, namely $Re_2(\mu\text{-}O)(\mu\text{-}O_2CR)(\mu\text{-}Cl)Cl_4(PPh_3)_2$ and $Re_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2(\mu\text{-}Cl)Cl_2(PPh_3)_2$. Others[13] appear to be perrhenate salts of carboxylate cations.[14]

Experimental

Microanalyses were by Pascher, Bonn, and Imperial College Laboratories. Spectrometers were as follows: JEOL FX90Q (^1H n.m.r., 89.55 MHz; ^{13}C n.m.r., 22.51 MHz), Perkin-Elmer 683 (i.r. spectra in Nujol mulls), and VG Micromass 7070 or Kratos Ms 25 (mass spectra). All operations were performed under dry, oxygen-free nitrogen or *in vacuo*. Ether and hydrocarbon solvents were refluxed over sodium benzophenone ketyl, dichloromethane and acetonitrile over calcium hydride, and all solvents were distilled immediately prior to use. Di-isopropylamine and bis(trimethylsilyl)amine were distilled from the corresponding sodium amide; tmen was distilled from sodium. Liquid carboxylic acids were refluxed with and fractionally distilled from the corresponding carboxylic anhydride. Liquid carboxylic anhydrides were fractionally distilled. Benzoic acid and benzoic anhydride were used directly. Dirhenium heptaoxide was prepared by the literature procedure[15] except that oxygen was passed over the heated metal in a horizontal tube allowing quantities of *ca.* 20 g to be made; literature methods for ReO_3Cl[1] and $ReO_3(OSiMe_3)$[5] were used. The silylethers Me_3SiOR were prepared by treating $SiMe_3Cl$ with the corresponding sodium alkoxide or phenoxide in diethyl ether followed by distillation (R = Me, b.p. 50 °C; R = CMe_3, b.p. 97.5 °C; R = Ph, b.p. 178 °C). Analytical data are collected in Table 2.

Preparation of t-Butoxotrioxorhenium(VII).—(*a*) *From* ReO_3Cl. To a solution of ReO_3Cl (0.25 g, 0.9 mmol) in hexane (20 cm^3) was added Me_3SiOBu^t (0.16 cm^3, 1.5 mmol). The yellow solution was stirred (0.5 h). The resulting colourless solution was concentrated to *ca.* 5 cm^3 *in vacuo*, filtered and cooled (−20 °C). The colourless needles were collected, washed with cold hexane (3 cm^3, −20 °C) and rapidly dried *in vacuo*. The crystals were thermally unstable, becoming black within minutes at ambient temperatures. They are stable for weeks at −20 °C. Yield 0.25 g, 87% based on ReO_3Cl. The compound is very soluble in aliphatic, aromatic, and chlorinated hydrocarbons as well as ethers. I.r.: 1 259s, 1 150w, 1 005s,br, 965s,br, 915s,br, 840s,br, 810s,br, 759s, 735m, 638m, and 310m,br cm^{-1}.

(*b*) *From* $ReO_3(OSiMe_3)$. To a solution of $ReO_3(OSiMe_3)$ (1 g, 3.1 mmol) in hexane (30 cm^3) was added Me_3SiOBu^t (1.20 cm^3, 6.2 mmol) and stirred (24 h). The colourless solution was filtered and the colourless needles isolated as above, or used directly for the preparation of the tmen adduct. Yield 0.81 g, 85% based on $ReO_3(OSiMe_3)$. The product is identical to that from ReO_3Cl (i.r. and n.m.r. data).

t-Butoxotrioxo(NNN′N′-*tetramethylethylenediamine*)-*rhenium*(VII).—To the filtered colourless solution of $ReO_3(OBu^t)$ obtained above was added, with vigorous stirring, tmen (1 cm^3, 6.6 mmol) and the resulting white suspension stirred (0.5 h). The solid was collected, washed with hexane (2 × 10 cm^3) and recrystallised from CH_2Cl_2–hexane mixtures by extraction into CH_2Cl_2 (20 cm^3), filtration, concentration (to *ca.* 10 cm^3) and addition of hexane followed by cooling (−20 °C). The colourless needles were collected, washed with hexane (2 × 5 cm^3) and dried *in vacuo*. Yield 1.2 g, 92% based on $ReO_3(OSiMe_3)$. The compound is soluble in aromatic and chlorinated hydrocarbons and ethers. I.r.: 1 310w, 1 288m, 1 255s, 1 243s, 1 192w, 1 180m, 1 168w, 1 150w, 1 127m, 1 100w, 1 065m, 1 048m, 1 021m, 1 008m, 970s,br, 910s,br, 880s,br, 832s,br, 805s,br, 771s, 750s, 688m, 632m, 605w, 566w, 519m, 492m, 467m,br, 391s, and 365m cm^{-1}.

