Molecular modeling of dimetal systems
Part 4. Dirhenium bonds

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Abstract

The relationship between bond order (N), harmonic force constant (k_r) and characteristic bond length free of strain (r_0) for dirhenium bonds has been studied by molecular-mechanics simulation of suitable structures well characterized by X-ray diffraction. It follows the same trend, $N = ak_r = abr_0^{-5}$, found before for dimolybdenum and dichromium bonds. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There exists a simple empirical relationship between the bond order (N), characteristic bond length (r_0) and harmonic force constant (k_r) of the dimetal bonds of molybdenum and chromium [1,2]. The relationship is

$$N = ak_r = abr_0^c$$

where the coefficients a and b are characteristic constants for different metals and $c = -5$. The relationship is not restricted to integral bond orders and is especially useful for the estimation of fractional bond orders.

It is interesting, but premature, to speculate about the theoretical significance of the correlation and more data are needed to substantiate its general validity. A suitable system for further investigation is the dirhenium center, also known to support a variety of multiple bond types. We report results for a study of dirhenium bonds.

2. Methods of study

The purpose of the work is to find a single equation that relates the bond order, harmonic force constant and characteristic bond length for all dirhenium bonds, irrespective of environment. The starting point is to identify a sufficient number of well-characterized dirhenium bonds of different order and steric type. For a given bond order, bonds of different steric type are analyzed by molecular mechanics in order to establish unique values of harmonic force constant and characteristic bond length free of strain. An illustration of this procedure is the comparison of bonds that are respectively stretched and compressed by steric factors. These different types have molecular-mechanics solution curves of different slope and intersect at a single point, which defines unique transferable values of k_r and r_0 for the common bond order. A solution curve is obtained by systematically varying either k_r or r_0 and finding the matching value of the second variable at each point by molecular-mechanics optimization of the molecular structure to fit a known crystallographic model. More detailed discussion of the method, convergence criteria and general force fields are provided in the earlier parts of the series. Applied to dirhenium, simulations of all bond orders from one to four were carried out.

3. Single bonds

Two different structures, characterized by X-ray diffraction, and of different steric type, are available for the analysis of Re–Re single bonds. These are the unbridged

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dinuclear complex $[Re_2(CO)_{10}]$ and the singly bridged $Re_2(CO)_8(C_4H_6)$. The C≡O and Re–C bond lengths in the X-ray structure of $Re_2(CO)_{10}$ [3] show some irregularities of an obviously random nature. The C≡O bond lengths are in the range 112.2–114.6 pm and the benchmark value for molecular mechanics was selected at 114.5 pm on the basis of a limited CSD search. Based

Table 1
Special force-field parameters used in this study

Bond	k_r (N m^{-1})	r_0 (pm)
Re–CO(ax)	390	191.5
Re–CO(eq)	370	197.5
Re–CH	175	237.0
Re–CH$_2$	150	234.0
C≡O(ax)	1770	114.5
C≡O(eq)	1770	114.5
H$_2$C=CH	960	139.7
HC–CH	500	108
Re–Cl	110	231.4
Re–P	100	231.4
P–H	325	142
P–C	345	179
Re–S	100	241
Re–S(ax)	100	281
S–Co	264	182
Angle	k_θ (10^{-10} rad^{-1} N)	θ_0 (rad)
Re–C≡O	3	3.142
C=C–C	55	2.129
H–C=C	36	2.094
H–C–H	32	2.077
Re–Re–P	7.8	1.571
Cl–Re–P	8.7	1.571
Re–P–C	10.0	2.095
C–P–C	25.0	1.763
P–C–H	30.0	1.919
Atom	r(vdW) (pm)	ϵ (J mol^{-1})
Re	263	79.50
C	190	184.10
O	170	230.12
H	144	100.42
P	218	702.9
Cl	204	1004.2
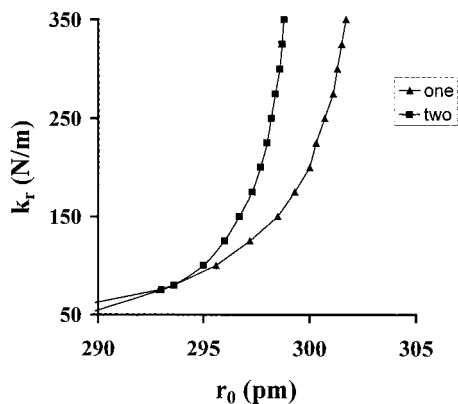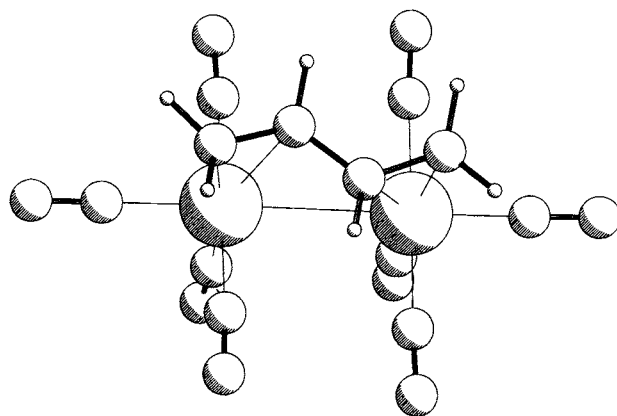
Fig. 2. The structure of $Re_2(CO)_8(C_4H_6)$.

