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STUDIES ON ORGANOMETALLIC COMPOUNDS WITH HETERO MULTIPLE BRIDGES

V *. CRYSTAL AND MOLECULAR STRUCTURE OF THE PARENT RHENIUM COMPLEX $Re_2Br_2(CO)_6(THF)_2$ AND SUBSTITUTED PRODUCTS OF TRICARBONYLRHENIUM(I) DERIVED FROM IT **

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Summary

Reactions of the tetrahydrofuran adduct $Re_2Br_2(CO)_6(THF)_2$ with some phosphorous- and nitrogen-containing donors under mild conditions are reported, which led to the formation of substituted products of tricarbonylrhenium(I). Bromide abstraction from the THF adduct by secondary amines and CS_2 produced the dithiocarbamato derivatives $Re(S_2CNR_2)(CO)_3(HNR_2)$ whose behaviour in solution with CO was also investigated. Mass spectral data for some of the substituted products have been measured. The title compound crystallizes in the space group $P2_1/n$ with cell constants a = 8.661(2), b = 11.251(3), c = 11.424(3) Å and β = 110.36(2)°, U = 1043.67 Å^3 and D_{calc} = 2.686 g cm^{-3}, Z = 2. The molecule consists of a planar Re_2Br_2 moiety, as demanded by symmetry. The two THF groups are on opposite sides of this plane and the three CO groups around each rhenium atom are arranged in a *fac* arrangement. The unique Re—Br distances are 2.642(5) and 2.644(4) Å, while the Re—O distance is 2.129(31) Å. The Re—Br—Re and Br—Re—Br angles are 97.3(2) and 82.7(1)°, respectively. The Re···Re nonbonding distance is 3.967(3) Å. The THF ligands consist of a nearly planar C_4 fragment (maximum deviation from planarity 0.06 Å), while the oxygen is 0.348 Å out of that plane, the angle defined by the C_4 plane and the C—O—C fragment of the THF ligand being 24.99°. Final values of the discrepancy indices are $R(F)$ = 0.074 and $R_w(F)$ = 0.095.

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* For parts I—IV see refs. 3—6.

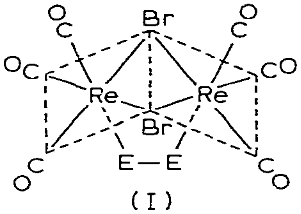
** Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

Introduction

In previous publications [1—6] it has been shown that the tetrahydrofuran adduct $Re_2Br_2(CO)_6(THF)_2$, as prepared [1] from $ReBr(CO)_5$ and THF und reflux conditions, can be used as a "solvent-stabilised intermediate" for the preparations of tricarbonylrhenium(I) derivatives under mild conditions. This concept has been successfully applied to the preparation of tricarbonylrhenium-(I) complexes containing nitrogen donors [1], isocyanides [1], S_2Ph_2 [2,3], S_2Me_2 [2,4] Se_2Ph_2 [6], and P_2Ph_4 [6] as ligands. While infrared spectroscopic evidence showed [1] that the THF adduct has a molecular structure in which the THF groups are on opposite sides of the $(OC)_2ReBr_2Re(CO)_2$ plane, the products resulting from reaction 1 contain a E_2R_{2n} bridge in addition to the bromide bridges, i.e. the E_2R_{2n} ligand is on the same side of the molecule, see structure I.

$$Re_2Br_2(CO)_6(THF)_2 + E_2R_{2n} \rightarrow Re_2Br_2(CO)_6E_2R_{2n} + 2\ THF \qquad (1)$$

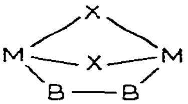
$(n = 1, E = S, Se; n = 2, E = P)$



(I)

(R groups attached to E are omitted)

It was therefore of interest to establish conclusively the molecular structure of the parent compound, since this had strong implications on the thermodynamic stability of the products resulting from reaction 1 and on the mechanism of their formation. It is worth mentioning, incidentally, that the products I represent rare examples of organometallic molecules containing the arrangement II, i.e., one in which two metal atoms are held together by bridging atoms of different



(II)

nature, one of the bridging ligands being, moreover, bidentate. Further justification for determination of the molecular structure of the dimeric tetrahydrofuran adduct was that in the products $Re_2Br_2(CO)_6E_2R_{2n}$ the Re_2Br_2 fragment of the dimer is bent such that the two $ReBr_2$ halves are folded along the Br···Br axis by angles ranging from 23 to 33° [3—6]. In the absence of a fully formed metal—metal bond the bending of the structure could be explained either by the presence of the relatively short E—E bridge or by the E···Br interaction. The latter postulate is based on the experimentally observed E···Br contacts, which are considerably shorter than the sum of the Van der Waals radii.

This paper reports the crystal and molecular structure of the dimeric THF adduct and the preparation of some new tricabonylrhenium(I) derivatives obtained from it.

Results and discussion

The molecules of $Re_2Br_2(CO)_6(THF)_2$ are shown in a stereodiagram in Fig. 1, where one can see that the Re_2Br_2 fragment is completely planar, which is demanded by crystallographic symmetry (space group $P2_1/n$; $Z = 2$ molecules per unit cell). The packing of the molecules in the unit cell is shown in Fig. 2. Crystallographic data of the THF adduct are in Table 1, while positional and thermal parameters are in Table 2. As shown in Table 3, the oxygens of the THF groups are nearly perpendicular to the Re_2Br_2 plane, the angle being approximately 85° for Br—Re—O(4), 95° for O(4)—Re—C(equatorial) and 177° for O(4)—Re—C(axial). It is significant, however, that the two Re—Br distances are identical within experimental error (1σ) since crystallographic symmetry does not demand this result. The Re_2Br_2 fragment could have a parallelogram shape with two different Re—Br distances and still obey the crystallographic symmetry requirement.

By taking also into consideration the data shown in Tables 4 and 5, one can see that the result of allowing the molecule to become planar has the following effects on bond length.