Preparation of Methoxotrioxorhenium(VII).—(*a*) *From* ReO_3Cl. To a solution of ReO_3Cl (1 g, 3.7 mmol) in hexane (20 cm^3) was added Me_3SiOMe (2 cm^3, 15 mmol) and the resulting white precipitate immediately filtered off, washed with hexane (5 cm^3) and dried *in vacuo*. The precipitate was extracted into CH_2Cl_2 (2 × 20 cm^3), filtered, concentrated (to *ca*. 10 cm^3 or until saturated) and cooled (−20 °C). The colourless prisms were collected, washed with hexane (5 cm^3) and dried *in vacuo*. Yield 0.73 g, 74% based on ReO_3Cl. The compound is insoluble in hydrocarbons, sparingly soluble in diethyl ether, and soluble in thf and chlorinated hydrocarbons. I.r.: 1 260w, 1 005m, 975s, 965s, 945s, 919m, 904m, 832s, 720w, 580s, 393w, 385w, 368m, 356w, and 322m cm^{-1}.

(*b*) *From* $ReO_3(OSiMe_3)$. The procedure was as above but $ReO_3(OSiMe_3)$ (1 g; 20 cm^3 of hexane, 1.7 cm^3 of Me_3SiOMe) was used. The product was identical to that from ReO_3Cl (i.r. and n.m.r. data). Yield 0.71 g, 87% based on $ReO_3(OSiMe_3)$.

Methoxotrioxo(NNN′N′-*tetramethylethylenediamine*)*rhenium*(VII).—The initial white precipitate obtained above was dissolved in thf (30 cm^3) and tmen (1 cm^3, 6.6 mmol) was added. The solution was stirred (0.5 h) concentrated (to *ca*. 15 cm^3) and cooled. The colourless prisms were collected, washed with hexane and dried *in vacuo*. Yield 1.00 g, 85% based on $ReO_3(OSiMe_3)$. The compound is soluble in chlorinated hydrocarbons and thf. I.r.: 1 302m, 1 293m, 1 245w, 1 193w, 1 165w, 1 153w, 1 127w, 1 098w, 1 070m, 1 050m, 1 038m,br, 1 012s, 1 010s, 962m, 931s, 913s, 892s, 880m, 829w, 609w, 541m, 511m, 492w, and 467w cm^{-1}.

(*Di-isopropylamido*)*trioxorhenium*(VII).—To a cold (−78 °C) solution of ReO_3Cl (2 g, 7.4 mmol) in diethyl ether (50 cm^3) was added di-isopropylamine (2.1 cm^3, 15 mmol) with vigorous stirring. A pale precipitate separated and the supernatant was orange-brown, The suspension was allowed to warm to ambient temperature with continued stirring when the supernatant was pale orange or yellow. Volatile materials were removed *in vacuo* and the residue extracted into hexane (3 × 20 cm^3), filtered, concentrated until saturated (to *ca*. 5 cm^3) and cooled (−20 °C). The canary yellow plates were separated, washed with cold hexane (2 cm^3, −78 °C) and dried *in vacuo*. The combined filtrate and washings were further concentrated and cooled to yield a further crop. Combined yield 1.93 g, 78% based on ReO_3Cl; m.p. 25—30 °C. The yield is depressed by performing the reaction in hexane. The compound is very soluble in aliphatic and aromatic hydrocarbons, ethers, and chlorinated hydrocarbons. I.r.: 1 190w, 1 166m, 1 145m,br, 1 104m, 1 016w, 989s, 950s,br, 882w, 841w, 801w, 540w, 509w, and 321m,br cm^{-1}.

(*Di-isopropylamido*)*trioxo*(NNN′N′-*tetramethylethylenediamine*)*rhenium*(VII).—To a solution of $ReO_3(NPr^i_2)$ (0.5 g, 30 mmol) in diethyl ether (20 cm^3) was added tmen (1 cm^3, 6.6 mmol) with vigorous stirring. The pale yellow solution immediately became orange-red. After stirring (0.5 h) the volatile materials were removed *in vacuo* and the orange residue extracted into hexane (2 × 20 cm^3), filtered, concentrated (to *ca*. 15 cm^3) and cooled (−20 °C). The orange needles were collected, washed with cooled (2 cm^3, −78 °C) hexane and dried *in vacuo*. The combined supernatant and washings yielded a further crop upon concentration and cooling. The combined yield was essentially quantitative. The compound is readily soluble in hydrocarbons, ethers, and chlorinated hydrocarbons and sublimes (60 °C, 10^{-3} mmHg) with minimal decomposition. I.r.: 1 310w, 1 265w, 1 197m, 1 162m, 1 157m, 1 136m, 1 121s, 1 113s, 1 104s, 1 027m, 1 009w, 998m, 960m, 930s, 912s, 894s, 873m, 848m, 820m, 803m, 731w, 572m, 520s, 458m, 342s, 335s, 320m, and 292w cm^{-1}.

