Inorganica Chimica Acta, *184* (1991) 221–228

Three new dicarboxylatodirhenium(III) compounds and their structures: a structure type not previously seen

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(Received January 21, 1991)

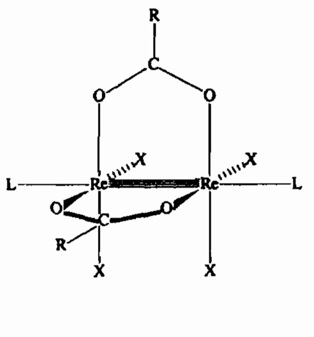
Abstract

Three new structures of compounds containing the $Re_2(O_2CR)_2X_4$ unit are reported and two are shown to contain features rarely or not previously observed. Reaction of trimeric $ReCl_3$ and PhCOONa in THF under reflux conditions for 24 h gave dark-green orthorhombic crystals of the THF solvate *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2\cdot THF$ (**1**). The crystals belong to the space group *Pbcm* with unit cell dimensions $a=8.867(2)$, $b=19.851(4)$, $c=18.022(4)$ Å, $V=3172(2)$ Å^3, and $D_{calc}=2.037$ g/cm^3 for $Z=4$. The structure was refined to $R=0.037$ and $R_w=0.046$ for 1825 reflections having $I>3\sigma(I)$. Reaction of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ and NaF in acetonitrile under reflux conditions for 4 days followed by work-up in acetone gave blue, monoclinic crystals of *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5]\cdot(CH_3)_2CO$ (**2**). The crystals belong to the space group $P2_1/n$ with unit cell dimensions $a=11.283(4)$, $b=13.577(5)$, $c=21.835(10)$ Å, $V=3345(4)$ Å^3, and $D_{calc}=1.923$ g/cm^3 for $Z=4$. The structure was refined to $R=0.056$ and $R_w=0.066$ for 2443 reflections having $I>3\sigma(I)$. Compound **3**, $[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6]\cdot CHCl_3$, contains the first example of an axially coordinated species with a transoid arrangement of the carboxylate ligands. **3** crystallizes in space group $P\bar{1}$ with $a=13.372(4)$, $b=14.067(6)$, $c=10.899(7)$ Å, $\alpha=99.694(5)°$, $\beta=103.030(5)°$, $\gamma=84.501(3)°$, $V=1966(3)$ Å^3, $Z=1$. The structure was refined to $R=0.067$ and $R_w=0.082$ for 2648 reflections with $I>3\sigma(I)$.

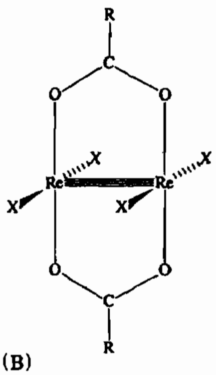
Introduction

Over a period of years a number of structurally characterized dirhenium compounds of the composition $Re_2(O_2CR)_2X_4L_n$, where X_4 represents four equatorial ligands and L, which may be X also or a neutral ligand, occupies an axial position; n may be 0 or 2. Table 1 contains a list of those for which structures have been reported. Inspection of this list reveals the following regularity: all compounds with $n=1$ or 2 have a cisoid arrangement (A) of the carboxyl groups, while all those with $n=0$ have a transoid arrangement (B). There are two cases where stoichiometrically $n=1$, but in one of them this ligand, μ-HCO_2^-, serves as a bidentate bridge between adjacent molecules, thus making the compound effectively an $n=2$ case.

On three different occasions in this laboratory we have unintentionally obtained other dicarboxylatodirhenium compounds and characterized them structurally. We report these compounds and their structures here because they show that the published literature affords an incomplete and partly misleading picture of this class of compounds. One of the new compounds has $n=1$, but becomes effectively an $n=2$ compound by sharing the axial ligand, and another is of the $n=2$ type but with a transoid arrangement of the carboxyl groups, the first instance of such a structure.



(A)



(B)

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TABLE 1. $Re_2(O_2CR)_2X_4L_n$ compounds of known structure

Compound	X_4	L_n	Structure type	Reference
$Re_2(O_2CPh)_4I_4$	I_4		transoid	1
$Re_2(O_2CCMe_3)_2Cl_4$	Cl_4		transoid	2
$Re_2(O_2CMe)_2Cl_4$	Cl_4		transoid	3, 4
$Re_2(O_2CMe)_2Br_4$	Br_4		transoid	5
$Re_2(O_2CMe)_2Cl_4(H_2O)_2$	Cl_4	$(H_2O)_2$	cisoid	6
$Re_2(O_2CH)_2Cl_4(Ph_2NCHO)_2$	Cl_4	$(Ph_2NCHO)_2$	cisoid	7
$Re_2(O_2CMe)_2Cl_4(Me_2SO)_2$	Cl_4	$(Me_2SO)_2$	cisoid	8
$Re_2(O_2CMe)_2Cl_4(Me_2NCHO)_2$	Cl_4	$(Me_2NCHO)_2$	cisoid	9
$(NH_4)_2Re_2(O_2CH)_2Cl_6$	Cl_4	Cl_2	cisoid	10
$Re_2(O_2CMe)_2Cl_2Me_2(Me_2SO)$	Cl_2Me_2	Me_2SO	cisoid	11
$(Et_3NH)Re_2(O_2CH)_2Cl_4(HCO_2)$	Cl_4	μ-OCHO	cisoid	12

