

# PHOTOCHEMICAL REACTION OF DECACARBONYLDIRHENIUM WITH THIOPHENE AND CRYSTAL STRUCTURE OF TETRADECACARBONYLHYDRIDOTRIRHENIUM

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**Key Word Index**—Photochemistry; rhenium; crystal structure.

The photochemical reaction of  $\text{Re}_2(\text{CO})_{10}$  with thiophene in hexane solution was investigated under vacuum. Three rhenium clusters:  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ ,  $\text{HRe}_3(\text{CO})_{14}$  and  $\text{Re}_4(\text{CO})_{17}(\text{OH})_4$  were isolated. The structure of Fellmann-Kaesetz cluster Complex  $\text{HRe}_3(\text{CO})_{14}$  was determined by use of the X-ray diffraction method. The three rhenium atoms form a plane of symmetry and  $\text{L:Re}_1\text{Re}_2\text{Re}_3$  is  $107^\circ$ . The ten carbonyl groups bonded to the two terminal rhenium atoms  $\text{Re}_1$  and  $\text{Re}_3$ , are staggered with respect to the central rhenium atoms. The bond lengths are 3.10 Å for  $\text{Re}_2\text{-Re}_3$  and 3.34 Å for  $\text{Re}_1\text{-Re}_2$ . The bridging hydride is between  $\text{Re}_1$  and  $\text{Re}_2$ .

Reduction of  $\text{Re}_2(\text{CO})_{10}$  with sodium borohydride yields several rhenium carbonyl cluster compounds:  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$ ,  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$ ,  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$ ,  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$  and  $[\text{Re}_4(\text{CO})_{17}]^{2-}$ . The other major reaction pathway leading to the formation of rhenium carbonyl cluster compounds is the reaction between  $\text{Re}_2(\text{CO})_{10}$  and ethanolic potassium hydroxide. It yields the unsaturated cluster compounds:  $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$ ,  $[\text{H}_3\text{Re}_3(\mu_3\text{-O})(\text{CO})_8]^{2-}$ ,  $[\text{H}_3\text{Re}_3(\text{CO})_{15}]^{2-}$  and  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$ . Most of other known rhenium carbonyl cluster compounds are prepared using the above cluster compounds as starting reagents. For example, in refluxing acetone,  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  can be converted to  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ .  $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$  and  $[\text{H}_3\text{Re}_3(\text{CO})_{15}]^{2-}$  can be prepared from  $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$ . This work will report that the rhenium carbonyl cluster compounds can also be prepared from photochemical reaction of  $\text{Re}_2(\text{CO})_{10}$  with thiophene.

Most of the known rhenium carbonyl cluster compounds have been characterized by X-ray structural determination. There are exceptions, though, which include the relatively simple compounds:  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $\text{HRe}_3(\text{CO})_{14}$ . The crystal disorder of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  prevents a meaningful X-ray structural determination. However, its main structural features can be deduced from  $[\text{HRe}_3(\text{CO})_{12}]^{2-}$  and  $[\text{H}_3\text{Re}_3(\text{CO})_{12}]^{2-}$ . A detailed structure of the Fellmann-Kaesetz complex,  $\text{HRe}_3(\text{CO})_{14}$ , known since 1966, on the other hand, has never been reported. It is the main product in the photochemical reaction between  $\text{Re}_2(\text{CO})_{10}$  and thiophene. It is our intention to determine the structure of this product.

## EXPERIMENTAL

### (A) Photochemical Reaction of $\text{Re}_2(\text{CO})_{10}$ with Thiophene:

0.4 mM  $\text{Re}_2(\text{CO})_{10}$  (obtained from the

Strem Chemical Co.) and excess ( $\approx 5$  mM) thiophene (obtained from the Aldrich Chemical Co.) were dissolved in 20 ml of hexane (purified by standard procedure). After standard vacuum degassing procedure, the solution was irradiated, under vacuum, with a Hanovia 450 W medium pressure mercury lamp. The gas generated in the reaction was pumped away in a vacuum line every 30 minutes. After photolysis for 10 hours, the solvent was removed by vacuum distillation. The yellowish-brown residue was dissolved in ethylacetate. Separation was accomplished by preparative TLC made from silica gel 60 PF<sub>254</sub> with hexane-benzene (6:1) mix solvent as eluent. Four compounds were obtained, besides 45% of unreacted Re<sub>2</sub>(CO)<sub>10</sub>. The instruments used to obtain various spectra of those compounds were Perkind Elmer 580 for IR; Jeol JNM-FX 100 for NMR; and Jeol JMS-D-100 (12eV) for Mass. The detailed spectroscopic data of three of the four compounds are presented below. The fourth compound, with a 7% yield, could not be identified.