(*Di-isopropylamido*)*trioxo*(*pyridine*)*rhenium*(VII).—A procedure similar to that above was followed except that after the addition of pyridine (1 cm^3, 12.4 mmol) to a solution of $ReO_3(NPr^i_2)$ (0.5 g, 3 mmol) in diethyl ether (20 cm^3) and stirring (0.5 h), the product was isolated by concentrating (to *ca*. 10 cm^3) and cooling (−20 °C) the solution. The orange-red needles were collected, washed with hexane (2 × 5 cm^3) and dried *in vacuo*. The combined washings and supernatant were concentrated and cooled to give a further crop. The combined yield was quantitative. The compound is soluble in chlorinated and aromatic hydrocarbons and ethers, and sparingly soluble in hexane. I.r.: 3 055w, 1 603s, 1 305w, 1 215m, 1 194m, 1 160s,br, 1 134m, 1 110s, 1 075m, 1 043m, 1 017m, 990m, 961m, 933s, 890s,br, 872s, 844s, 775s, 712s, 660w, 638m, 563m, 525m, 460m, 339s, 323m, and 282w cm^{-1}.

Preparation of [*Bis*(*trimethylsilyl*)*amido*]*bis*(*trimethylsiloxo*)*bis*(*trimethylsilylimido*)*rhenium*(VII).—(*a*) *From* ReO_3Cl. To a solution of ReO_3Cl (0.5 g, 1.9 mmol) in diethyl ether (20 cm^3), held at −78 °C, was slowly added a solution of $Li[N(SiMe_3)_2]$ (6 cm^3, 1 mol dm^{-3} in Et_2O, 6 mmol). The solution, which became bright red, was warmed to ambient temperature and stirred (0.5 h). Volatile materials were removed *in vacuo* and the dark red residue extracted into hexane (50 cm^3), filtered, and the filtrate washed (by vigorous stirring) with degassed water (20 cm^3, 10 min). The mixture was allowed to settle, cooled (−20 °C) to freeze the water, filtered, and the red solution dried over molecular sieves (type 4A, 24 h). The solution was concentrated *in vacuo* (to *ca*. 5 cm^3 or until saturated) and cooled (−78 °C) to give red prisms which were collected, washed with cold hexane −78 °C, 2 cm^3) and dried *in vacuo*. The combined washings and filtrate were concentrated and cooled to give a further crop. Combined yield 0.87 g, 67% based on ReO_3Cl. The compound is very soluble in aliphatic, aromatic, or chlorinated hydrocarbons and ethers, slightly soluble in acetonitrile and acetone, and insoluble in water. I.r. (KBr disc): 2 960m, 2 925m, 2 855w, 1 260s, 1 246s, 1 099m, 1 020m,br, 980w, 902s,br, 860m, 836s,br, 773m, 693m, 659s, 437m, 368w, and 329m cm^{-1}.

(*b*) *From* $ReO_3(OSiMe_3)$. A procedure similar to that above was employed, except for the use of $ReO_3(OSiMe_3)$ (3 g, 9.3 mmol) in diethyl ether (50 cm^3) and $Li[N(SiMe_3)_2]$ (30 cm^3, 1 mol dm^{-3} in Et_2O, 30 mmol). Yield (two crops) 59%.

Carboxylatotrioxorhenium(VII) *Compounds*.—The procedures for the preparation of $ReO_3(O_2CMe)(thf)$, $ReO_3(O_2CMe)(tmen)$, and $ReO_3(O_2CMe)(py)$ are described. The trifluoroacetate and pivalate were obtained similarly.

(*a*) $ReO_3(O_2CMe)(thf)$. Tetrahydrofuran (60 cm^3) was added to yellow crystalline Re_2O_7 (2.42 g, 10 mmol) and the mixture stirred until all the oxide had dissolved. To this was added acetic anhydride (1.9 cm^3, 20 mmol) and the solution stirred (12 h). The volatile materials were removed *in vacuo* and the off-white crystalline residue extracted into diethyl ether (60 cm^3; warming may be necessary), filtered, concentrated until saturated (to *ca*. 30 cm^3, with warming to redissolve precipitated product) and cooled (−20 °C). The white needles were collected, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. The supernatant and washings were combined, concentrated and cooled to give a further crop. Combined yield 3.18 g, 87% based on Re_2O_7. I.r.: 1 480s,br, 1 347s, 1 245m, 1 174m, 1 073m, 1 044m, 1 018s, 976s, 965s, 940s,br, 860s,br, 713s,br, 622s, 381s, and 361s cm^{-1}.