TABLE 2. Crystal data for *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2 \cdot THF$ (1), *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5] \cdot (CH_3)_2CO$ (2) and *trans*-$[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6] \cdot CHCl_3$ (3)

	1	**2**	**3**
Formula	$C_{26}H_{34}Cl_4O_7Re_2$	$C_{23}H_{48}Cl_5NO_5Re_2$	$C_{73}H_{66}Cl_8P_4O_4Re_3$
Formula weight	972.8	968.31	2068.81
Space group	*Pbcm*	$P2_1/n$	$P\bar{1}$
Systematic absences	$0kl$: $k=2n+1$ $h01$: $l=2n+1$	$h0l$: $h+1=2n+1$ $0k0$: $k=2n+1$	none
a (Å)	8.867(2)	11.283(4)	13.372(4)
b (Å)	19.851(4)	13.577(5)	14.067(6)
c (Å)	18.022(4)	21.835(10)	10.899(7)
α (°)	90.0	90	99.694(5)
β (°)	90.0	90.02(1)	103.030(5)
γ (°)	90.0	90	84.501(3)
V Å^3	3172(2)	3345(4)	1966(3)
Z	4	4	1
d_{calc} (g/cm^3)	2.037	1.923	1.750
Crystal size (mm)	0.45×0.35×0.25	0.50×0.05×0.05	0.3×0.2×0.15
μ(Mo Kα) (cm^{-1})	81.096	77.649	51.788
Data collection instrument	CAD-4	CAD-4	CAD-4
Radiation (monochromated in incident beam)		Mo Kα ($\lambda=0.71073$ Å)	
Orientation reflections, no., range (2θ) (°)	25, $12<2\theta<25$	25, $18.5<2\theta<27.5$	20, $15<2\theta<27$
Temperature (°C)	27	−80	22
Scan method	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ (°)	$4\leqslant 2\theta\leqslant 50$	$4\leqslant 2\theta\leqslant 50$	$4\leqslant 2\theta\leqslant 45$
No. unique data, total	2306	4485	5563
with $F_o^2>3\sigma(F_o^2)$	1825	2443	2648
No. parameters refined	168	245	248
Transmission factors, max., min.	0.999, 0.920	0.999, 0.956	0.997, 0.636
R[a]	0.037	0.056	0.067
R_w[b]	0.046	0.066	0.082
Quality-of-fit indicator[c]	1.164	1.400	1.737
Largest shift/e.s.d., final cycle	0.02	0.39	0.18
Largest peak (e/Å^3)	0.84	1.55	1.95

[a] $R=\Sigma\||F_o|-|F_c\||/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(|F_o|)$. [c] Quality-of-fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Experimental

General procedures

In general manipulations were carried out in an atmosphere of oxygen-free argon or nitrogen using Schlenk technique. Solvents were dried and deoxygenated by refluxing over appropriate drying agents. The (±)-*trans*-1,2-bis(diphenylphosphino)-cyclopentane, dpcp, was prepared as previously described [13], and $Re_2(O_2CPh)_4Cl_2$ was prepared by a literature method [14].

Preparations

cis-$Re_2(O_2CPh)_2Cl_4(THF)_2 \cdot THF$ (*1*)

$ReCl_3$ (0.1 g, 0.3 mmol) and PhCOONa (0.1 g, 0.7 mmol) were refluxed together in 10 ml of THF for 24 h. The dark-green reaction mixture was filtered into a Schlenk tube and layered with 20 ml of hexane. After a few days a crop of small, dark-green, X-ray quality crystals was formed. Yield: 0.04 g, 24%.

TABLE 3. Positional parameters and their e.s.d.s for *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2 \cdot THF$ (**1**)

