terminal CO's. In contrast, in benzene or toluene the bridging CO peak is substantially weaker, and the terminal CO region is more complex, indicating an equilibrium between the bridged structure found in the solid state and at least one other structure is present in these solvents. This is supported by the ^{1}H NMR, which shows three peaks in the normal Cp region. The two Cp ligands in I are nearly equivalent[14] and should give only a single peak. Analogous behavior has been observed for $Co_2(CO)_8$, which in solution is an equilibrium mixture of doubly CO-bridged (the solid-state structure) and nonbridged isomers.[15] Because of the low overall symmetry of I, it is not possible to use the total CO-stretching absorption pattern to reach any firm conclusions about the other structures in solution, although the relative intensity of the peak assigned to C_B-O_B suggests that they may well be nonbridged too.

Registry No. I, 69927-38-4; Cp_2NbH_3, 11105-67-2; $Co_2(CO)_8$, 10210-68-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

Some Reactions of the Octahalodirhenate(III) Ions. 10. Further Study of the Tetrakis(pivalato)dirhenium Dihalides†

DOUGLAS M. COLLINS, F. ALBERT COTTON,* and LARRY D. GAGE

The previously known compounds $Re_2(O_2CCMe_3)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Br_2$ have been further studied structurally and spectroscopically. The two compounds are isomorphous, crystallizing in the space group $I4/m$ with $Z = 2$ and the following cell dimensions, where those for the bromide follow those for the chloride in each case: $a = 11.469$ (4), 11.601 (3) Å, $c = 10.733$ (1), 11.154 (3) Å, $V = 1411.8$ (2), 1501.1 (2) Å^3. The molecules have crystallographically imposed $4/m$ (C_{4h}) symmetry and, neglecting the rotational orientations of the CMe_3 groups, approximate very closely to D_{4h} symmetry. The XReReX groups are perfectly linear and parallel to the crystal c axis. The most important molecular dimensions are as follows: for the chloride Re–Re = 2.236 (1) Å, Re–Cl = 2.477 (3) Å, Re–O = 2.025 (4) Å, Re–Re–O = 89.82 (9)°; for the bromide Re–Re = 2.234 (1) Å, Re–Br = 2.603 (1) Å, Re–O = 2.029 (5) Å, Re–Re–O = 89.54 (10)°. The visible spectra are also reported and discussed in a preliminary way.

Introduction

Considerable effort, in several laboratories, has now been devoted to understanding the electronic structures and electronic spectra of compounds with quadruple,[1] triple,[2] and other high-order bonds[3] between transition-metal atoms. With regard to the $M_2X_8^{n-}$ species such as $Re_2Cl_8^{2-}$, $Tc_2Cl_8^{3-}$, and $Mo_2Cl_8^{4-}$ the picture seems reasonably clear. The theoretical descriptions are fairly detailed and the interpretation of spectra is rather complete.[1,3] The bonding in the $Mo_2(NR_2)_6$ and $Mo_2(OR)_6$ species is also understood.[2] For the carboxylato-bridged molecules, as exemplified particularly by the $Mo_2(O_2CR)_4$ compounds, the spectra are replete with subtle details[4] which are not yet fully understood and it cannot yet be said that there is a completely straightforward assignment of the electronic absorption spectra, although a recent study[5] has clarified many points.

For the somewhat more complicated $Re_2(O_2CR)_4X_2$ systems there has not as yet been any serious attempt to study and assign the electronic absorption spectra or to provide a detailed, quantitative description of their electronic structures. It is our intention to undertake both of these tasks by using single-

crystal spectroscopy for the former and SCF–Xα–SW calculations, including relativistic corrections, for the latter. Our first step has been to find crystalline compounds well adapted to the spectroscopic studies. The principal requirements are to have favorable orientations of the molecules in the unit cell, crystal symmetry sufficient to define uniquely a set of optic axes, and only one crystallographic type of molecule.