on the observed structure, Re–C distances were simulated to match axial and equatorial values of 193 and 199 pm, respectively. The observed Re–Re distance is 304.1 pm. The overall conformation is staggered, with an average 3° tilt of the Re–C bonds towards the molecular center. The force field, based on literature preference and applicable to all structures analyzed in this work, is summarized in Table 1.

Angles around Re atoms were modeled by 1,3-interactions. Like non-bonded interactions, these were based on Buckingham potentials derived from van der Waals radii and hardness parameters, ϵ. Simulations were terminated successfully when reproducing all observed structure parameters within 1 pm or 3°.

The parameter k_r for Re–Re was varied in the range 30–450 N m^{-1} and at each point a matching value of r_0 was found, such that the observed structure was reproduced by the (k_r, r_0) pair according to the stated criteria. The solution curve $\{k_r, r_0\}$ through all matching pairs is shown in Fig. 1.

As the second example of a structure with a Re–Re single bond, the butadiene bridged complex $Re_2(CO)_8(C_4H_6)$ was analyzed. The observed structure [4] is shown in Fig. 2. The structure was simulated by the same criteria as before, ignoring minor discrepancies from the symmetrical arrangement, especially those involving angles of the olefin. The solution curve is also shown in Fig. 1.

The intersection of the two solution curves defines the unique values of (k_r, r_0) = (75 N m^{-1}, 293 pm) of the Re–Re bond. The characteristic bond length of 293 pm is considerably shorter than any of the observed bond lengths. This means that the dimetal bond in both compounds is sterically stretched, as could be expected from the low force constant.

Fig. 1. Intersecting solution curves for single bonds.

4. Double bonds

The structure of the only compound [5] known to contain a Re=Re bond, the cyclopentadienyl complex

$\{Re(CO)_2[C_5(CH_3)_5]\}_2$, is shown in Fig. 3. Each of the bridging carbonyl groups is associated more closely with one of the Re atoms. The two Re–C distances are 192(1) and 248(1) pm, respectively. For this compound to obey the 18-electron rule the two 16-electron fragments must be joined via a double bond. The distance between Re atoms (272.3 pm) is considerably shorter than in the dirhenium single bond.

A convenient way to model Cp compounds is in terms of a single interaction between the centroid of the Cp ring and the metal atom [6]. Asymmetric bridging was modeled by adjusting the force constants and characteristic bond length, up and down from the listed values. The solution curve is shown in Fig. 4.

Fig. 4. Solution curve for the assumed Re=Re bond.