(a) The Re—Br distances of 2.642(5) and 2.644(4) Å are longer (by 0.040 Å; 8σ) than in the diphenyl disulphide derivative; however, given the stated deviations, the Re—Br distances in the THF adduct and in the P_2Ph_4 derivative (2.649 Å, average value) are the same despite the variations in the folding angle (the THF adduct is planar, for the S_2Ph_2 derivative the angle is 33°, while for the phosphorous compound the same angle is 23.4°). Thus, this parameter alone cannot account for the variation in the Re—Br distances, which is probably a complicated function of the folding angle, of the nature of the ligand donor atom (P, S) and of the geometrical arrangement (in *cis* or *trans* pairs) of those ligands.

(b) The Re···Re distance of 3.967(3) Å is the longest found until now for the dimeric rhenium derivatives, as listed in Table 5. Since we have already seen that the Re—Br distance in the THF adduct and in the P_2Ph_4 complex are the same but now find that the Re···Re distance changes significantly, it is not surprising

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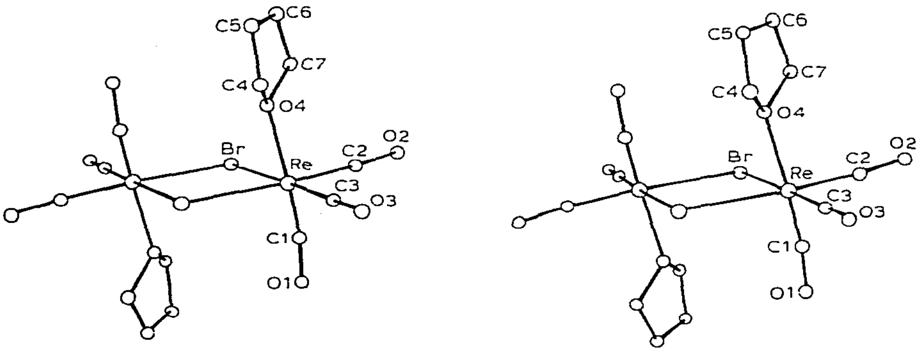


Fig. 1. A general view of the molecule with the labelling system used in the crystallographic study. Only those atoms constituting the asymmetric unit are labelled; the others are related to the first set by an inversion center.

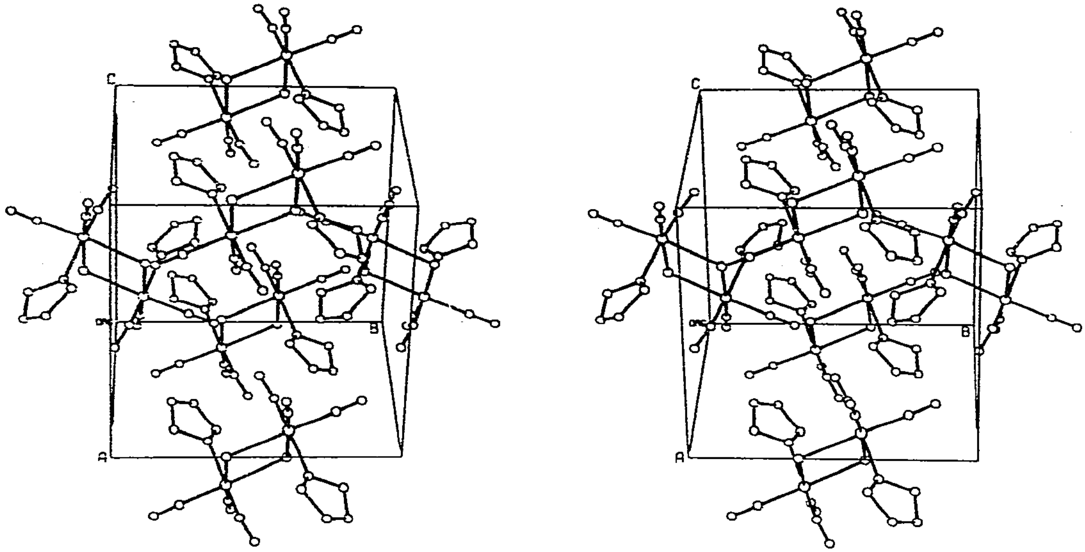


Fig. 2. The packing of the molecules in the unit cell.

TABLE 1

CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION

Molecular formula	$C_{14}H_{16}Br_2O_8Re_2$
Molecular weight	844.48 g mol^{-1}
Space group	$P2_1/n$
Cell constants (Mo-K_α, λ 0.71069 Å)	a = 8.661(2) Å b = 11.251(3) c = 11.424(3) β = 110.36(2)
Unit cell volume	U = 1043.67 Å^3
Density	D_c = 2.686 g cm^{-3} [a]
Z	2
Standards for intensity control (every 30 data)	[0, 1, $\bar{3}$; 2, 0, 0]
Description of the data crystal: plate	Along [100] = 0.10 mm [010] = 0.23 mm [001] = 0.23 mm
Scanning range for 2θ:	$6.00 \leqslant 2\theta \leqslant 50.0$
Scan width for each reflection	$\Delta 2\theta = (2.0 + 0.7 \tan\theta)^\circ$
Maximum scan time	5 minutes
Minimum number of counts above background for each reflection	2000
Range of scan speeds	0.4 to 5.0°/min
Absorption coefficient used in correcting data	μ = 155.6 cm^{-1}
Total number of data points collected	2077
Number above two standard deviations	1522
Number of total variables	118
Final $R(F)$ [b]	0.074
Final $R_w(F)$ [c]	0.095
Goodness of fit	1.71
Weighting scheme	$w = 1/\sigma^2(F)$