We report here that the pivalates, $Re_2(O_2CCMe_3)_4X_2$, with X = Cl and Br, not only fulfill these minimal requirements but also have structures that are ideal for the purpose of spectroscopic study. The unit cell for these two isomorphous substances (1) contains only molecules related by translation (thus eliminating Davydov splittings), (2) has all molecules rigorously parallel to one another and to one crystallographic axis, and (3) has each molecule at a site of $4/m$ symmetry. An additional favorable property of these substances is that they appear to be sufficiently volatile to allow the measurement of their valence shell ionization spectra in the vapor phase.

Experimental Section

Microanalyses were performed by the Center for Trace Characterization, Texas A&M University. The solution UV–visible spectra were recorded on a Beckman Acta III spectrophotometer in dichloromethane. The pellet spectra were recorded on a Cary 14

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

no.	name	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1	Re	0.0000 (0)	0.0000 (0)	0.10417 (6)	1.90 (4)	$=B_{11}$	1.86 (3)	0	0	0
2	Cl	0.0000 (0)	0.0000 (0)	0.3350 (5)	5.9 (4)	$=B_{11}$	1.7 (2)	0	0	0
3	O	−0.0826 (7)	−0.1561 (7)	0.1036 (6)	2.9 (3)	2.5 (3)	2.5 (3)	−0.5 (3)	0.2 (2)	−0.1 (2)
4	C(1)	−0.111 (1)	−0.205 (1)	0.000 (0)	2.3 (6)	2.4 (6)	2.9 (5)	0.0 (5)	0	0
5	C(2)	−0.180 (1)	−0.313 (1)	0.000 (0)	3.9 (7)	2.8 (6)	4.3 (7)	−1.1 (6)	0	0
6	C(3)	−0.158 (2)	−0.385 (2)	0.121 (1)	9 (1)	4.1 (7)	5.9 (7)	−1.4 (8)	−1.3 (6)	1.3 (5)
7	C(4)	−0.309 (2)	−0.275 (2)	0.000 (0)	3.9 (9)	6 (1)	8 (1)	−0.6 (8)	0	0

[a] The form of the anisotropic thermal parameter is $\exp[-^{1}/_{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

no.	name	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1	Re	0.0000 (0)	0.0000 (0)	0.10012 (9)	2.77 (6)	$=B_{11}$	2.83 (4)	0	0	0
2	Br	0.0000 (0)	0.0000 (0)	0.3335 (3)	5.5 (3)	$=B_{11}$	3.0 (1)	0	0	0
3	O	0.155 (1)	−0.081 (1)	0.0987 (7)	3.3 (4)	4.1 (5)	3.4 (3)	0.5 (4)	0.1 (4)	−0.2 (4)
4	C(1)	0.202 (2)	−0.109 (2)	0.000 (0)	2.7 (9)	2.7 (9)	4.9 (9)	−0.1 (8)	0	0
5	C(2)	0.310 (2)	−0.180 (3)	0.000 (0)	2.0 (9)	7 (2)	6 (1)	1 (1)	0	0
6	C(3)	0.380 (2)	−0.152 (3)	−0.118 (2)	3.2 (8)	10 (2)	9 (1)	2.4 (9)	1.9 (7)	2 (1)
7	C(4)	0.265 (3)	−0.307 (2)	0.000 (0)	8 (2)	3 (1)	12 (2)	2 (1)	0	0

[a] The form of the anisotropic thermal parameter is $\exp[-^{1}/_{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

spectrophotometer by using a compressed KBr wafer immersed in liquid nitrogen.

Syntheses. The tetra-*n*-butylammonium salts of $Re_2X_8^{2-}$, where X = Cl or Br, were prepared by literature methods.[6] All reactions were carried out in a nitrogen atmosphere.

$Re_2[O_2CC(CH_3)_3]_4Cl_2$. The compound was prepared according to a previously published method[7] by allowing $[(n-C_4H_9)_4N]_2Re_2Cl_8$ (0.5 g) to react with pivalic acid (0.5 g) at ca. 150 °C for 48 h. The residue when washed with 30 mL of *n*-hexane and 10 mL of acetone yielded large red crystals. Anal. Calcd for $Re_2C_{20}O_8H_{36}Cl_2$: C, 28.34; H, 4.25. Found: C, 28.5; H, 4.18. IR: ν_{max} 2972, 1481, 1449, 1422, 1376, 1358, 1208, 625, 462 cm^{-1} and others.