**Compound I:** White solid stable in air. Easily sublimable at 60°C under vacuum.  $R_f$ : 0.65 (hexane-benzene 6:1 mix solvent). Purified yield: 4.5%.  $\nu_{C=O}$  and  $\nu_{Re-H}$  (in cyclohexane): 2093 (*m*), 2030 (*vs*), 2005 (*m*), 1982 (*m*)  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  (CDCl<sub>3</sub>): -16.98 *ppm*. Mass: 899, 898, 897, 896, 895, 894, 893 (M-*n*H, M=H<sub>2</sub>Re<sub>2</sub>(CO)<sub>10</sub>); 870, 868, 866, 864 (M-CO-2H); 842, 840, 838, 836 (M-2CO-2H); 814, 812, 810, 808 (M-3CO-2H); 785, 783, 781, 779 (M-4CO-3H); 654, 652, 650; 626; 624, 622; 598, 596, 594; 570, 568, 566; 542, 540, 538; 514, 512, 510; 486, 482; 458, 456, 454; 431, 429, 427; 327, 325; 299, 297.

**Compound II:** Yellow crystal, stable in air. m.p.: 115°C.  $R_f$ : 0.45 (in hexane-benzene 6:1 mix solvent). Yield: 17%.  $\nu_{C=O}$  and  $\nu_{Re-H}$  (in cyclohexane): 2140 (*vw*), 2100 (*w*), 2040 (*vs*), 2008 (*m*), 1990 (*s*), 1978 (*m*), 1965 (*w*), 1930 (*m*)  $cm^{-1}$ .  $^1H$  NMR (acetone-*d*<sub>6</sub>): -15.96 *ppm*. Mass: 954, 952, 950, 948 (M=HRe<sub>2</sub>(CO)<sub>10</sub>); 926, 924, 922, 920 (M-CO); 898, 896, 894, 892 (M-2CO); 870, 868, 866, 864 (M-3CO). There are low mass peaks

starting from 654. These peaks are identical to those presented in compound I.

**Compound III:** Light yellow crystal.  $R_f$  (hexane-benzene 4:1 mix solvent): 0.35. Yield: 7.3%. Decomposition temperature: 80°.  $\nu_{C=O}$  (CHCl<sub>3</sub>): 2020 (*s*), 1920 (*vs*)  $cm^{-1}$ .  $^1H$  NMR: 3.34 *ppm*.  $^{13}C$  NMR: 196.4 *ppm*. Mass: 108, 90, 74, 73, 64, 58, 46, 44, 30, 18. Found Re: 63.4% (neutron activation analysis).

#### (B) X-ray Structural Determination of HRe<sub>2</sub>(CO)<sub>10</sub>

A 0.1×0.4×0.5 mm crystal of compound II was chosen for study by X-ray diffraction of the molecular and crystal structure. Compound II crystallizes in orthorhombic cell *Pnma* with  $a=9.812$  (1),  $b=12.582$  (3),  $c=17.010$  (3) Å,  $z=4$ . A total of 3458 reflections were measured by  $w/2\theta$  scan technique, the scan range was calculated according to  $(1.6+0.7\tan\theta)^\circ$ . The absorption corrections were applied on the basis of measured faces, the transmission coefficients varied from 0.019 to 0.177 ( $\mu=175$   $cm^{-1}$ ,  $Mok\alpha$ ). The calculated and experimental  $\Psi$  rotation on 3 reflections do give very good agreement. The structure was solved by means of the heavy atom method. Three Re atoms are on the crystallographic mirror plane. All the carbonyl groups appeared in the subsequent Fourier synthesis maps. The model was then refined by the least square process based on 1217 reflections ( $I \geq 3\sigma(I)$ ). The process, however, was not successful. Nevertheless, the agreement indices ( $R=0.088$ ,  $R_w=0.075$ ) are acceptable. Thus the model is believed to be correct; the failure of the refinement is probably due to the inconsistency of the relative intensities which may be resulted from the contamination of the impurity.