[a] The density was not measured because of the air instability of the compound. [b] Defined as $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] Defined as $R_w(F) = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS IN $Re_2Br_2(CO)_6(THF)_2$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0615(2)	0.6027(2)	0.1504(2)	0.0359(9)	0.0192(7)	0.0376(9)	−0.0013(13)	0.0037(7)	−0.0038(12)
Br	0.1354(5)	0.3905(4)	0.0857(4)	0.050(3)	0.022(2)	0.049(3)	0.0096(28)	−0.011(2)	−0.0030(25)
O(1)	−0.183(6)	0.507(3)	0.229(3)	0.14(5)	0.07(3)	0.05(3)	0.05(3)	−0.04(3)	0.01(2)
O(2)	0.324(6)	0.576(4)	0.419(3)	0.26(6)	0.11(4)	0.05(2)	−0.14(4)	0.00(3)	0.00(2)
O(3)	−0.035(4)	0.854(2)	0.212(3)	0.07(2)	0.04(2)	0.09(3)	0.03(2)	0.02(2)	−0.02(2)
O(4)	0.240(3)	0.665(2)	0.075(2)	0.03(2)	0.03(2)	0.04(2)	0.02(1)	0.00(1)	0.03(1)
C(1)	−0.070(7)	0.556(5)	0.200(6)	0.08(5)	0.06(4)	0.09(4)	0.07(4)	0.05(4)	0.04(3)
C(2)	0.214(5)	0.588(3)	0.314(4)	0.05(3)	0.00(2)	0.07(3)	0.00(2)	−0.02(2)	−0.01(2)
C(3)	0.000(4)	0.764(3)	0.189(3)	0.02(2)	0.04(2)	0.00(2)	0.00(2)	0.00(2)	0.00(2)
C(4)	0.221(7)	0.785(5)	0.017(6)	0.10(5)	0.09(5)	0.15(6)	−0.03(4)	0.09(5)	0.03(4)
C(5)	0.368(9)	0.794(5)	−0.010(6)	0.14(6)	0.04(3)	0.11(5)	0.03(4)	0.05(5)	0.04(4)
C(6)	0.488(8)	0.715(6)	0.069(6)	0.10(6)	0.13(7)	0.12(6)	−0.07(5)	0.02(5)	0.05(5)
C(7)	0.412(6)	0.632(4)	0.134(6)	0.04(3)	0.04(3)	0.20(7)	−0.02(3)	0.01(4)	0.00(4)

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°). STARRED ATOMS LOCATED AT INVERSION CENTERS

Bond	Length	Angle	
Re—Br	2.642(5)	Re—Br—Re *	97.3(1)
Re—Br *	2.644(4)	Br—Re—Br *	82.7(1)
Re—O(4)	2.13(3)	Re—C(1)—O(1)	172(5)
Re—C(1)	1.60(7)	Re—C(2)—O(2)	176(5)
Re—C(2)	1.88(4)	Re—C(3)—O(3)	178(4)
Re—C(3)	1.93(4)	Re—O(4)—C(4)	120(6)
C(1)—O(1)	1.22(8)	Re—O(4)—C(7)	120(3)
C(2)—O(2)	1.25(5)	Br—Re—O(4)	84.4(7)
C(3)—O(3)	1.16(5)	Br—Re—C(1)	94(2)
O(4)—C(4)	1.50(7)	Br—Re—C(2)	93(1)
O(4)—C(7)	1.45(5)	Br—Re—C(3)	177.2(8)
C(4)—C(5)	1.42(10)	O(4)—Re—C(1)	177(2)
C(5)—C(6)	1.43(8)	O(4)—Re—C(2)	94(2)
C(6)—C(7)	1.49(10)	O(4)—Re—C(3)	95(2)
		C(1)—Re—C(2)	88(2)
Non-bonded contacts		C(1)—Re—C(3)	86(2)
Re—Re	3.967(3)	C(2)—Re—C(3)	90(2)
Br—Br	3.494(6)	C(4)—O(4)—C(7)	112(4)
		O(4)—C(4)—C(5)	101(5)
		C(4)—C(5)—C(6)	110(6)
		C(5)—C(6)—C(7)	111(6)
		O(4)—C(7)—C(6)	110(5)

to note that the Re—Br—Re angle has become larger in the THF adduct. Interestingly, the Br—Re—Br angles have remained exactly the same, i.e. 82.7°.

To summarize the comparison of structural parameters for the Re_2Br_2 frag-

TABLE 4

LEAST SQUARES PLANES THROUGH SELECTED ATOMS AND DEVIATIONS OF ATOMS FROM THOSE PLANES (Å) [a]

1. Plane defined by C(4), C(5), C(6) and C(7)

$0.04773x + 0.63249y + 0.77310z = 5.78154$

C(4)	0.035	C(6)	0.058
C(5)	−0.060	C(7)	−0.034
		O(4)	−0.348

2. Plane defined by C(4), C(7) and O(4)

$-0.31217x + 0.40781y + 0.85804z = 3.18205$

C(4)	0.000	C(6)	−0.510
C(5)	−0.638	C(7)	0.000

3. Plane defined by Re, Re*, Br and Br*

$0.87891x + 0.40371y - 0.25405z = 2.27108$

Plane	Plane	Dihedral angles (°)
1	2	24.99
1	3	84.21
2	3	70.87

[a] All planes are given in the form $ax + by + cz = s$, and are expressed in orthogonal angstrom space.
* Designates an atom related to a non-starred one by an inversion of coordinates.

TABLE 5

STRUCTURAL DATA FOR DIMERIC COMPLEXES OF RHENIUM(I)

Compound	Re···Re (Å)	E—E (Å)	Folding angles [a] (°)	Re—Br—Re (°)	Br—Re—Br (°)	Ref.
$Re_2Br_2(CO)_6(THF)_2$	3.967(3)			97.3(1)	82.7(1)	This study
$Re_2Br_2(CO)_6S_2Ph_2$	3.782(2)	2.140(9)	33.0	93.0(1)	81.7(1)	3
$Re_2Br_2(CO)_6S_2Me_2$	3.790(2)	2.111(13)	28.0	94.1(2)	82.4(2)	4
$Re_2Br_2(CO)_6Se_2Ph_2$	3.90(4)	2.411(23)	31.1	94.4(1)	81.3(1)	5
$Re_2Br_2(CO)_6P_2Ph_4$	3.890(1)	2.308(6)	23.4	94.5(1)	82.7(1)	6

[a] This is the angle between the normals to the $(OC)_2ReBr_2$ planes.

ments in the THF adduct and in the P_2Ph_4 complex, which have the same Re—Br distance, the unfolding of the fragment from 23.4° to 0° results in an increase of the Re···Re contact by 0.077 Å, in no change of the Br—Re—Br angle and in a change of 2.8° in the Re—Br—Re angle.