$Re_2[O_2CC(CH_3)_3]_4Br_2$. A procedure similar to the above but using $[(n-C_4H_9)_4N]_2Re_2Br_8$ and heating for 4 days afforded red-brown crystals of the desired product. Anal. Calcd for $Re_2C_{20}O_8H_{36}Br_2$: C, 25.65; H, 3.87. Found: C, 26.01; H, 3.86. IR: ν_{max} 2970, 1480, 1450, 1425, 1375, 1362, 1215, 1115, 626, 462 cm^{-1} and others.

X-ray Crystallography. $Re_2(O_2CCMe_3)_4Cl_2$. A crystal in the shape of a rectangular parallelepiped measuring 0.43 × 0.22 × 0.08 mm was mounted on a glass fiber with epoxy cement. It was inspected under a polarizing microscope and appeared to be suitable for X-ray data collection. Data were collected on a Syntex $P\bar{1}$ autodiffractometer at 23 ± 2 °C using Mo Kα radiation with a graphite crystal monochromator in the incident beam. Fifteen of the most intense reflections in the range $20° < 2\theta < 30°$ were centered automatically and the setting angles were used in standard autoindexing procedure. By least-squares refinement the following unit cell constants for a tetragonal cell were obtained: 11.469 (4) Å, 10.733 (1) Å, and V = 1411.8 (2) Å^3. With a formula weight of 847.8 it follows that Z = 2.

Data were collected by using the θ–2θ scan technique in the range $0 < 2\theta < 50°$. The scan range was from 1.0° below Kα_1 to 1.0° above Kα_2 with intensity-dependent scan rates of 4.0–24.0° min^{-1}. Three standard profiles were monitored periodically. Since the linear absorption coefficient is 93 cm^{-1} and the calculated transmission factors vary from 0.115 to 0.235, an absorption correction was needed. The faces of the crystal were measured on an optical goiniometer and external parameters for an absorption correction were calculated analytically.[8a]

$Re_2[O_2CC(CH_3)_3]_4Br_2$. A crystal with the dimensions of 0.33 × 0.22 × 0.14 mm was fixed on a glass fiber and inspected with a polarizing microscope. The cell parameters were determined in the same manner as above. Tetragonal cell constants are 11.601 (3) Å, 11.154 (3) Å, and V = 1501.1 (2) Å.

Data were collected at 23 °C as described above. The linear absorption coefficient is 114 cm^{-1}. The transmission factors, calculated analytically from measured crystal dimensions, varied from 0.083 to 0.328.

Solution and Refinement of Structure. $Re_2[O_2CC(CH_3)_3]_4Cl_2$. The Laue symmetry was $4/m$ and the systematically absent reflections

indicated body centering. The approximate rhenium atom position was found from a three-dimensional Patterson map and refinement was initiated in space group $I\bar{4}$. One cycle of least-squares refinement on the positional and isotropic thermal parameters and scale factor for the single atom gave agreement indices of

$$R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0.25$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.28$$

The six other atoms in the asymmetric unit were found in a difference map and were refined isotropically to convergence. It was observed that the methyl carbons were situated on a mirror plane indicative of space group $I4/m$. An additional refinement cycle in $I4/m$ reduced R_1 and R_2 to 0.098 and 0.147, respectively. The absorption correction was applied to the data at this point. After three cycles of refinement on the positional and anisotropic thermal parameters R_1 and R_2 were converged to values of 0.044 and 0.060, respectively. The final refinement involved a total of 43 variables and 597 observations with $I > 3\sigma(I)$. A final difference map revealed only peaks believed to be associated with hydrogen atoms about the methyl groups but no attempt was made to locate and refine the hydrogen atoms.

$Re_2[O_2CC(CH_3)_3]_4Br_2$. This compound gave every indication of being isomorphous with the chloro compound. The positions of the rhenium and bromine atoms were therefore taken from the results for $Re_2[O_2CC(CH_3)_3]_4Cl_2$. Two cycles of least-squares refinement and a subsequent difference map revealed the remaining five atoms and confirmed the presumed isomorphicity. Two cycles of isotropic refinement on all atoms produced values of 0.111 and 0.128 for R_1 and R_2, respectively. An absorption correction substantially reduced the discrepancy indices and three cycles of anisotropic refinement effected convergence with final values for R_1 and R_2 of 0.054 and 0.064. For refinement on 43 variables, 552 observations with $I > 3\sigma(I)$ were employed.