Atom	x	y	z	B (Å^2)[a]
Re(1)	0.15300(7)	0.12923(3)	0.250	3.12(1)
Re(2)	0.31856(7)	0.04501(3)	0.250	3.09(1)
Cl(1)	0.2385(4)	0.2002(2)	0.3417(2)	4.88(7)
Cl(2)	0.4851(3)	0.0754(2)	0.1583(2)	4.64(7)
O(1)	0.1942(7)	−0.0053(3)	0.3262(4)	3.3(1)
O(2)	0.0274(7)	0.0791(3)	0.3271(4)	3.4(1)
C(1)	0.066(1)	0.0199(5)	0.3484(6)	3.5(2)
C(11)	0.004(1)	−0.0847(6)	0.4152(7)	4.9(3)
C(12)	−0.088(1)	−0.1221(6)	0.4628(8)	5.9(3)
C(13)	−0.220(1)	−0.0903(7)	0.4927(8)	5.5(3)
C(14)	−0.254(1)	−0.0226(7)	0.4740(7)	5.6(3)
C(15)	−0.161(1)	0.0133(6)	0.4248(7)	4.5(3)
C(16)	−0.031(1)	−0.0187(5)	0.3982(6)	3.5(2)
O(3)	−0.068(1)	0.1942(5)	0.250	4.6(3)
C(31)	−0.220(3)	0.169(1)	0.250	7.3(6)*
C(32)	−0.325(3)	0.231(1)	0.250	8.6(7)*
C(33)	−0.225(4)	0.290(2)	0.250	14(1)*
C(34)	−0.066(3)	0.266(1)	0.250	7.7(6)*
O(4)	0.442(1)	−0.0666(6)	0.250	4.7(3)
C(41)	0.506(2)	−0.0936(7)	0.1825(8)	6.8(3)
C(42)	0.651(2)	−0.120(1)	0.210(1)	12.4(6)
O(5)	0.479(4)	0.750	0.500	26(1)*
C(51)	0.369(2)	0.688(1)	0.504(1)	13.2(7)*
C(52)	0.228(4)	0.725(2)	0.475(2)	10(1)*
C(53)	0.260(3)	0.711(1)	0.548(2)	7.5(8)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

TABLE 4. Positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5] \cdot (CH_3)_2CO$ (**2**)

Atom	x	y	z	B (Å^2)
Re(1)	0.16980(9)	0.06542(6)	0.23631(5)	1.67(2)
Re(2)	0.24402(8)	−0.07789(6)	0.20349(5)	1.50(2)
Cl(1)	0.1657(6)	0.1600(4)	0.1467(4)	2.4(1)
Cl(2)	−0.0367(6)	0.0483(4)	0.2305(4)	2.8(2)
Cl(3)	0.2724(6)	−0.0584(4)	0.0979(4)	2.8(1)
Cl(4)	0.0701(6)	−0.1688(4)	0.1845(4)	3.0(2)
Cl(5)	0.3600(5)	−0.2573(4)	0.1986(3)	2.1(1)
O(1)	0.161(1)	0.018(1)	0.323(1)	3.0(5)
O(2)	0.337(2)	0.108(1)	0.253(1)	2.7(4)
O(3)	0.245(2)	−0.123(1)	0.293(1)	4.5(6)
O(4)	0.408(1)	−0.032(1)	0.2140(8)	1.3(3)*
C(21)	0.204(2)	−0.067(2)	0.335(1)	1.9(4)*
C(22)	0.201(3)	−0.102(2)	0.399(2)	4.3(8)
C(23)	0.430(2)	0.053(1)	0.244(1)	0.5(3)*
C(24)	0.547(3)	0.082(2)	0.250(1)	3.3(6)
N	0.319(2)	0.203(1)	0.896(1)	1.7(4)*
C(1)	0.431(2)	0.170(2)	0.932(1)	1.9(4)*
C(2)	0.420(3)	0.184(2)	0.998(2)	3.4(6)*
C(3)	0.537(3)	0.157(2)	1.029(2)	3.2(6)*
C(4)	0.530(3)	0.157(2)	1.102(2)	5(1)
C(5)	0.349(3)	0.181(2)	0.829(2)	3.0(6)*
C(6)	0.261(3)	0.220(2)	0.783(2)	3.7(6)*
C(7)	0.268(3)	0.162(2)	0.725(2)	3.6(6)*
C(8)	0.388(3)	0.174(2)	0.691(2)	4.0(7)*
C(9)	0.208(3)	0.151(2)	0.921(2)	3.2(6)*
C(10)	0.219(3)	0.035(2)	0.913(2)	2.8(5)*
C(11)	0.103(3)	−0.004(2)	0.945(2)	4.6(7)*
C(12)	0.112(4)	−0.116(3)	0.940(2)	7(1)
C(13)	0.290(2)	0.312(2)	0.906(1)	2.4(5)*
C(14)	0.393(3)	0.384(2)	0.889(2)	3.3(6)*
C(15)	0.343(3)	0.488(2)	0.890(2)	8(1)
C(16)	0.353(5)	0.540(2)	0.936(2)	10(1)
O(5)	0.493(4)	0.080(2)	0.404(1)	10(1)
C(31)	0.441(4)	0.127(2)	0.445(2)	5(1)
C(32)	0.318(4)	0.171(2)	0.442(3)	9(1)
C(33)	0.496(3)	0.140(2)	0.503(2)	7(1)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

cis-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5] \cdot (CH_3)_2CO$ (*2*)

A mixture of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (0.16 g, 0.14 mmol), NaF (0.072 g, 1.71 mmol) and 10 ml of acetonitrile was stirred at 70 °C for 4 days. The initial blue–green color changed to dark blue. The reaction mixture was filtered, reduced in volume to about 3 ml and then about 50 ml of ethyl ether was added to it. The blue solid that precipitated was filtered, redissolved in acetone and layered with ether to give needle shaped crystals. Yield: 0.08 g, 60%.