Inasmuch as there are no other structural studies of Re—THF complexes, it is difficult to assess the meaning of the Re—O distance we found. The nearest result available in the literature is the study by Fredette and Lock [7] reporting the data for a rhenium complex containing a "monodentate, neutral, β-ketoenol" in which the Re—O distance is 2.16 Å, which is the same as our value of 2.13(3) Å, see Table 3. The molecular parameters of the THF ligands resemble the results obtained by Atwood and Smith [8], by Huttner et al. [9], by Krausse et al. [10],

TABLE 6

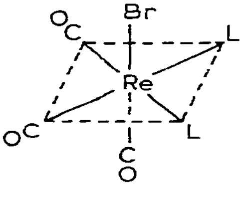
INFRARED DATA FOR CARBONYL DERIVATIVES OF RHENIUM(I)

Compound	Solvent	$\nu(CO)$ (cm^{-1})			
$ReBr(CO)_3en$	THF	2018	1903		1876
$ReBr(CO)_3(PPh_2Cl)_2$	CCl_4	2052	1985		1929
	Benzene	2050	1980		1925
$ReBr(CO)_3(PPh_2H)_2$	CCl_4	2041	1970		1902
$Re_2Br_2(CO)_6(PPh_2H)_2$	CCl_4	2036	1947		1916
	THF	2033	1935		1896
$ReBr(CO)_3(HNMe_2)_2$	CCl_4	2039	1930		1901
	Benzene	2025	1914		1887
	THF	2022	1910		1885
$Re(S_2CNMe_2)(CO)_3(HNMe_2)$ [a]	CCl_4	2022	1916		1901
	Benzene	2019		1904	
	THF	2016		1899	
$Re(S_2CNEt_2)(CO)_3(HNEt_2)$ [b]	Heptane	2024	1918		1906
	CCl_4	2022	1916		1899
	Toluene	2019	1909		1896
	THF	2015		1899	
$Re(S_2CNEt_2)(CO)_4$ [c,d]	CCl_4	2102	1998	1984	1945

[a] ^1H NMR data in benzene-d_6 (τ values, int. TMS): 7.95 (NH), 7.63 (singlet, 3H), 7.57 (singlet, 3H), 7.53 (singlet, 6H). [b] ^1H NMR data in CCl_4: 8.72 (triplet, 6H, J 6.4 Hz), 8.65 (triplet, 6H, J 6.4 Hz), 8.10 (NH), 6.79 (quartet, 2H, J 7 Hz), 6.69 (quartet, 2H, J 7 Hz), 6.26 (quartet, 4H, J 7 Hz). [c] ^1H NMR data in benzene-d_6: 9.28 (triplet, 6H, J 7.5 Hz), 6.84 (quartet, 4H, J 7.5 Hz). [d] Similar IR data in dichloromethane solution were given in ref. 20.

by Behrens et al. [11] and by Daly and Sneeden [12] for THF containing complexes, but our THF ligands are not planar and the OC_2 vs. C_4 dihedral angle of 24.99° (see Table 4) is close to the average value of 21° reported in ref. 12 for $CrCl_2(p\text{-tolyl})(THF)_3$.

Addition of ligands to $Re_2Br_2(CO)_6(THF)_2$ produced the mononuclear complexes $ReBr(CO)_3L_2$ (L = PPh_2Cl, PPh_2H, $C_6H_{11}NC$) [1] and $ReBr(CO)_3LL$ (LL = ethylenediamine (en), 9,10-phenanthroline [1] (phen) and 2,2′-bipyridyl [1] (bipy)). The monomeric nature of the complexes with monodentate ligands has been established cryoscopically or by mass spectrometry (vide infra); this paper reports the mass spectral data for the amine complexes, for which no cryoscopic measurements are possible because of the low solubility. The IR spectra in the carbonyl stretching region (see Table 6) are generally in agreement with the assumption of monomeric *fac* structures (III and IV) of idealised C_s symmetry, for which three intense $\nu(CO)$ are expected. The decrease of $\nu(CO)$ in the sequence $PPh_2Cl > PPh_2H >$ en is consistent with a corresponding increase of π-back-bonding, as expected on the basis of electronegativity arguments (PPh_2Cl, PPh_2H) and of σ-donor capacity of the ligand (en).



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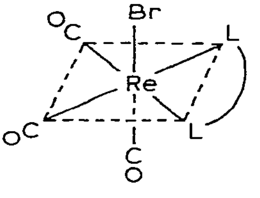


(IV)

The presence of an intact PPh_2H ligand in $ReBr(CO)_3(PPh_2H)_2$ has been established spectroscopically ($\nu(P—H)$ at 2320 cm^{-1} and ^1H NMR peak at τ 3.44, $J(P—H)$ 378 Hz; to be compared with similar values for complexes of Cr^0, Mo^0, W^0 and Fe^0 [13]).

The reaction of $Re_2Br_2(CO)_6(THF)_2$ with PPh_2H has been studied at different PPh_2H/Re molar ratios. When this ratio was two or higher monomeric $ReBr(CO)_3$-(PPh_2H_2) was obtained (eq. 2). However, it was also possible to establish conclusively that when the molar ratio was well below that required by the stoichiometry of reaction 2 a product analysing for $ReBr(CO)_3PPh_2H$ and spectroscopically different (see Table 6) from the other one was obtained. Due to low solubility and volatility, cryoscopic or mass spectral molecular weight could not be measured. By analogy with the established structure for the THF adduct, we suggest a dimeric structure for this compound resulting from the displacement of the THF groups by PPh_2H (eq. 3). The analytically pure product became isolable only when the PPh_2H/Re molar ratio was about 0.5 and by virtue of its lower solubility with respect to the starting THF adduct.

$$Re_2Br_2(CO)_6(THF)_2 + 4\ PPh_2H \rightarrow 2\ ReBr(CO)_3(PPh_2H)_2 + 2\ THF \qquad (2)$$

$$Re_2Br_2(CO)_6(THF)_2 + 2\ PPh_2H \rightarrow Re_2Br_2(CO)_6(PPh_2H)_2 + 2\ THF \qquad (3)$$

$Re_2Br_2(CO)_6(PPh_2H)_2$ has probably a dimeric structure (V) of idealised C_{2h} symmetry, for which three $\nu(CO)$ are expected, to be compared (see Table 6) with the same number of bands observed. Absence of coupling between the two

TABLE 7

MASS SPECTRAL DATA OF CARBONYL DERIVATIVES OF RHENIUM(I) [a]