$ReO_3(O_2CCF_3)(thf)$. Yield 79%, m.p. >50 °C (decomp.). I.r.: 1 470s, 1 350m, 1 333m, 1 285w, 1 250w, 1 235w, 1 190w, 1 160m, 1 035w, 1 000s, 943s, 936s, 920s, 862, 828s,br, 718m, and 375m cm^{-1}.

$ReO_3(O_2CCMe_3)(thf)$. Yield 72%, m.p. 98—100 °C. I.r.: 1 902w, 1 869w, 1 699w, 1 485s,br, 1 342m, 1 314w, 1 297w, 1 212s, 1 174m, 1 145w, 1 035m, 1 012s, 969s, 930s,br, 852s,br, 818s, 789m, 720m, 675w, 623s, 437m, 389w, 369m, 348m, and 312m cm^{-1}.

(*b*) $ReO_3(O_2CR)(py)$ *and* $ReO_3(O_2CR)(tmen)$. The preparation of the pyridine and tmen acetate complexes is described; the procedures for the trifluoroacetate, pivalate, and benzoate are similar. The procedures for the tmen complexes are also analogous to those for the pyridine complexes.

To a solution of $ReO_3(O_2CMe)(thf)$ (1.1 g, 3 mmol) in diethyl ether (30 cm^3) was added either tmen (1 cm^3, 6.6 mmol) or pyridine (0.5 cm^3, 6 mmol), producing a white crystalline precipitate. After stirring (0.5 h) volatile materials were removed *in vacuo* and the residue extracted into dichloromethane (20 cm^3) which was filtered, concentrated (to *ca.* 10 cm^3), saturated by the addition of hexane, and cooled (−20 °C). The colourless needles were collected, washed with diethyl ether (5 cm^3) and dried *in vacuo*. The combined supernatant and washings yielded a further crop upon concentration and cooling. The initial precipitate obtained (from Et_2O) was found to be of sufficient purity (^1H n.m.r.) for most purposes. Yields of all complexes >90%. I.r.: $ReO_3(O_2CMe)(py)$, 1 609m, 1 588m,br, 1 226w, 1 160w, 1 078m, 1 053m, 1 028w, 979m, 969m, 930s,br, 884m,br, 776m, 732m, 719m, 707m, 653m, 632w, 465w, 386s, 360w, 336w, and 279w cm^{-1}; $ReO_3(O_2CMe)(tmen)$, 1 658s, 1 285s, 1 270s,br, 1 190w, 1 150w, 1 123w, 1 066w, 1 043w, 1 011m, 1 003m, 957m, 948m, 910s,br, 807m, 769m, 726w, 663m, 661w, 540w, 524w, 460w, 449w, 409w, 378s, 327w, and 289w cm^{-1}; $ReO_3(O_2CCF_3)(py)$, 1 610s, 1 230w, 1 197m,br, 1 159w, 1 080m, 1 051m, 1 030m, 975m, 965s, 940s, 929s,br, 878m,br, 772m, 771m, 650m, 611m, and 571w cm^{-1}; $ReO_3(O_2CCF_3)(tmen)$, 1 730s,br, 1 282w, 1 200s,br, 1 172s,br, 1 126s,br, 1 039w, 1 002m, 992m, 944s, 912s,br, 840m, 820m, 779w, 764m, 722s, 611m, 524m, and 449w cm^{-1}; $ReO_3(O_2CCMe_3)(py)$, 1 609s, 1 490s,br, 1 235m, 1 226m, 1 176w, 1 157m, 1 074m, 1 052m, 1 023m, 975m, 947s, 929s,br, 830m, 800m, 772m, 733m, 706m, 651m, 636m, 447m, 379m, 361w, and 328m cm^{-1}; $ReO_3(O_2CCMe_3)(tmen)$, 1 668s, 1 362m, 1 289s, 1 269w, 1 188s, 1 103w,br, 1 070w, 1 051w, 1 019m, 965m, 953s, 934s, 911s, 816s, 778w, 733w, 627m, 580w, and 532w cm^{-1}; $ReO_3(O_2CPh)(py)$, 1 698m, 1 610s, 1 601s, 1 540m, 1 507s, 1 323w, 1 292w, 1 219m, 1 185w, 1 160w, 1 102w, 1 073m, 1 054w, 1 035w, 1 028m, 972m, 967m, 935s,br, 890m,br, 780m, 732s, 709m, 691m, 650m, and 496m cm^{-1}; $ReO_3(O_2CPh)(tmen)$, 1 662s, 1 625w, 1 582w, 1 318s, 1 299s, 1 179w, 1 159w, 1 128m, 1 079m, 1 052w, 1 029w, 1 018w, 1 007w, 960m, 951s, 932s, 913s, 813m, 776m, 724s, 691m, 600w, 533w, 509w, 467w, 418w, 386m, and 334 cm^{-1}.