$[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6] \cdot CHCl_3$ (*3*)

A mixture of $Re_2(O_2CPh)_4Cl_2$ (0.124 g, 0.143 mmol) and dpcp (0.125 g, 0.286 mmol) was stirred in 30

TABLE 5. Positional and isotropic equivalent thermal parameters for *trans*-$[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6] \cdot CHCl_3$ (**3**)[a,b]

Atom	x	y	z	B (Å^2)
Re1	0.0189(1)	0.42744(9)	0.0317(1)	5.00(5)
Re2	0.5000	0.0000	0.5000	1.79(4)
Cl1	0.069(1)	0.2597(7)	0.1017(9)	8.6(3)
Cl2	−0.1428(8)	0.3826(7)	0.0419(8)	7.6(3)
Cl3	0.198(1)	0.4091(9)	0.052(1)	9.6(4)
Cl4	0.5386(5)	0.0620(5)	0.7149(5)	3.2(2)
Cl5	0.244(2)	0.404(2)	0.732(2)	7.8(5)[c]
Cl6	0.423(2)	0.358(2)	0.905(2)	9.6(6)[c]
Cl7	0.398(2)	0.541(2)	0.821(3)	12.6(8)[c]
P1	0.3161(5)	0.0599(5)	0.4865(6)	2.5(2)
P2	0.5098(5)	0.1540(5)	0.4156(6)	2.5(2)
O1	−0.042(2)	0.510(1)	−0.217(2)	5.2(6)
O2	−0.004(2)	0.362(1)	−0.152(2)	5.3(6)
CCl3	0.335(4)	0.445(4)	0.859(4)	4(1)[c]
C1	0.248(2)	0.070(2)	0.619(2)	3.0(5)[c]
C2	0.290(2)	0.130(2)	0.732(2)	3.9(6)[c]
C3	0.237(2)	0.141(2)	0.834(3)	4.4(6)[c]
C4	0.141(2)	0.100(2)	0.815(3)	4.9(6)[c]
C5	0.098(2)	0.045(2)	0.696(3)	5.7(7)[c]
C6	0.153(2)	0.032(2)	0.598(3)	4.3(6)[c]
C11	0.232(2)	−0.001(2)	0.348(2)	3.3(5)[c]
C12	0.224(2)	−0.100(2)	0.341(3)	4.8(6)[c]
C13	0.168(2)	−0.154(2)	0.232(3)	5.1(7)[c]
C14	0.123(3)	−0.107(3)	0.125(3)	6.4(8)[c]
C15	0.124(3)	−0.008(3)	0.124(3)	6.9(9)[c]
C16	0.184(2)	0.047(2)	0.240(3)	5.0(7)[c]
C21	0.566(2)	0.261(2)	0.518(2)	3.4(5)[c]
C22	0.584(2)	0.276(2)	0.643(3)	5.8(7)[c]
C23	0.629(3)	0.358(3)	0.721(3)	6.5(8)[c]
C24	0.659(2)	0.423(2)	0.665(3)	5.8(8)[c]
C25	0.647(3)	0.411(3)	0.528(4)	8(1)[c]
C26	0.599(2)	0.328(2)	0.452(3)	5.5(7)[c]
C31	0.560(2)	0.143(2)	0.267(2)	3.5(5)[c]
C32	0.666(2)	0.141(2)	0.278(3)	4.2(6)[c]
C33	0.703(2)	0.132(2)	0.173(3)	4.8(6)[c]
C34	0.642(2)	0.122(2)	0.054(3)	5.5(7)[c]
C35	0.535(2)	0.123(2)	0.045(3)	5.2(7)[c]
C36	0.495(2)	0.132(2)	0.152(3)	4.7(6)[c]
C37	−0.030(2)	0.414(2)	−0.238(3)	4.6(6)[c]
C41	−0.052(2)	0.371(2)	−0.375(3)	4.3(6)[c]
C42	−0.78(2)	0.428(2)	−0.466(3)	4.3(6)[c]
C43	−0.095(2)	0.382(3)	−0.596(3)	6.0(8)[c]
C44	−0.077(2)	0.284(2)	−0.628(3)	5.8(7)[c]
C45	−0.043(2)	0.227(2)	−0.533(3)	4.7(6)[c]
C46	−0.025(2)	0.269(2)	−0.401(3)	4.8(6)[c]
C51	0.373(2)	0.196(2)	0.365(2)	3.2(5)[c]
C52	0.343(2)	0.303(2)	0.337(3)	4.7(6)[c]
C53	0.256(3)	0.336(3)	0.389(3)	6.0(8)[c]
C54	0.215(2)	0.253(2)	0.439(3)	5.3(7)[c]
C55	0.320(2)	0.187(2)	0.465(2)	3.0(5)[c]

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. [b] e.s.d.s in the least significant digits are given in parentheses. [c] Refined isotropically.

ml of chloroform. Me_3SiCl (0.5 ml) was added and the mixture allowed to reflux for 4 h. The resulting red solution was filtered through a medium glass frit and 5 ml of the filtrate was covered with a layer of hexane in a Schlenk tube. After one day red crystals of the starting material began to appear, but after 4 weeks green crystals of the product had also appeared.