A final difference map contained only a few low-intensity peaks near the metal atom in addition to some which may have been due to hydrogen atoms associated with the methyl groups. No attempt was made to refine the hydrogen atoms.

Atomic scattering factors used in both structure refinements were from Cromer and Waber.[8b] Incorporated into the calculation of scattering factors for each atom were corrections for anomalous dispersion effects.[9] All calculations were carried out on a PDP 11/45 computer programmed with the Enraf-Nonius structure determination package.[10] Tables of the observed and calculated structure factors for both compounds are available.

Results and Discussion

Structures. The atomic positional and thermal parameters are listed in Tables I and II for the chloride and bromide,

Table III. Interatomic Distances (Å)[a]

| atoms | tetrapivalato compounds | | tetrabenzoato chloride[b] |
	chloride	bromide	
Re-Re	2.236 (1)	2.234 (1)	2.235 (2)
-Cl(Br)	2.477 (3)	2.603 (1)	2.489 (5)
-O	2.025 (4)	2.029 (5)	2.02 ± 0.01
C(1)-O	1.284 (5)	1.272 (6)	1.29 ± 0.03
C(1)-C(2)	1.475 (11)	1.496 (14)	
C(2)-C(3)	1.564 (9)	1.577 (10)	
C(3)-C(4)	1.538 (14)	1.563 (18)	

[a] Figures in parentheses are esd's occurring in the least significant figure listed. [b] From ref 11. For averages over several crystallographically independent values, the mean deviation from the mean is given.
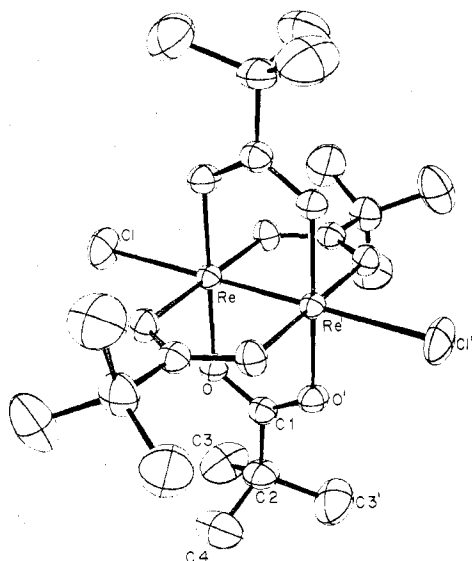
Figure 1. An ORTEP drawing of the formula unit of Re_2-$(O_2CCMe_3)_4Cl_2$ showing the numbering scheme. Atoms are represented by ellipsoids of thermal vibration scaled to include 40% of their electron density.

respectively. Figures 1 and 2 show the molecule of Re_2-$(O_2CCMe_3)_4Cl_2$ and a stereoview of the molecular packing in the unit cell, respectively, for the chloride. Figure 1 also defines the numbering scheme which applies also to the bromide. Tables III and IV give the interatomic distances and the angles, respectively, for both structures and also make comparisons to corresponding distances and angles in the $Re_2(O_2CC_6H_5)_4Cl_2\cdot 2CHCl_3$ structure.[11]

The molecules have rigorous crystallographic $4/m$ (C_{4h}) symmetry and are arranged in infinite parallel chains running in the c direction. Adjacent nonbonded Cl···Cl and Br···Br contacts are at distances of 3.543 (3) and 3.714 (3) Å, respectively. These may be compared with the commonly accepted van der Waals radii which are 3.60/2 and 3.90/2 Å for Cl and Br.