Ion	$ReBr(CO)_3en$		$ReBr(CO)_3bipy$		$ReBr(CO)_3phen$	
	m/e	Rel. int.	*m/e*	Rel. int.	*m/e*	Rel. int.
$M^{+\cdot}$	410	100	506	68	530	48
$(M-CO)^{+\cdot}$	382	65	478	30	502	28
$(M-2\,CO)^{+\cdot}$	354	42	450	66	474	54
	352	40				
$(M-3\,CO)^{+\cdot}$	326	20	422	100	446	100
	324	24				
	322	24				
$(M-3\,CO-HBr)^{+\cdot}$					366	57
$(M-3\,CO)^{++}$			211	30	223	39
$LL^{+\cdot}$			156	32	180	23

$ReBr(CO)_3(NCC_6H_{11})_2$

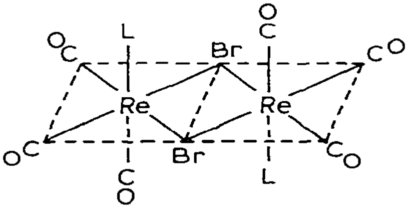
Ion	*m/e*	Rel. int.
$M^{+\cdot}$	568	29
$(M-CO)^{+\cdot}$	540	18
$(M-2\,CO)^{+\cdot}$	512	100
$(M-2\,CO-C_6H_{10})^{+\cdot}$	430	74
$(M-2\,CO-2\,C_6H_{10})^{+\cdot}$	348	99
$(M-3\,CO-2\,C_6H_{10})^{+\cdot}$	320	28

$Re(S_2CNEt_2)(CO)_3(HNEt_2)$

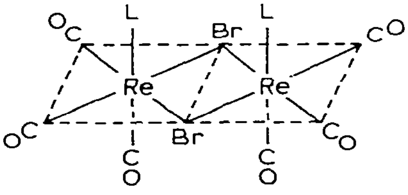
Ion	*m/c*	Rel. int.
M^{+}	492	100
$(M-CO)^{+}$	464	52
$(M-CO-CH_2O)^{+}$	434	22
$(M-HNEt_2)^{+}$	419	96
$(M-2\,CO-CH_2O)^{+}$	406	33
$(M-HNEt_2-CO)^{+}$	391	81
$(M-HNEt_2-2\,CO)^{+}$	363	55
$(M-HNEt_2-3\,CO)^{+}$	335	55

[a] Only peaks with ^{79}Br are reported.

$Re(CO)_3$ units would, of course, result in reduction of the number of bands in less symmetrical structures, for example VI of C_{2v} symmetry. However, vibrational coupling has been found in the complexes $Re_2Br_2(CO)_6E_2R_{2n}$, for which structures I were established by X-ray diffraction methods. In view of these results we do not see any reason to neglect vibrational coupling and we therefore suggest that $Re_2Br_2(CO)_6(PPh_2H)_2$ should have a rather symmetrical structure.



(V)



(VI)

$Re_2Br_2(CO)_6(PPh_2H)_2$ is unstable with respect to $ReBr(CO)_3(PPh_2H)_2$ as shown by the fact that treatment of the dimer with one equivalent of PPh_2H per rhenium formed the monomeric species, presumably by halogen-bridge cleavage (eq. 4).

$$Re_2Br_2(CO)_6(PPh_2H)_2 + 2\,PPh_2H \rightarrow 2\,ReBr(CO)_3(PPh_2H)_2 \qquad (4)$$

The reaction with PPh_2H and the isolation of the dimer appear to us as key-points for the understanding of the reactivity of the dimeric THF adduct, $Re_2Br_2(CO)_6(THF)_2$, with Lewis bases.

The behaviour observed in this case (displacement of THF by PPh_2H, followed by the cleavage of the Br bridge in the intermediate dimer) may be reasonably well regarded to be a quite general pattern of reactivity of $Re_2Br_2(CO)_6(THF)_2$ towards Lewis bases.

The reaction of $Re_2Br_2(CO)_6(THF)_2$ with dimethylamine resulted in the formation of a compound analysing for $ReBr(CO)_3(HNMe_2)_2$ (see Table 8, experimental section). The moderate solubility in aromatic hydrocarbons and the volatility both suggest that this compound is monomeric with a structure similar to III. However, further support of this hypothesis must come from an X-ray investigation, which is now in progress. In this paper, the dimethylamine complexes have been used simply as an intermediate to the dithiocarbamato complexes (vide infra). For the time being we can only say that no evidence has been found for the abstraction of bromide ion from the coordination sphere of rhenium with formation of ionic products, as has been reported by Hieber et al. [14] for pyrrolidine.

Bromide abstraction has, however, been found from the amine complex in the presence of CS_2 or from the dimeric THF adduct by preformed $Et_2NCS_2^-$:

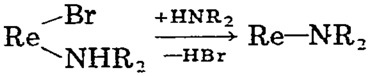
$$ReBr(CO)_3(HNMe_2)_2 + CS_2 + HNMe_2 \rightarrow Re(S_2CNMe_2)(CO)_3(HNMe_2) + Me_2NH_2^+Br^- \qquad (5)$$

$$Re_2Br_2(CO)_6(THF)_2 \quad 2\,NEt_2CS_2^- + 2\,NHEt_2 \rightarrow 2\,Re(S_2CNEt_2)(CO)_3(HNEt_2) + 2\,Br^- + 2\,THF \qquad (6)$$

The known methods of preparation of dithiocarbamato complexes of transition metals are: (i) the insertion of CS_2 in a preformed metal—dialkylamido bond [15], (ii) the treatment of a metal—halogen bond with $M'E_2CNR_2$ [16—20] (M' = alkali metal, Tl), (iii) treatment of low-valent transition-metal complex with $(S_2CNR_2)_2$ resulting in the oxidative addition across the S—S bond [21], and (iv) the direct reaction of a metal—halogen bond with CS_2 and amine [22]. The latter method, which has been applied recently to the synthesis of the tetracarbamato complexes of uranium(IV), is further exemplified by reaction 5.

Dithiocarbamato complexes of formula $Re(CO)_3(S_2CNR_2)L$ (L = CO, PPh_3, py) have been prepared earlier [20] by the reaction of TlS_2CNR_2 with $ReBr(CO)_5$ at the reflux temperature of benzene. Triphenylphosphine-substituted derivatives of rhenium(I)-containing carbamato and dithiocarbamato groups of formula $Re(CO)_2(E_2CNR_2)(PPh_3)_2$ have been reported [23], their preparation involving the amido group displacement from $Re(CO)_3(NHCOR)(PPh_3)_2$ by CE_2 (E = O, S) and the secondary amine.