X-ray crystallographic procedures

All crystals used in this study were mounted and sealed with epoxy glue in thin-walled capillaries filled with degassed mineral oil to prevent decomposition in the air. Axial lengths and Laue class were confirmed with oscillation photographs. The general procedures were those routinely used in this laboratory and have been described elsewhere [15]*. Lorentz, polarization, and empirical absorption corrections were applied to the data. The positions of heavy atoms were deduced from the Patterson maps. Additional least-squares cycles and difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. All atoms were refined anisotropically in **1** and **2**, but in **3** only the Re atoms and those attached directly to them were refined anisotropically. The choice of *Pbcm* as the correct space group for **1** was confirmed by successful refinement. Successful refinement of **2** in the space group $P2_1/n$ showed that the choice of monoclinic system with $\beta \approx 90°$ from the axial photograph was also correct. In the final difference Fourier map for **2** there were 14 peaks above 1 e/Å^3, all of which were ghosts of the heavy

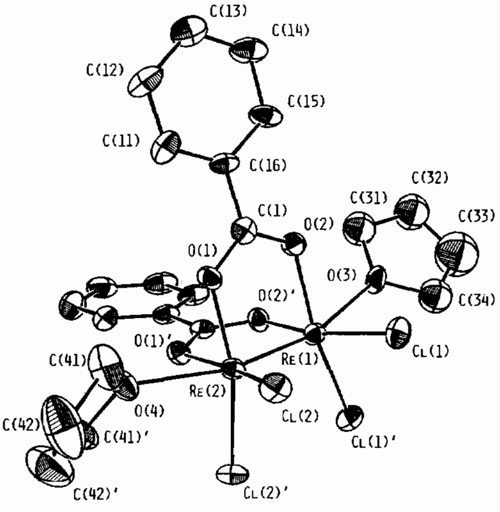

Fig. 1. ORTEP drawing of *cis*-$Re_2(O_2CC_6H_5)_2Cl_4(THF)_2$ (**1**) with the atom labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level.

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*The calculations were performed on the Microvax II computer at the Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, TX 77843, U.S.A.

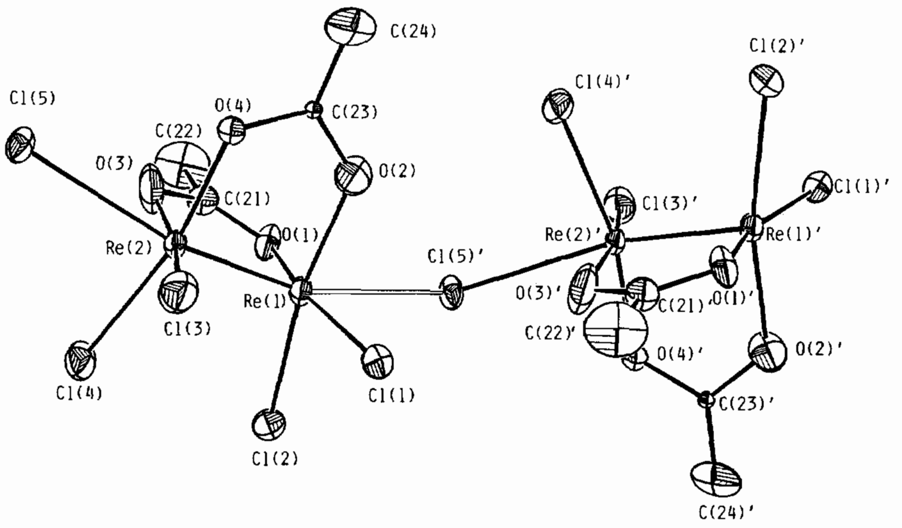

Fig. 2. ORTEP drawing of two adjacent anions of *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5]\cdot(CH_3)_2CO$ (**2**) with the atom labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level.

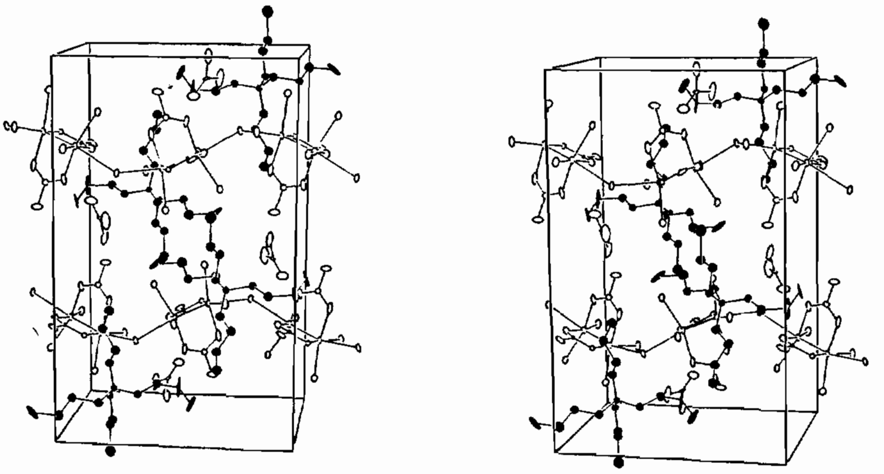

Fig. 3. A unit cell diagram for *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5]\cdot(CH_3)_2CO$ (**2**). Open circles represent atoms of the anions while the filled circles represent atoms of the cations. Atoms are represented by their ellipsoids at the 20% probability level.