Reactions of $ReO_3(O_2CMe)(thf)$ *with Benzoic Acid and 2-Hydroxypyridine.*—(*a*) *Benzoatotrioxo*(*tetrahydrofuran*)-*rhenium*(VII). To a solution of $ReO_3(O_2CMe)(thf)$ (1 g, 2.7 mmol) in diethyl ether (30 cm^3) was added benzoic acid (0.33 g, 2.7 mmol) and the solution stirred (24 h). The colourless solution was evaporated to dryness *in vacuo* and the residue extracted into diethyl ether (2 × 20 cm^3), filtered, concentrated (to *ca.* 15 cm^3) and cooled (−20 °C). The colourless prisms were collected, washed with light petroleum (5 cm^3) and dried *in vacuo*. Concentration and cooling of the supernatant provided a further crop; the combined yield was quantitative. The compound is soluble in chlorinated hydrocarbons, thf, and diethyl ether, but insoluble in hydrocarbons. I.r.: 1 697m, 1 600s, 1 508s, 1 481s, 1 347m, 1 328m, 1 313m, 1 291m, 1 187m, 1 104w, 1 079m, 1 031s, 981s, 973w, 945s,br, 892s,br, 874s, 712m, 697m, 503s, 383m, 366m, 332m, and 284m cm^{-1}.

(*b*) *Acetato*(*2-hydroxypyridine*)*trioxorhenium*(VII). The procedure was as above but 2-hydroxypyridine (0.26 g, 2.7 mmol) was used. The white prisms were isolated from diethyl ether and could be recrystallised from thf–hexane or dichloromethane–hexane. The yield was quantitative. An identical product was isolated using a 100% excess of 2-hydroxypyridine. The compound is soluble in thf, diethyl ether, chlorinated hydrocarbons and is insoluble in hydrocarbons. I.r.: 3 360m, 1 905w, 1 873w, 1 770w, 1 645s,br, 1 589s, 1 535m, 1 270m, 1 240w, 1 168m, 1 155m, 1 121w, 1 098m, 1 049m, 1 022m, 1 001s, 968m, 909s,br, 863m, 769s, 721s, 619m, 598s, 559m, 531s, 510s, 373s, 357s, 323m, and 300m cm^{-1}.

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References

1 P. G. Edwards, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 2467.
2 R. H. A. Bosma, G. C. N. Van den Aardweg, and J. C. Mol, *J. Organomet. Chem.*, 1983, **255**, 159 and refs. therein.
3 (*a*) See, for example, W. A. Nugent, *Inorg. Chem.*, 1983, **22**, 965; (*b*) D. S. Edwards, L. V. Biondi, J. W. Ziller, M. R. Churchill, and R. R. Schrock, *Organometallics*, 1983, **2**, 1505.
4 I. R. Beattie and P. J. Jones, *Inorg. Chem.*, 1979, **18**, 2318.
5 H. Schmidt and H. Schmidbauer, *Chem. Ber.*, 1959, **92**, 2667.
6 J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.
7 K. W. Chiu, W. K. Wong, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *Polyhedron*, 1982, **1**, 37.
8 D. A. Edwards and R. T. Ward, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 89.
9 D. A. Edwards and R. T. Ward, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1043.
10 G. LaMonica, S. Cenini, F. Porta, and M. Pizzotti, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 1777.
11 R. C. Mehrotra and R. Bohra, 'Metal Carboxylates,' Academic Press, New York, 1983.
12 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' Wiley, New York, 1982.
13 F. Taha and G. Wilkinson, *J. Chem. Soc.*, 1963, 5406.
14 G. Calvo, N. C. Jayadevan, C. J. L. Lock, and R. Restivo, *Can. J. Chem.*, 1970, **48**, 219.
15 A. D. McLaven, J. N. Fowle, W. Bricknell, and C. F. Hiskey, *Inorg. Synth.*, 1950, **3**, 188.

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