Such a phenomenon is known for other Re compounds.<sup>6,10</sup> The crystal structure analysis of this very compound, HRe<sub>2</sub>(CO)<sub>10</sub>, has been mentioned in the literature.<sup>10</sup> But the completed work did not appear later on in the literature. It is somewhat

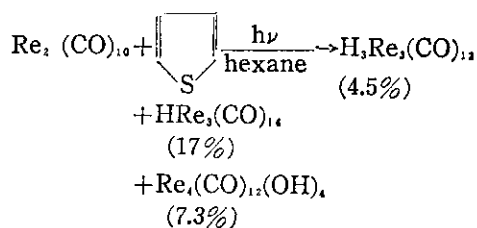
doubtful that the analysis of other Re compounds encountered the similar problems.

## RESULTS AND DISCUSSION

After photolysis of a hexane solution containing  $\text{Re}_2(\text{CO})_{10}$  and thiophene using a 450W mercury lamp for ten hours, four compounds I-IV were obtained, besides the unreacted  $\text{Re}_2(\text{CO})_{10}$  (45%). On comparison with the reported IR data<sup>23</sup>, Compound I was identified to be  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ . Based on the IR data<sup>12,13</sup>, Compound II was identified as  $\text{HRe}_3(\text{CO})_{14}$ . The mass spectroscopic data furnished further support of the identification. Though the molecular ion  $\text{M}^+$  peaks of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  were not detected, the deprotonated peaks  $(\text{M}-\text{nH})^+$  could be observed between 899 and 893. The  $(\text{M}-\text{nCO}-\text{mH})^+$  peaks were also detected for  $n$  up to 4. The  $\text{M}^+$  of  $\text{HRe}_3(\text{CO})_{14}$  could be easily recognized at 954, 952, 950 and 948 with an intensity ratio 4.9:8.8:5.2:1 as expected from the isotope abundance distribution. The decarbonylated peaks:  $[\text{M}-\text{CO}]^+$ ,  $[\text{M}-2\text{CO}]^{2+}$  and  $[\text{M}-3\text{CO}]^+$ , were clearly observed for  $\text{HRe}_3(\text{CO})_{14}$ . Both compounds decomposed in the mass spectrometer to yield  $\text{Re}_2(\text{CO})_{10}$ , which was responsible for the mass peaks observed between 654 and 297.

The simple IR spectrum of Compound III is identical to the reported spectrum of  $\text{Re}_4(\text{CO})_{12}(\text{OH})_4$ .<sup>14</sup> The  $^1\text{H}$  NMR signal at 3.34 ppm and  $^{13}\text{C}$  NMR signal at 196.4 ppm are also the characteristics of  $\text{Re}_4(\text{CO})_{12}(\text{OH})_4$ . The result of elemental analysis of Re (Found: 63.4%, Calc. 64.8%) leaves no doubt that compound III is  $\text{Re}_4(\text{CO})_{12}(\text{OH})_4$ . The parent peak and other peaks with  $m/e$  above 1000 could not be observed because of the limitation of our mass spectrometer. However, no mass peak containing rhenium could be observed below 1000. It is indicated that the decomposition of  $\text{Re}_4(\text{CO})_{12}(\text{OH})_4$  does not go through the  $\text{Re}_2(\text{CO})_{10}$  intermediate as observed for  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $\text{HRe}_3(\text{CO})_{14}$ .

Thus, the photochemical reaction between  $\text{Re}_2(\text{CO})_{10}$  and thiophene can be expressed as:



The numbers in the parenthesis are the purified yield based on the amount of reacted  $\text{Re}_2(\text{CO})_{10}$ .

After photolyzing a sealed NMR tube containing  $\text{Re}_2(\text{CO})_{10}$  and thiophene, a  $^1\text{H}$  NMR signal at  $-14.7$  ppm, different from those of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  ( $-16.98$  ppm) and  $\text{HRe}_3(\text{CO})_{14}$  ( $-15.96$  ppm), was observed. This signal is very close to the signal of bridging hydride in  $(\mu\text{-H})\text{Re}_2(\text{CO})_8(\text{CO})_2$ ,  $(\mu\text{-C}_5\text{H}_4\text{N})^{13}$  ( $-14.52$  ppm), and  $(\mu\text{-H})\text{Re}_2(\text{CO})_8$ ,  $(\mu\text{-CH}=\text{CH}_2)^{16}$  ( $-14.72$  ppm). Thus, one of the key intermediates in the photoreactions of  $\text{Re}_2(\text{CO})_{10}$  with thiophene is very likely to be  $(\mu\text{-H})\text{Re}_2(\text{CO})_8$ ,  $(\mu\text{-C}_5\text{H}_4\text{N})$ . This intermediate then decomposed to yield  $\text{HRe}_3(\text{CO})_{14}$ , which reacted further to produce various rhenium carbonyl cluster compounds. This proposed mechanism is similar to that proposed by Graham<sup>13</sup> *et al.* to account for the production of  $\text{HRe}_3(\text{CO})_{14}$  in the photochemical reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{HSiCl}_3$ .