TABLE 6. Selected bond distances (Å) and angles (°) for *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2\cdot THF$ (**1**)

Distances					
Re(1)–Re(2)	2.225(1)	Re(1)–O(3)	2.347(10)	Re(2)–O(4)	2.470(11)
Re(1)–Cl(1)	2.300(3)	Re(2)–Cl(2)	2.296(3)	O(1)–C(1)	1.304(12)
Re(1)–O(2)	2.040(7)	Re(2)–O(1)	2.025(7)	O(2)–C(1)	1.283(12)
Angles					
Re(2)–Re(1)–Cl(1)	104.04(8)	O(2)–Re(1)–O(2)'	85.9(3)	Cl(2)–Re(2)–O(1)	89.5(2)
Re(2)–Re(1)–O(2)	89.7(2)	O(2)–Re(1)–O(3)	79.1(3)	Cl(2)–Re(2)–O(4)	87.2(2)
Re(2)–Re(1)–O(3)	164.6(2)	Re(1)–Re(2)–Cl(2)	103.12(8)	O(1)–Re(2)–O(1)'	85.4(3)
Cl(1)–Re(1)–Cl(1)'	91.9(1)	Re(1)–Re(2)–O(1)	90.7(2)	O(1)–Re(2)–O(4)	78.4(3)
Cl(1)–Re(1)–O(2)	89.4(2)	Re(1)–Re(2)–O(4)	165.0(3)	Re(2)–O(1)–C(1)	119.5(6)
Cl(1)–Re(1)–O(2)'	165.5(2)	Cl(2)–Re(2)–Cl(2)'	92.0(1)	Re(1)–O(2)–C(1)	120.3(6)
Cl(1)–Re(1)–O(3)	86.5(2)	Cl(2)–Re(2)–O(1)'	165.4(2)	O(1)–C(1)–O(2)	119.6(9)

Numbers in parentheses are e.s.d.s in the least significant digits.

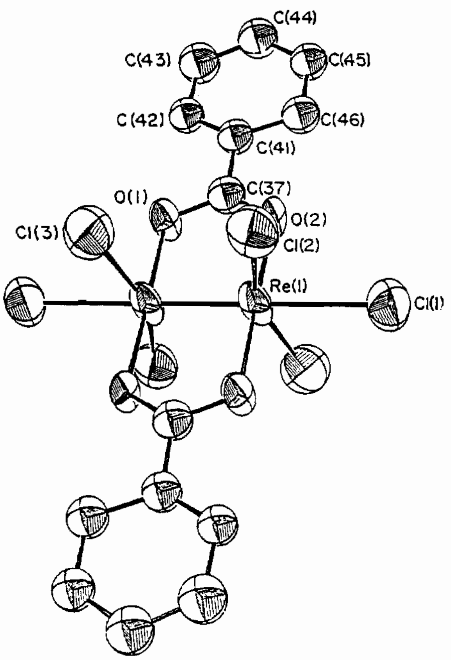

Fig. 4. ORTEP drawing of the dinuclear anion in $[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6]$ (**3**) with the atom labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level.

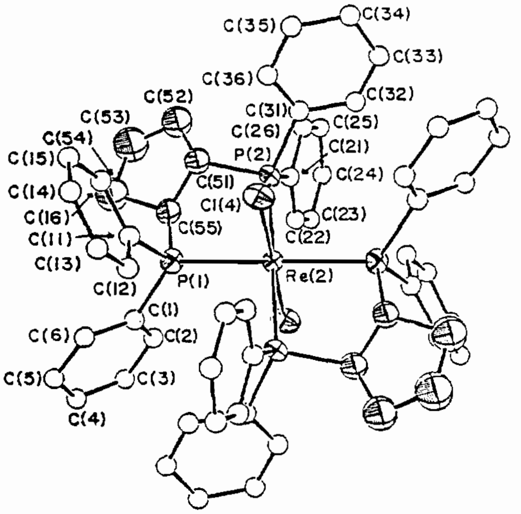

Fig. 5. ORTEP drawing of the cation in **3**.

atoms. No disorder or other non-routine problems arose. A summary of crystal and refinement data is presented in Table 2. The atomic positional parameters for *cis*-$Re_2(O_2CPh)_2Cl_4(THF)_2 \cdot THF$ (**1**), *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5] \cdot (CH_3)_2CO$ (**2**) and *trans*-$[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6] \cdot CHCl_3$ (**3**) are given in Tables 3, 4 and 5, respectively.