5. Triple bonds

The compound $Re_2Cl_4(dppm)_2$, dppm = bis(diphenylphosphino)methane [7], contains a dirhenium center bridged by the dppm ligands. The compound $Re_2Cl_4[P(CH_3)_3]_4$ [8] contains an unbridged dirhenium center. It is therefore likely that molecular-mechanics solution curves of these two compounds may intersect in a point to define a unique (k_r, r_0) pair for Re≡Re. In both cases the ligands are so bulky that their staggered arrangement dictates the overall conformation at the dirhenium center. To substantiate this conclusion both structures and their simplified versions, obtained by replacing phenyl and methyl groups, respectively, by H atoms, were simulated by molecular mechanics. Not only was the observed structures reproduced, but the
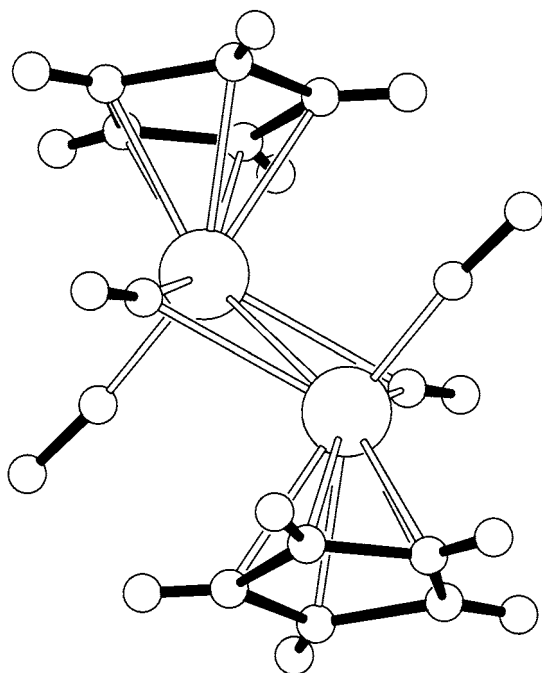
stripped down versions were also found to have the same minimum energy conformations as the observed structures. This meant that the smaller molecules $Re_2Cl_2(dp)_2$, dp = diphosphinomethane, $Re_2Cl_4(PH_3)_4$ could serve equally well for the calculation of of the (k_r, r_0) pair for dirhenium triple bonds. The optimized structures shown in Figs. 5 and 6 faithfully reproduce all observed features of the bigger molecules, significantly, without any restraints on torsions around the dimetal bonds.

Plots of solution curves for $Re_2Cl_2(dp)_2$ and $Re_2Cl_4(PH_3)_4$ are shown in Fig. 7. There is not a big difference in the shape and slope of the curves, which run together in the region $225 \leq k_r \leq 300$ N m^{-1} and $218.0 \leq r_0 \leq 219.4$ pm.

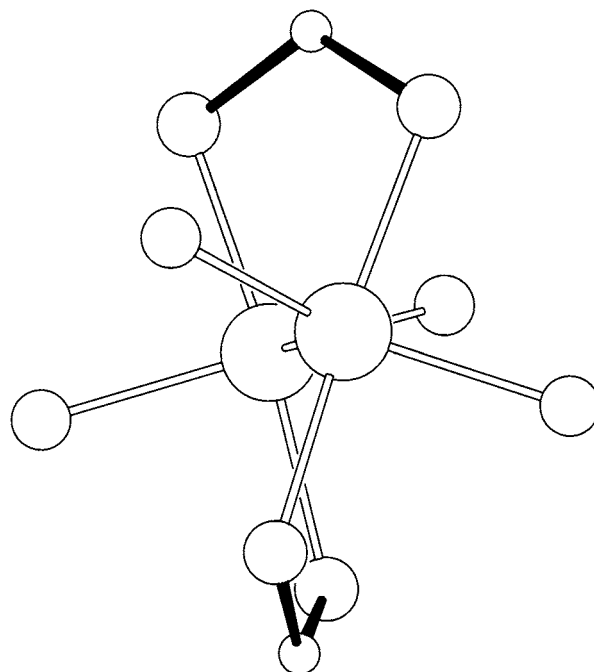Fig. 3. The structure of $\{Re(CO)_2[C_5(CH_3)_5]\}_2$.

Fig. 5. The optimized structure of $Re_2Cl_2(dp)_2$.

6. Quadruple bonds

An unsupported Re$\underline{4}$Re center occurs in the anion $\{(ReCl_4)_2\}^{2-}$, studied crystallographically [9]in the compound $K_2(ReCl_4)_2 \cdot 2H_2O$. The optimized eclipsed structure of the anion is shown in Fig. 8. The modeling followed a procedure described before [10]. A suitable structure for comparison, with a carboxylate bridge supporting the Re$\underline{4}$Re bond, is that of the dinuclear $Re_2Cl_4(CH_3COO)_2$ compound [11], shown in Fig. 9. A third possibility examined here is the product obtained by reacting $(ReCl_4)_2^{2-}$ with dithiahexane (dth) [12]. The dth chelates one Re atom by replacing a Cl ligand and inserting a second S in axial coordination. The structure is shown in Fig. 10.
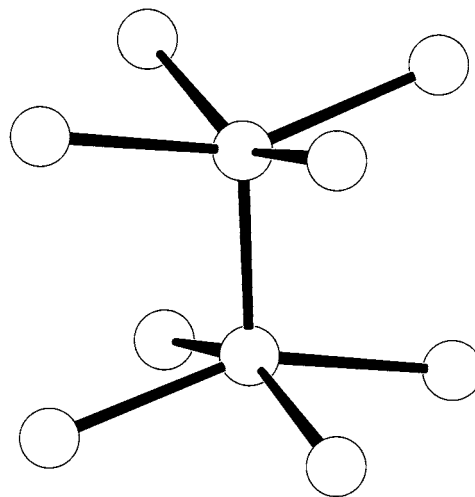