The molecular structure of  $\text{HRe}_3(\text{CO})_{14}$  is shown in Fig. 1, the atomic coordinates are given in Table 1. Bond lengths and angles are listed in Table 2. There are slightly distorted octahedral geometries around the three Re atoms: the terminal Re, Re, atoms have one carbonyl group on the mirror plane trans to Re-Re bond, the other two pairs of carbonyl groups are on a plane perpendicular to the Re-Re bond. The central  $\text{Re}_2$  atom has two carbonyl groups on the mirror plane trans to Re-Re bonds, the other pair serves as axial ligands perpendicular to this plane. The on-plane Re-C distances (1.71-1.93 Å)

Table 1. Fractional atomic coordinates and thermal<sup>†</sup> parameters\* ( $\times 10^{-2}\text{\AA}^2$ )

Atom	X	Y	Z
Re <sub>1</sub>	0.0359(3)	0.2500	0.0753(5)
Re <sub>2</sub>	0.3568(4)	0.2500	0.0137(4)
Re <sub>3</sub>	0.3508(4)	0.2500	-0.1628(4)
O <sub>11</sub>	-0.250	0.250	0.158
O <sub>12</sub>	0.150	0.432	0.190
O <sub>13</sub>	-0.083	0.077	-0.042
C <sub>11</sub>	-0.134	0.250	0.134
C <sub>12</sub>	0.140	0.352	0.156
C <sub>13</sub>	-0.036	0.137	0.001
C <sub>21</sub>	0.411	0.250	0.117
C <sub>22</sub>	0.544	0.250	-0.008
C <sub>23</sub>	0.350	0.409	0.001
O <sub>21</sub>	0.432	0.250	0.192
O <sub>22</sub>	0.669	0.250	-0.011
O <sub>23</sub>	0.345	0.503	-0.008
O <sub>31</sub>	0.350	0.250	-0.337
O <sub>32</sub>	0.570	0.422	-0.161
O <sub>33</sub>	0.134	0.062	-0.149
C <sub>31</sub>	0.355	0.250	-0.269
C <sub>32</sub>	0.495	0.363	-0.157
C <sub>33</sub>	0.217	0.125	-0.154
H <sub>1</sub>	0.185	0.250	0.025

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>13</sub>
Re <sub>1</sub>	2.5(2)	5.7	2.8(5)	-0.2(4)
Re <sub>2</sub>	1.5(2)	6.3(5)	3.1(5)	-0.1(3)
Re <sub>3</sub>	3.0(5)	5.2(6)	4.4(5)	0.2(3)

\* U<sub>12</sub>=U<sub>23</sub>=0 for Re atoms.

The isotropic thermal parameters are fixed at 0.06 Å<sup>2</sup> for carbon and oxygen atoms and at 0.08 Å<sup>2</sup> for hydrogen atom.

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$$

<sup>†</sup> The estimated standard deviation for non-rhenium atoms is 0.003-0.006.

trans to carbonyl groups. This may be explained as better back-bonding on the carbonyl groups which are trans to Re-Re bond than on those trans to another carbonyl group. The carbonyl groups around Re<sub>1</sub> and Re<sub>2</sub> atoms are staggered from those of Re<sub>3</sub>. The torsion angles between the carbonyl groups on neighbo-

Table 2. Selected bond lengths (Å) and angles (°)