The dimensions of the $Re_2(O_2CR)_4$ moiety are essentially unaltered upon changing the halogen atoms from Cl to Br or
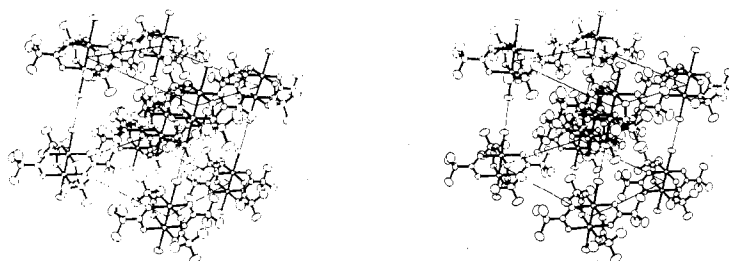
Table IV. Bond Angles (deg)[a]

| atoms | tetrapivalato compounds | | tetrabenzoato chloride[c] |
	chloride	bromide	
Re-Re-Cl	180.00[b]	180.00[b]	177.1 (1)
-O	89.82 (9)	89.54 (10)	90.1 ± 0.4
-O-C(1)	120.2 (4)	120.5 (5)	120 ± 1
O-C(1)-O	120.0 (7)	119.8 (9)	120.5 ± 0.5
O(1)-C(1)-C(2)	120.0 (4)	120.0 (4)	
C(1)-C(2)-C(3)	110.9 (5)	108.5 (7)	
-C(4)	106.6 (8)	103.7 (10)	
C(3)-C(2)-C(4)	107.6 (6)	111.4 (8)	
O-C(1)-O	120.0 (7)	119.8 (9)	120.5 ± 0.5

[a] Figures in parentheses are esd's occurring in the least significant figure listed. [b] Fixed by symmetry. [c] From ref 11. For averages over several crystallographically independent values, the mean deviation from the mean is given.

upon changing R from $(CH_3)_3C-$ to C_6H_5-, as may be seen in Tables III and IV. It is also notable that the Re-Cl distances are insignificantly different in the two chloro compounds and that the Re-Cl and Re-Br distances differ by an amount, 0.126 (3) Å, that is very close to the difference in the accepted single bond covalent radii of Cl and Br, namely, 0.15 Å. The Re-Cl and Re-Br bonds are relatively weak since their lengths are much greater than those in species such as $Re_2Cl_8^{2-}$ (ca. 2.32 Å[12]) and $Re_2Br_8^{2-}$ (ca. 2.48 Å[13]). The long distances are consistent with the low Re-Cl stretching frequencies,[14] 199 and 223 cm^{-1} in the Raman and infrared, respectively, for $Re_2(O_2CCH_3)_4Cl_2$, as compared to frequencies[4] of ca. 360 cm^{-1} for $Re_2Cl_8^{2-}$.

Spectra. One of the ultimate objectives in studying these compounds is to arrive, through spectroscopic work, at a detailed understanding of their electronic structures. The most effective tool for this will be the measurement of polarized single-crystal spectra at low temperatures. Such measurements have been undertaken and will be the subject of a future report. In this paper we present some preliminary spectral data which serve to define the scope of the spectroscopic problem as a whole. Figure 3 shows the spectra of the chloro and bromo compounds recorded in dichloromethane solution at ca. 300 K. Clearly the two are very similar, the main difference being in the displacement of the strong near-UV band some 3800 cm^{-1} to lower energy in the bromide. It is likely from their positions and intensities and the shift in energy from the chloro to the bromo compound that these bands are due to allowed L → M charge-transfer transitions.