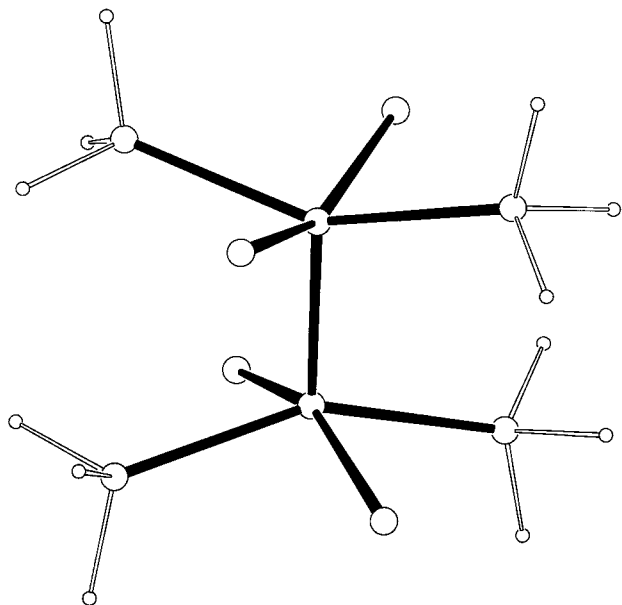Fig. 8. The optimized eclipsed structure of $(ReCl_4)_2^{2-}$.
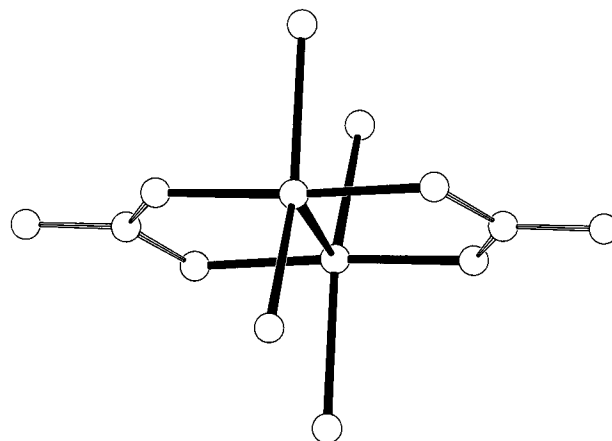

Fig. 6. The optimized structure of $Re_2Cl_4(PH_3)_4$.

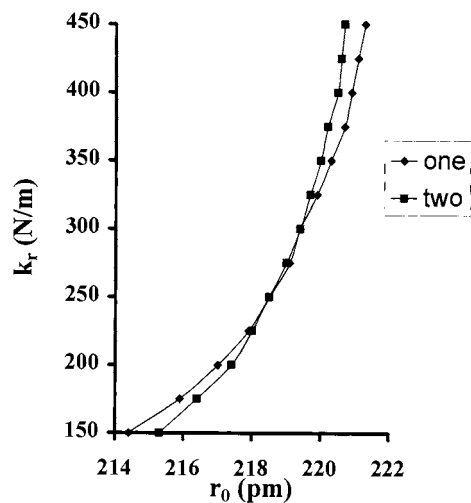Fig. 9. The structure of $Re_2Cl_4(CH_3COO)_2$.
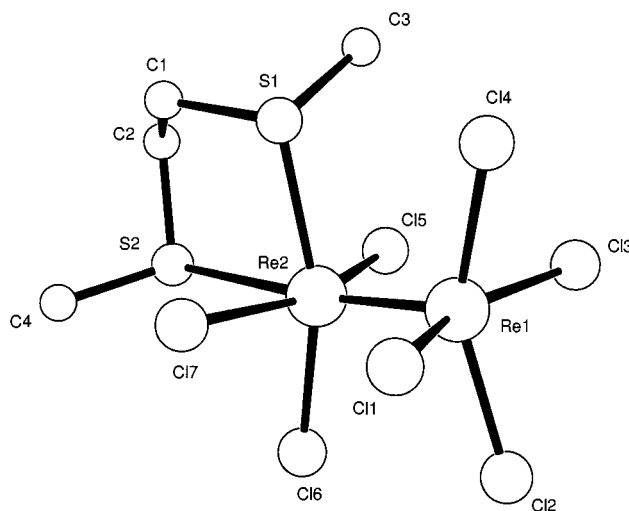

Fig. 7. Solution curves for triple bonds.