Re <sub>1</sub> -Re <sub>2</sub>	3.34(1)	Re <sub>2</sub> -Re <sub>3</sub>	3.10(1)
Re <sub>1</sub> -H <sub>1</sub>	1.70	Re <sub>2</sub> -C <sub>21</sub>	1.84
Re <sub>1</sub> -C <sub>11</sub>	1.93	Re <sub>2</sub> -C <sub>22</sub>	1.84
Re <sub>1</sub> -C <sub>12</sub>	2.00	Re <sub>2</sub> -C <sub>23</sub>	2.02
Re <sub>1</sub> -C <sub>13</sub>	2.02	Re <sub>2</sub> -H <sub>1</sub>	1.74
Re <sub>3</sub> -C <sub>31</sub>	1.71	C <sub>11</sub> -O <sub>11</sub>	1.21
Re <sub>3</sub> -C <sub>32</sub>	2.02	C <sub>12</sub> -O <sub>12</sub>	1.24
Re <sub>3</sub> -C <sub>33</sub>	2.04	C <sub>13</sub> -O <sub>13</sub>	1.15
C <sub>21</sub> -O <sub>21</sub>	1.28	C <sub>31</sub> -O <sub>31</sub>	1.16
C <sub>22</sub> -O <sub>22</sub>	1.23	C <sub>32</sub> -O <sub>32</sub>	1.05
C <sub>23</sub> -O <sub>23</sub>	1.18	C <sub>33</sub> -O <sub>33</sub>	1.13
Re <sub>2</sub> -Re <sub>1</sub> -C <sub>11</sub>	167	Re <sub>1</sub> -Re <sub>2</sub> -Re <sub>3</sub>	107
Re <sub>2</sub> -Re <sub>1</sub> -C <sub>12</sub>	84	Re <sub>1</sub> -Re <sub>2</sub> -C <sub>12</sub>	88
Re <sub>2</sub> -Re <sub>1</sub> -C <sub>13</sub>	98	Re <sub>2</sub> -Re <sub>1</sub> -C <sub>13</sub>	98
Re <sub>2</sub> -Re <sub>2</sub> -C <sub>21</sub>	173	C <sub>11</sub> -Re <sub>1</sub> -C <sub>12</sub>	90
C <sub>11</sub> -Re <sub>1</sub> -C <sub>13</sub>	91	Re <sub>3</sub> -Re <sub>2</sub> -C <sub>21</sub>	165
C <sub>12</sub> -Re <sub>1</sub> -C <sub>12'</sub>	80	Re <sub>3</sub> -Re <sub>2</sub> -C <sub>22</sub>	80
C <sub>12</sub> -Re <sub>1</sub> -C <sub>13</sub>	175	Re <sub>3</sub> -Re <sub>2</sub> -C <sub>23</sub>	84
C <sub>12</sub> -Re <sub>1</sub> -C <sub>13'</sub>	96	C <sub>21</sub> -Re <sub>2</sub> -C <sub>22</sub>	85
C <sub>13</sub> -Re <sub>1</sub> -C <sub>13</sub>	89	C <sub>21</sub> -Re <sub>2</sub> -C <sub>23</sub>	97
Re <sub>2</sub> -Re <sub>3</sub> -C <sub>31</sub>	177	C <sub>22</sub> -Re <sub>2</sub> -C <sub>23</sub>	91
Re <sub>2</sub> -Re <sub>3</sub> -C <sub>32</sub>	83	C <sub>23</sub> -Re <sub>2</sub> -C <sub>23'</sub>	167
Re <sub>2</sub> -Re <sub>3</sub> -C <sub>33</sub>	84	Re <sub>1</sub> -H <sub>1</sub> -Re <sub>2</sub>	156
C <sub>31</sub> -Re <sub>3</sub> -C <sub>32</sub>	94	Re-C-O	168-179 <sup>o</sup>
C <sub>31</sub> -Re <sub>3</sub> -C <sub>33</sub>	98		
C <sub>32</sub> -Re <sub>3</sub> -C <sub>32'</sub>	89		
C <sub>32</sub> -Re <sub>3</sub> -C <sub>33</sub>	16		
C <sub>32</sub> -Re <sub>3</sub> -C <sub>33'</sub>	84		
C <sub>33</sub> -Re <sub>3</sub> -C <sub>33'</sub>	100		

\* The estimated standard deviation of Re-Cis 0.02 Å and of C-O is 0.03 Å.

ring Re atoms are 42-45°. The angle of Re<sub>1</sub>-Re<sub>2</sub>-Re<sub>3</sub> (107°) is larger than that of Re<sub>1</sub>-Re<sub>2</sub>-Mn in HMnRe<sub>3</sub>(CO)<sub>12</sub><sup>22</sup>.