Results and discussion

As noted in the 'Introduction', the three compounds reported here were all prepared inadvertently. The preparative procedures are therefore in no sense optimal. Actually for **1** the procedure, which is simple, employs easily available starting materials, and gives a yield of 24%, is not bad from a practical point of view. The procedure for **2**, which was carried out with the goal of obtaining $[(C_4H_9)_4N]_2Re_2F_8$, provides a remarkably good yield (60%) even though no acetic acid or acetate was employed. Evidently, the acetate ligands arose by hydrolysis of CH_3CN, so that we must assume that the NaF used was wet. The reaction from which **3** arose was intended to give $Re_2Cl_6(dpcp)_2$. The yield of **3** was not large, probably about 10%.

The structures of the three compounds are shown in Figs. 1–5, and the more important molecular dimensions are listed in Tables 6, 7 and 8. We shall now discuss them individually.

Compound 1

As seen in Fig. 1 and Table 6, this is a molecular compound with normal dimensions for such a molecule. It adopts a cisoid disposition of the carboxyl groups and thus conforms with the previously established pattern, since n, the number of axial ligands, equals 2. A packing diagram is available, see 'Supplementary material', but it shows no unusual features.

Compound 2

This compound constitutes only the second example of a compound with stoichiometrically one axial ligand in which sharing occurs to form infinite chains. The dimensions are presented in Table 7 and a portion of the structure is shown in Fig. 2. Figure 3 shows the entire unit cell where the parallel infinite chains separated by $(C_4H_9)_4N^+$ ions are clearly visible. Because of the shared axial chlorine atoms, this compound is, effectively, an $n = 2$ case and follows the established pattern by having a cisoid arrangement of its carboxyl groups.

Compound 3

The anion and cation comprising this compound are shown in Figs. 4 and 5, respectively, and the important metrical properties are listed in Table 8. Both ions reside on centers of inversion. For the cation this means that there is one *S,S* and one *R,R* dcpc ligand bound to each rhenium atom. However, because of the conformational demands of the dpcp ligands this 'equatorial' plane is appreciably tilted from perpendicular to the Cl–Re–Cl axis. The

TABLE 7. Selected interatomic distances (Å) and angles (°) for *cis*-$[(n\text{-}C_4H_9)_4N][Re_2(O_2CCH_3)_2Cl_5]\cdot(CH_3)_2CO$ (**2**)

Distances					
Re(1)–Re(2)	2.236(1)	Re(2)–Cl(3)	2.343(8)	O(2)–C(23)	1.30(3)
Re(1)–Cl(1)	2.341(7)	Re(2)–Cl(4)	2.355(6)	O(3)–C(21)	1.29(3)
Re(1)–Cl(2)	2.345(7)	Re(2)–O(3)	2.04(3)	O(4)–C(23)	1.35(2)
Re(1)–O(1)	2.01(2)	Re(2)–O(4)	1.967(15)	C(21)–C(22)	1.47(4)
Re(1)–O(2)	2.01(2)	O(1)–C(21)	1.27(3)	C(23)–C(24)	1.38(4)
Angles					
Re(2)–Re(1)–Cl(1)	102.5(2)	Re(1)–Re(2)–Cl(3)	105.6(2)	Re(1)–O(1)–C(21)	118.0(2)
Re(2)–Re(1)–Cl(2)	105.6(2)	Re(1)–Re(2)–Cl(4)	101.5(2)	Re(1)–O(2)–C(23)	124.0(1)
Re(2)–Re(1)–O(1)	92.4(4)	Re(1)–Re(2)–O(3)	87.4(5)	Re(2)–O(3)–C(21)	121.0(2)
Re(2)–Re(1)–O(2)	87.6(5)	Re(1)–Re(2)–O(4)	92.2(4)	Re(2)–O(4)–C(23)	120.0(1)
Cl(1)–Re(1)–Cl(2)	89.4(3)	Cl(3)–Re(2)–Cl(4)	90.0(3)	O(1)–C(21)–O(3)	122.0(3)
Cl(1)–Re(1)–O(1)	165.0(5)	Cl(3)–Re(2)–O(3)	166.5(6)	O(1)–C(21)–C(22)	119.0(3)
Cl(1)–Re(1)–O(2)	90.4(6)	Cl(3)–Re(2)–O(4)	87.2(5)	O(3)–C(21)–C(22)	120.0(2)
Cl(2)–Re(1)–O(1)	88.2(5)	Cl(4)–Re(2)–O(3)	90.9(6)	O(2)–C(23)–O(4)	114.0(2)
Cl(2)–Re(1)–O(2)	166.6(5)	Cl(4)–Re(2)–O(4)	166.2(4)	O(2)–C(23)–C(24)	126.0(2)
O(1)–Re(1)–O(2)	88.5(8)	O(3)–Re(2)–O(4)	88.8(8)	O(4)–C(23)–C(24)	118.0(2)
Non-bonding distances					
Re(1)–Cl(5)	2.816(6)	Re(2)–Cl(5)	2.767(5)		
Non-bonding angles					
Re(2)–Re(1)–Cl(5)	161.9(1)	Cl(5)–Re(1)–O(2)	77.0(5)	Cl(5)–Re(2)–O(3)	76.8(5)
Cl(1)–Re(1)–Cl(5)	87.2(2)	Re(1)–Re(2)–Cl(5)	162.8(2)	Cl(5)–Re(2)–O(4)	80.8(4)
Cl(2)–Re(1)–Cl(5)	89.6(2)	Cl(3)–Re(2)–Cl(5)	89.8(2)	Re(1)–Cl(5)–Re(2)	132.5(3)
Cl(5)–Re(1)–O(1)	78.0(5)	Cl(4)–Re(2)–Cl(5)	85.8(2)		