Fig. 10. Structure of the axially coordinated compound.

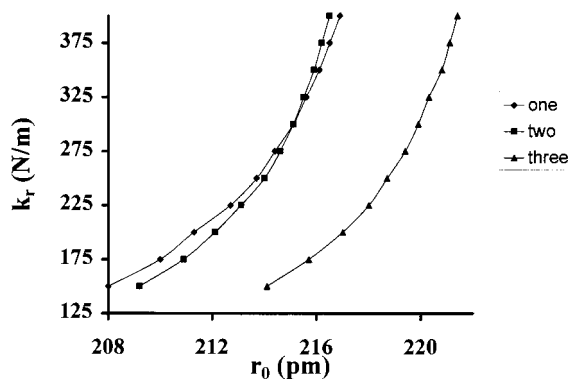Fig. 11. Solution curves for assumed quadruple bonds.

Fig. 12. The relationship between harmonic force constant and characteristic bond lengths free of strain for dirhenium bonds.

The solution curves of the three compounds are shown in Fig. 11. The curves of the first two compounds intersect at a point $(k_r, r_0) = (325$ N m^{-1}, 215.6 pm), but the curve of the compound with an axial ligand is sufficiently far displaced from the others. As in the case of Cr [1], axial ligation therefore has a marked effect on dimetal bond order.

7. The bond-order function

Three points in terms of which to define a general relationship between N, k_r and r_0 for dirhenium bonds have been established as follows:

N	k_r (N m^{-1})	r_0 (pm)
1	75	293
3	265 ± 37	218.7 ± 0.7
4	325 ± 50	215.6 ± 0.9

Assuming a relationship of the form

$$k_r = br_0^{-5}$$

the solution $b = 1.52 \times 10^{14}$ N m^{-1} pm^5 defines a curve that accounts for all experimental points, as shown in Fig. 12. This result fixes the auxiliary relationships:

$$N = ak_r = abr_0^{-5}$$

where $a = 1.23 \times 10^{-2}$ N m^{-1} and $c = ab = 1.864 \times 10^{12}$ pm^5.

The $N = 2$ point in Fig. 12 corresponds to the point of intersection between the Re≡Re solution curve with the sampling curve, defining the parameters, $(k_r, r_0) = (106$ N m^{-1}, 270.3 pm). These values do not satisfy the relationship between N and r_0 for $N = 2$, but rather for $N \sim 1.5$. This is not too surpris-
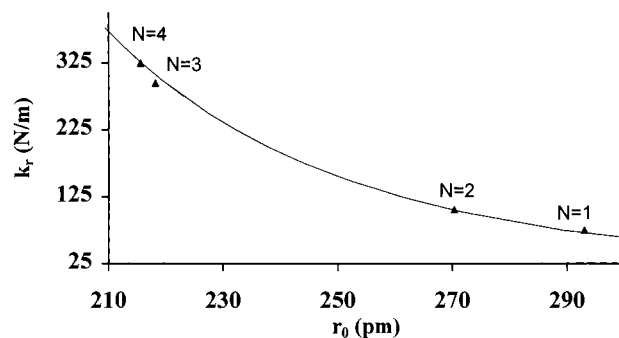
ing in view of the expected electronic effects of the bridging carbonyl groups.

One of the referees commented on how r_0 values tend to be bunched up for all solution curves representing bond orders greater than three, compared with those of lower order. It was correctly inferred that the reduced sensitivity of r_0 to bond order implies that δ-bonds are relatively weak compared to σ and π. This observation provides further evidence that molecular mechanics may be used to identify electronic effects in chemical interaction.

8. Conclusions

This analysis of dirhenium bonds confirms that their characteristic parameters for all bond orders obey the rule

$$k_r = br_0^{-5}$$

within reasonable limits. The calculated values of the proportionality constant depend on the reliability of the assigned bond orders. There is sufficient evidence that bond orders depend on several ligand effects and are particularly sensitive to axial ligation. The current values for the three metals Cr, Mo and Re of 0.45, 1.37 and 1.52 ($\times 10^{12}$ N m^{-1} pm^5), are therefore subject to refinement, but reflect an acceptable periodic trend.

A reasonable expectation now exists that the modeling procedure initiated here could be successfully extended to other dimetal bonds, including Mn, W, and other transition metals, as well as mixed-metal bonds. In the final analysis this could produce a single function that links the bond characteristics of many metals and all bond orders, based on some fundamental feature of chemical bonding in general. The procedure may also influence the way in which transferable force-field parameters could be selected more critically for molecular mechanics simulations.

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