The distance between Re<sub>2</sub> and Re<sub>3</sub> atoms (3.10 Å) is longer than that in Re<sub>3</sub>(CO)<sub>10</sub><sup>22</sup> (3.02 Å) and the other known rhenium cluster compounds<sup>19</sup>. The distance between Re<sub>1</sub> and Re<sub>2</sub> atoms (3.34 Å) is even longer, which is comparable with hydrogen bridged Re-Re distances. Such distances do vary over a wide range, e.g. 3.09 Å in H<sub>2</sub>Re<sub>2</sub>(CO)<sub>10</sub><sup>21</sup>, 3.144 Å in (HRe<sub>3</sub>(CO)<sub>12</sub>)<sub>2</sub><sup>20</sup>,

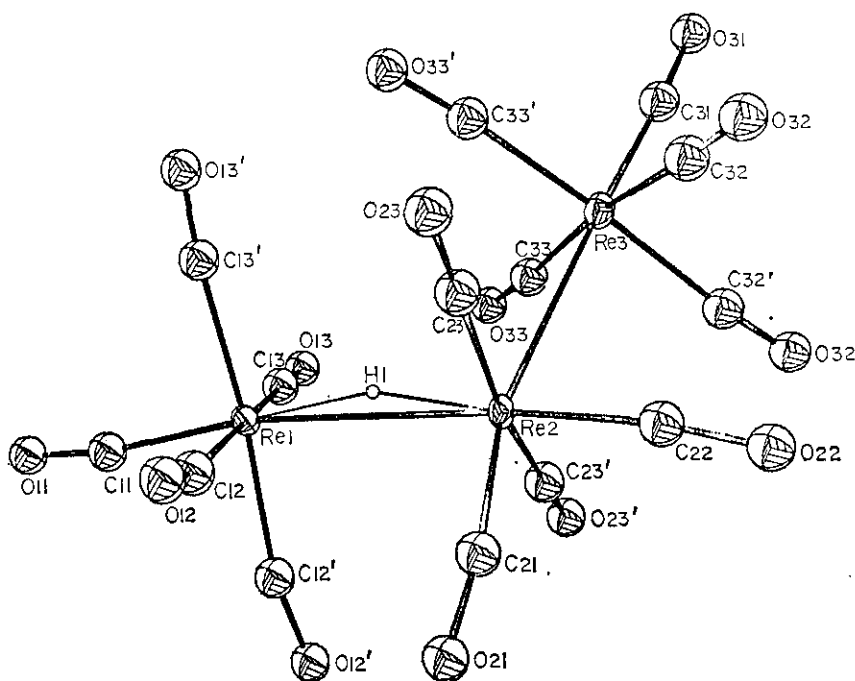


Fig. 1.

2.16 Å in  $(\text{H}_2\text{Re}_2(\text{CO})_{10})^{2-}$  and 3.39 Å in  $\text{HMnRe}_2(\text{CO})_{10}$ .<sup>22</sup> The variation in bond lengths is believed to be correlated with the variation in Re-H-Re angles. Unfortunately, the location of hydrogen atoms in the X-ray analysis is not well-defined enough for confirmation.

There are some subtle structural differences between the two very similar compounds:  $\text{HRe}_2(\text{CO})_{10}$  (II) and  $\text{HMnRe}_2(\text{CO})_{10}$  (V). Their simplified structures are depicted in Fig. 2.

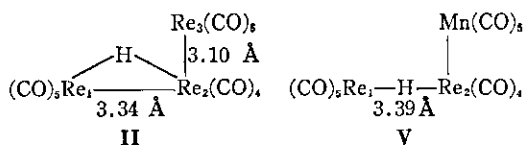


Fig. 2. The simplified structure of  $\text{HRe}_2(\text{CO})_{10}$  and  $\text{HMnRe}_2(\text{CO})_{10}$ .

The  $\text{Re}_1$ - $\text{Re}_2$  bond distances are 3.34 Å in (II) and 3.39 Å in (V). The carbonyl groups around  $\text{Re}_1$  and  $\text{Re}_2$  assume the staggered configuration in (II) and eclipsed configuration in (V). The bond length of  $\text{Re}_2$  and  $\text{Re}_1$  in (II) is the longest of all

known simple Re-Re bonds, while the  $\text{Re}_2$ -Mn bond length of (V) is that expected from  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Mn}_2(\text{CO})_{10}$ . The eclipsed carbonyl configuration in (V) indicates that the carbonyl groups interact only weakly through van der Waals force,<sup>19</sup> while the staggered configuration suggests a possible direct interaction between the  $\text{Re}_1$  and  $\text{Re}_2$ . The bond lengths between the central  $\text{Re}_2$  and the other metal atoms may be a reflection of the different degree of interaction between  $\text{Re}_1$  and  $\text{Re}_2$ .

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