The lowest energy band which has essentially the same energy and intensity in each case is likely to be the $\delta \rightarrow \delta^*$ transition. Its energy and intensity should be insensitive to the change from Cl to Br in the axial sites since the halogen atoms (a) are remote, (b) are at distances in accord with their inherent covalent radii, and (c) have no significant ability to interact directly with metal orbitals of δ symmetry. If this transition is the $\delta \rightarrow \delta^*$ transition, it is dipole allowed and should therefore show no significant change in intensity as a function of temperature. However, the band envelope will cover a progression in the totally symmetric Re-Re stretching
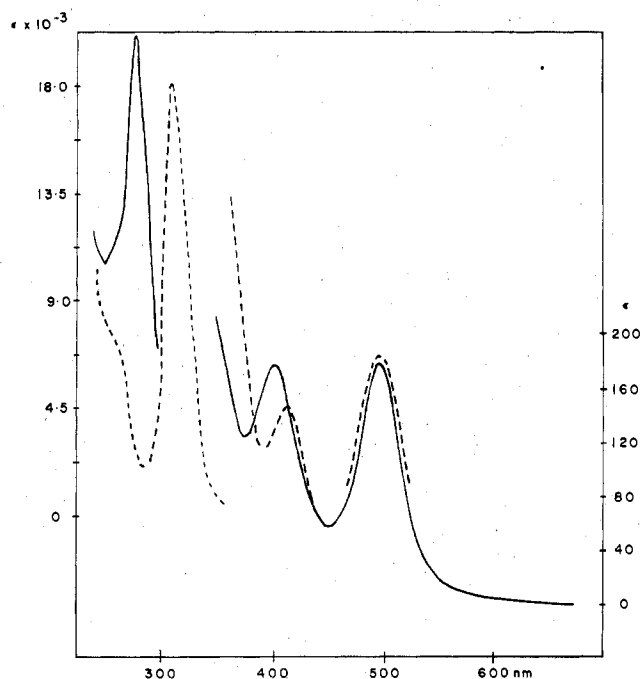

Figure 2. An ORTEP stereoview of the unit cell of $Re_2(O_2CCMe_3)_4Cl_2$.

Figure 3. Electronic absorption spectra of $Re_2(O_2CCMe_3)_4Cl_2$ (—) and $Re_2(O_2CCMe_3)_4Br_2$ (---) in CH_2Cl_2 solution.
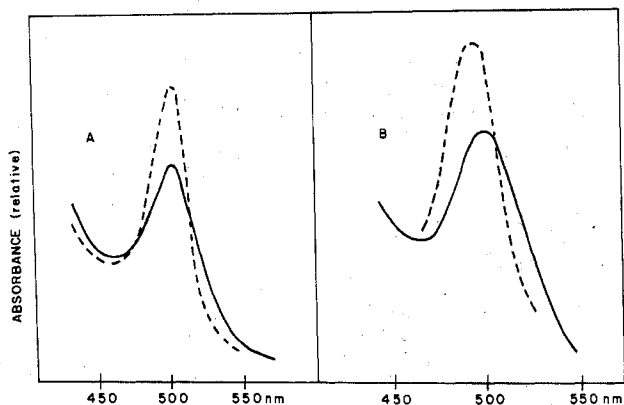
Figure 4. Low-energy electronic absorption band in Re_2-$(O_2CCMe_3)_4Cl_2$ (A) and $Re_2(O_2CCMe_3)_4Br_2$ (B) at 300 K (—) and 77 K (---).

mode, which has a value of ca. 280 cm^{-1} in the ground state[14] and may be expected to have a value of only 230–250 cm^{-1} in the excited state. The low value of the ground-state frequency means that the low-energy edge of the band at room temperature should be due in part to some vibronic transitions from excited vibrational levels. Hence, on cooling of the compounds, the $\delta \rightarrow \delta^*$ transition should sharpen, losing intensity on the lower energy side, but remain essentially the same in overall intensity. Figure 4 shows the band for each of the two compounds measured at 300 and 77 K with the powder in a compressed KBr wafer. Using a cut and weigh method on the spectral traces, we estimate that the intensities are equal within 10% at the two temperatures in each case.

If the suggested assignment of the $\delta \rightarrow \delta^*$ transition, at ca. 20 000 cm^{-1}, is correct, then we shall have to explain why it occurs at a significantly higher energy in the $Re_2(O_2CR)_4X_2$ species than in the $Re_2X_8^{2-}$ and closely related ones, e.g., $Re_2Cl_6(PEt_3)_2$, where it is found at about 14 000 cm^{-1}. Tentatively, we might attribute this to the lesser ability of the oxygen atoms to interact effectively with the rhenium $d\delta$ orbitals as compared with the Cl and Br ligands, thus leaving the $d\delta$ orbitals freer to interact with each other. A stronger δ component in the quadruple bond would not be expected to produce any observable shortening of the Re–Re distance as indicated in a recent discussion.[15]

Supplementary Material Available: Tables of observed and calculated structure factors for both compounds (6 pages). Ordering information is given on any current masthead page.

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