Reaction 5 may occur by two possible mechanisms a (eq. 7, 8) and b (eq. 9, 10).



$$Re(Br)(NHR_2) \xrightarrow[-HBr]{+HNR_2} Re{-}NR_2 \qquad (7)$$

(a)

$$Re{-}NR_2 + CS_2 \rightarrow Re(S_2CNR_2) \qquad (8)$$

i.e., formation of the dialkylamido complex first, followed by CS_2 insertion, or:

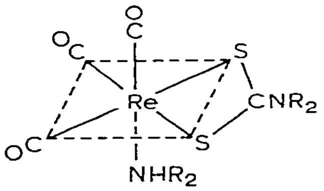
$$2\ NHR_2 + CS_2 \rightleftharpoons R_2NH_2^+R_2NCS_2^- \qquad (9)$$

(b)

$$Re{-}Br + R_2NCS_2^+ \rightleftharpoons Re(S_2CNR_2) + Br^- \qquad (10)$$

Equilibrium 9 was shown [22] spectroscopically to be rapidly established and shifted almost completely to the right. Pathway b appears therefore as a real possibility, in view also of the fact that the diethyldithiocarbamato complex could be obtained from pre-formed $R_2NH_2^+R_2NCS_2^-$ (see eq. 6).

According to IR data (Table 6), to cryoscopic molecular weight measurements (Table 7) in benzene and to mass spectral data (vide infra) showing the parent peak, the dithiocarbamato complexes $Re(CO)_3(S_2CNR)(HNR_2)$ are monomeric. They are therefore suggested to have structure VII. The intense IR absorption at 1505—1520 cm^{-1} is attributed to the C—N stretching vibration of the bidentate dithiocarbamato group [22]. In solvents of high spectral resolution such as heptane and CCl_4, the complexes show three strong carbonyl absorptions, which is in agreement with the proposed structure VII of idealised symmetry C_s.



(VII)

The ^1H NMR spectra of the methyl derivative $Re(S_2CNMe_2)(CO)_3(HNMe_2)$ (see Table 6) show a broad resonance at τ 7.95 due to the NH proton and three other resonances due to the methyl groups which may be interpreted to arise from the methyl groups of the amine ligand (τ 7.53), while the other two resonances are probably caused by the nonequivalent methyl groups of the dithiocarbamato group. The nonequivalence should originate from restricted rotation around the C—N bond of the $S_2C{-}NMe_2$ group. Support for this comes from the observation [24] that the carbamoyl derivative $Re(CONMe_2)(CO)_5$ shows two resonances for the methyl groups separated by 10 Hz (reported for our experimental conditions) and the nonequivalence was also in this case explained by restricted rotation around the C—N bond.

It is interesting to note that the tetracarbonyldithiocarbamato complex, $Re(S_2CNEt_2)(CO)_4$, whose NMR was not reported in ref. 20, shows a quadruplet for the methylene protons and a triplet for the methyl protons, with no indication of restricted rotation around the C—N bond of the dithiocarbamato group.

The tetracarbonyl derivatives $Re(S_2CNR_2)(CO)_4$, R = Me, Et, were prepared by bromide abstraction from $Re_2Br_2(CO)_8$ (eq. 11).

$$Re_2Br_2(CO)_8 + 2\ NR_2H_2^+NR_2CS_2^- \rightarrow 2\ NR_2H_2^+Br^- + 2\ Re(S_2CNR_2)(CO)_4 \qquad (11)$$

The tetracarbonyl derivative was also shown to be formed from the tricarbonylamine complex and carbon monoxide (eq. 12).

$$\mathrm{Re(S_2CNEt_2)(CO)_3(HNEt_2) + CO \rightleftharpoons Re(S_2CNEt_2)(CO)_4 + HNEt_2} \qquad (12)$$

The equilibrium is almost completely shifted to the right at ordinary pressure and temperature. However, in view of the competing coordinating ability of the amine in solution, reaction 11 is a better method of preparation of the tetracarbonyl.

Experimental

Unless otherwise stated, all the operations were carried out in an atmosphere of prepurified nitrogen.

Solvents were purified by conventional methods before use.

Infrared spectra were measured with Perkin—Elmer 337 and 283 instruments on expanded abscissa scale. The nujol and $(C_2ClF_3)_n$ mulls were prepared under a nitrogen atmosphere.

Nuclear magnetic resonance spectra were measured with Varian EM-360 and Jeol PS-100 spectrometers.

Low resolution (RP 1000) mass spectra were measured with a LKB 9000 spectrometer and high resolution (RP 10000) mass spectra with an AEI MS 902 S spectrometer attached to an AEI DS 30 data system.

Bromopentacarbonylrhenium(I), $ReBr(CO)_5$ was prepared according to the literature method [1] in THF as solvent.

The amine complexes $ReBr(CO)_3LL$ (L = 2,2′-bipyridyl, bipy, 9,10-phenanthroline, phen) were prepared according to the method reported previously [1]. The still unknown ethylenediamine complex $ReBr(CO)_3en$ was prepared similarly from the tetrahydrofuran adduct $Re_2Br_2(CO)_6(THF)_2$ and the stoichiometric amount of the amine in toluene at room temperature (89% yield). The combined nujol and $(C_2ClF_3)_n$ infrared spectra of the ethylenediamine complex have

TABLE 8

ANALYTICAL DATA OF CARBONYL DERIVATIVES OF RHENIUM(I)