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 8. Principal bond distances (Å) and bond angles (°) in *trans*-$[ReCl_2(dpcp)_2][Re_2(O_2CPh)_2Cl_6]\cdot CHCl_3$ (**3**)

Distances			
Re(1)–Re(1)	2.237(2)	P(1)–C(1)	1.85(2)
Re(1)–Cl(1)	2.579(10)	P(1)–C(11)	1.81(2)
Re(1)–Cl(2)	2.341(12)	P(1)–C(55)	1.847(7)
Re(1)–Cl(3)	2.345(13)	P(2)–C(21)	1.83(2)
Re(1)–O(1)	2.030(20)	P(2)–C(31)	1.87(3)
Re(1)–O(2)	2.020(20)	P(2)–C(51)	1.85(2)
Re(2)–Cl(4)	2.317(6)		
Re(2)–P(1)	2.501(6)		
Re(2)–P(2)	2.515(7)		
Angles			
Re(1)–Re(1)–Cl(1)	177.9(3)	Cl(4)–Re(2)–P(1)	90.3(2)
Re(1)–Re(1)–Cl(2)	102.1(3)	Cl(4)–Re(2)–P(2)	97.4(2)
Re(1)–Re(1)–Cl(3)	102.2(3)	P(1)–Re(2)–P(2)	82.6(2)
Re(1)–Re(1)–O(1)	90.4(5)	Re(2)–P(1)–C(1)	124.3(7)
Re(1)–Re(1)–O(2)	90.6(5)	Re(2)–P(1)–C(11)	41.7(8)
Cl(1)–Re(1)–Cl(2)	79.8(4)	Re(2)–P(1)–C(55)	101.7(3)
Cl(1)–Re(1)–Cl(3)	75.9(4)	Re(2)–P(2)–C(21)	122.4(9)
Cl(1)–Re(1)–O(1)	90.4(6)	Re(2)–P(2)–C(31)	117.2(8)
Cl(1)–Re(1)–O(2)	88.7(6)	Re(2)–P(2)–C(51)	103.4(9)
Cl(2)–Re(1)–O(1)	90.4(7)		
Cl(2)–Re(1)–O(2)	89.1(7)		
Cl(3)–Re(1)–O(2)	91.3(7)		

Cl(4)–Re(2)–P(2) angle is 90.3(2)° but the Cl(4)–Re(2)–P(1) angle is 97.4(2)°.

For the anion the inversion symmetry is consistent only with a transoid disposition of the ligands. Indeed, the $[Re_2(O_2CPh)_2Cl_6]^{2-}$ ion has D_{2h} symmetry within the experimental errors. The Re–Re distance, 2.237(2) Å, is quite normal for a quadruple bond and the Re–O and Re–Cl distances to the equatorial atoms are also quite normal. The axial Re–Cl bonds are significantly longer than the equatorial ones, as is expected.

This compound affords the first example of an exception to the previous pattern whereby all compounds with two axial ligands (or even one) were cisoid. It raises the question of the extent to which the previous pattern may be only the result of non-representative sampling.

We think that the general pattern probably *is* valid although the result for compound **3** shows that it is possible to have occasional violations. The reason why we believe in the general, though not rigorous, validity of the pattern is as follows. When no axial ligands are present, the four unidentate ligands (e.g. the four halogen atoms in the $Re_2(O_2CR)_2X_4$ molecules) can readily lessen the close contacts with each other by moving towards the empty axial positions. Of course they could also do this in a cisoid structure, so perhaps for simple $Re_2(O_2Cr)_2X_4$ molecules we see here evidence that the transoid relationship of the RCO_2 ligands is inherently more favorable than the cisoid one. On the other hand, when the axial positions are occupied, crowding is best avoided by having the RCO_2 ligands cisoid, because, owing to the constraint within each RCO_2 ligands, the pairs of oxygen atoms are kept close together and the Re–Re–X(eq) angles can expand by pushing the axial ligands towards the adjacent oxygen atoms.

Supplementary material

Full listing of bond distances, bond angles, isotropic equivalent displacement parameters, observed and calculated structure factors for **1**, **2** and **3** and a stereoview of the unit cell of **1** are available on request from author F.A.C.

Acknowledgements

We thank Professor Richard A. Walton for helpful discussions and the National Science Foundation for support.

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