Compound	Found (calcd.) (%)						
	C	H	Br	Cl	N	P	S
$ReBr(CO)_3(NH_2CH_2CH_2NH_2)$	15.74	2.18	19.56		7.11		
	(14.64)	(1.97)	(19.48)		(6.83)		
$ReBr(CO)_3(PPh_2Cl)_2$	41.86	2.53	9.65	8.70		8.16	
	(40.98)	(2.55)	(10.10)	(8.96)		(7.83)	
$ReBr(CO)_3(PPh_2H)_2$	44.79	3.05	11.02			8.17	
	(44.88)	(3.07)	(11.06)			(8.57)	
$Re_2Br_2(CO)_6(PPh_2H)_2$	33.28	2.05	14.50			5.20	
	(33.59)	(2.07)	(14.90)			(5.78)	
$ReBr(CO)_3(NHMe_2)_2$	19.58	3.00	17.90		6.27		
	(19.09)	(3.20)	(18.15)		(6.36)		
$Re(S_2CNMe_2)(CO)_3(HNMe_2)$	22.24	3.08			6.12		15.01
	(22.06)	(3.01)			(6.43)		(14.72)
$Re(S_2CNEt_2)(CO)_3(HNEt_2)$	29.27	4.34			5.62		12.90
	(29.32)	(4.31)			(5.70)		(13.04)
$Re(S_2CNMe_2)(CO)_4$ [a]	20.24	1.46			3.34		14.66
	(20.09)	(1.45)			(3.35)		(15.32)

[a] The corresponding ethyl derivative has been reported in ref. 20.

bands at 3340w, 3325, 3250(sh), 3230m, 3160w, 2960w, 2020s, 1920(sh), 1880s, 1730w, 1585m, 1455m-w, 1290w, 1165w, 1135w, 1120m, 1095w, 1050m, 990w, and 520w-m cm^{-1}.

Analytical data of the compounds prepared are shown in Table 8.

Collection of X-ray data

Data were collected by using the same technique described in previous papers of this series [3—6]. The only difference is the values of the parameters used to program the CAD-4 diffractometer for data collection and those are listed in Table 1. The crystal used for data collection was obtained by recrystallization of the tetrahydrofuran adduct from a THF/iso-octane mixture in the following manner. At room temperature under nitrogen, the rhenium complex was dissolved in tetrahydrofuran and iso-octane was then added. The solution was then maintained in the refrigerator at about 0°C for some hours: the crystals were then filtered by section under nitrogen and dried in vacuo. The approximate size of the crystal used in data collection is given in Table 1; however, the values are clearly not sufficiently accurate to permit a useful absorption correction, as we found out when the structure was solved and the data refined. We refined the molecular structure, first without an absorption correction and, later, with an absorption correction based on the coefficient of 155.6 cm^{-1} (calculated from the values in the International Tables) and the size described in Table 1. The results are worse than without an absorption correction and here is why. The crystals are air sensitive and fragile and they cannot be pressed into the capillary with a glass rod so as to clamp them into a steady position, since they shatter. Therefore, we had to coat the inside of the capillary with grease and push the crystal into it. All of these manipulations were carried out in a dry box filled with nitrogen. Attempts to measure the crystal were difficult because both the crystal and the grease were milky white and it was, thus, problematic to decide where the edges of the crystal were. As a result, the data presented in this paper are not corrected for absorption.

Solution and refinement of structure

The structure was solved using a Patterson function from which the Re and Br atoms of the asymmetric unit were readily located. Difference maps showed the positions of the missing atoms. Anisotropic refinement converged eventually to the $R(F)$ and $R_w(F)$ factors listed in Table 1. However, note that atoms C(1), C(3) and O(4) have anisotropic thermal parameters whose tensor components constitute a non-positive definite set which is characteristic of data sets afflicted by either lack of absorption corrections or imperfect corrections of that type. Above, we explained the nature of the problem associated with obtaining suitable physical data for an absorption correction.

Preparation of $ReBr(CO)_3(PPh_2Cl)_2$ (I)

The tetrahydrofuran adduct $Re_2Br_2(CO)_6(THF)_2$ (1.28 g, 1.52 mmol) was suspended in 75 ml toluene and treated with chlorodiphenylphosphine (1.6 ml, 8.63 mmol) with stirring for 48 h at room temperature. After filtration from traces of suspended solid, heptane was added to the solution and the colourless precipitate was filtered and dried in vacuo (1.85 g, 77% yield). By cryoscopy in benzene for a 0.027 *M* solution, mol. wt. 721 was found (calcd. 791.4). Infrared bands of the complex in nujol are at 3060w, 2040s, 1985m-s, 1970s, 1940s, 1920(sh), 1890m, 1435m, 1190m, 1164w, 1085s, 995m, 740w, 730m, 665s, 610w and 545m cm^{-1}.

Reaction between $Re_2Br_2(CO)_6(THF)_2$ *and* PPh_2H

(A) Molar ratio $PPh_2H/Re > 2$. *Preparation of* $ReBr(CO)_3(PPh_2H)_2$. The tetrahydrofuran adduct (1.14 g, 1.35 mmol) was suspended in 10 ml toluene and treated with diphenylphosphine (2.2 ml, 13.0 mmol). The solid dissolved rapidly, and the resulting solution was stirred for about 65 h, which caused partial precipitation of the colourless complex to occur. The latter was then filtered and dried in vacuo (0.93 g, 48% yield). By cryoscopy in benzene for a 0.039 *M* solution, mol. wt. 693 was found (calcd. 722.5). The infrared spectrum of the complex as nujol mull has bands at 3058w, 2320w (P—H), 2040s, 2020 (sh), 1960s, 1920s, 1870w, 1735w, 1580w, 1570w, 1560w, 1440m, 1305w, 1275w, 1185w, 1168w, 1160w, 1110w, 1090w, 1028w, 1000w, 935w, 918w, 895s, 890s, 870s, 860s, 855(sh), 745m, 738(sh), 735s, 705w, 695w, 615m-s, 605m, 585m, 535m, 515m, 510m, 500m, 490(sh), 465w, 455s, 440w, and 410w cm^{-1}.

(B) Molar ratio $PPh_2H/Re \sim 0.5$. *Preparation of* $Re_2Br_2(CO)_6(PPh_2H)_2$. The tetrahydrofuran adduct (1.73 g, 2.05 mmol) was dissolved in toluene (200 ml) and treated with 0.36 ml (2.13 mmol) of PPh_2H. After stirring overnight, the reaction mixture was filtered and the colourless solid was washed with toluene and dried in vacuo (0.085 g, 39% yield). The nujol infrared spectrum has bands at 3070w, 2370w (P—H), 2030s, 1930s, 1920s, 1430m, 1190m, 1160w, 1110w, 1095w, 1030w, 1000w, 890s, 855s, 845m, 840w, 745m, 735s, 710w, 690s, 640m, 610m, 515m-s and 495m cm^{-1}.

(C) Reaction of $Re_2Br_2(CO)_6(PPh_2H)_2$ *with* PPh_2H. The product resulting from *B* (0.12 g, 0.112 mmol) was suspended in toluene (10 ml) and treated with PPh_2H (0.04 ml, 0.236 mmol). After stirring for 16 h the original solid had dissolved almost completely and the solution showed only the bands at 2040, 1965 and 1905 cm^{-1} due to $ReBr(CO)_3(PPh_2H)_2$.

Reaction between $Re_2Br_2(CO)_6(THF)_2$ *and* Me_2NH

The tetrahydrofuran adduct (2.104 g, 2.49 mmol) was added at about —10°C to a solution of dimethylamine (1.4 g, 31.1 mmol) in toluene (12 ml). Within about 30 min, the tetrahydrofuran adduct dissolved out and then a colourless solid began to precipitate. After 48 h stirring, the reaction mixture was filtered and the solid was recrystallised from toluene by heating at about 70°C and then allowing the solution to reach ambient temperature slowly. The precipitation of the complex was facititated by cooling at about 0°C. The well formed crystals of $ReBr(CO)_3(Me_2NH)_2$ were filtered and dried in vacuo (1.55 g, 71% yield). The compound was sublimed at about 100°C/ca. 10^{-3} mmHg as a microcristalline colourless substance: the yield of sublimation was 78%. The product before and after sublimation had similar analytical composition and identical infrared spectra. The combined nujol and $(C_2ClF_3)_n$ IR spectra showed bands at 3210m (N—H), 3030m, 2980w, 2940m, 2850w, 2805w, 2515w, 2415w, 2300w, 2025s, 1920s, 1875s, 1660w, 1465m, 1430m, 1410w, 1285w, 1265w, 1215w, 1125m, 1080m, 1055w, 1035m-s, 1015m, 1010m, 900s, 662s, 635s-m 540s, 530m-s and 495m cm^{-1}.

Preparation of $Re(CO)_3(S_2CNMe_2)(NHMe_2)$

The dimethylamine complex $ReBr(CO)_3(NHMe_2)_2$ (1.609 g, 3.65 mmol) was suspended in 20 ml toluene and treated with CS_2 (0.22 ml, 3.64 mmol) and dimethylamine (43.5 mmol) at room temperature for three days. After filtration of $Me_2NH_2^+Br^-$, the filtrate was concentrated in vacuo and then heptane was added, which caused the precipitation of the complex. The latter was filtered and dried in vacuo (0.96 g, 60% yield). The dithiocarbamato complex is colourless and shows an intense band at 1520 cm^{-1} due to the C—N stretching vibration of the S_2CNMe_2 group. The mol. wt. found by cryoscopy in benzene for a 0.046 *M* solution was 457 (calcd. 435.5). The nujol infrared spectrum has bands at 3260w (N—H), 3210w (N—H), 2010s, 1900 (sh), 1890s, 1875s, 1520m (C—N), 1250m, 1145w, 1120w, 1075w, 1035m-s, 1010w, 975m, 898m, 640m, 630w, 570w, 530m, 520m-s, 500w, 485w, 480w and 440w cm^{-1}.

Preparation of $Re(S_2CNEt_2)(CO)_3(HNEt_2)$

Diethylammonium diethyldithiocarbamate, $Et_2NH_2^+Et_2NCS_2^-$ (0.595 g, 2.67 mmol), prepared from CS_2 and Et_2NH in a molar ratio 1/2 in toluene, was dissolved in toluene (25 ml). The tetrahydrofuran adduct $Re_2Br_2(CO)_6(THF)_2$ (1.13 g, 1.34 mmol) was then added together with 3.3 ml diethylamine (31.6 mmol). After stirring overnight, the precipitate of $Et_2NH_2^+Br^-$ was separated by filtration. The volume of the filtrate was reduced to about 6 ml under reduced pressure and heptane was then added to complete the precipitation of the complex. The latter was filtered and dried in vacuo (0.609 g, 46% yield). The mol. wt. found for a 0.0398 *M* solution by cryoscopy in benzene was 517 (calcd.: 491.6). The combined nujol and $(C_2ClF_3)_n$ infrared spectra have bands at 3240w (N—H), 2980w, 2940w, 2040w, 2020s, 2010s, 1890s, 1870s, 1505m (C—N), 1460w, 1440w, 1380w, 1360w, 1300m, 1280m, 1205m, 1145m, 1035w, 1025m, 910w, 845w, 785w, 640w, 630w, 620w, 520w, and 480w cm^{-1}.

Preparation of $Re(S_2CNMe_2)(CO)_4$

The rhenium tetracarbonyl dimer $Re_2Br_2(CO)_8$ (1.307 g, 1.73 mmol) was treated at room temperature with $Me_2NCS_2^-Me_2NH_2^+$ (0.584 g, 3.51 mmol) in toluene (20 ml) under an atmosphere of carbon monoxide. After two days the reaction mixture was filtered and heptane was added to the filtrate. The colourless precipitate obtained was filtered under CO and dried briefly in vacuo (0.26 g, 18% yield).

Preparation of $Re(S_2CNEt_2)(CO)_4$

This compound was prepared similarly to the methyl derivative reported above from $Re_2Br_2(CO)_8$ and $Et_2NCS_2^-Et_2NH_2^+$ in toluene under an atmosphere of carbon monoxide. Addition of heptane to the filtrate and cooling down to ca. —78°C caused crystallization of the compound to occur. This was filtered under CO and dried in vacuo (46% yield).

The equilibrium 12 between the tricarbonylamine and the tetracarbonyl derivatives was shown to occur at room temperature by letting a 1.63×10^{-2} *M* solution of the dithiocarbamato complex in toluene react with CO at atmospheric pressure for several hours at room temperature. After 65 h, a trace amount of the starting material was observed spectroscopically (band at 1909 cm^{-1}), while the four bands of the tetracarbonyl derivative were found in the carbonyl stretching region at 2100, 2000, 1980 and 1940 cm^{-1}. A similar experiment carried out in a heptane suspension led to only partial conversion of the tricarbonyl compound to the tetracarbonyl one.

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