ELSEVIER

Coordination Chemistry Reviews
153 (1996) 175–198

COORDINATION
CHEMISTRY
REVIEWS

Reparameterized Herschbach–Laurie empirical relationships between metal–metal distances and force constants applied to homonuclear bi- and polynuclear complexes (M = Cr, Mo, Rh, Pd, Ag, W, Re, Ir, Pt, Au, Hg)

Pierre D. Harvey

Département de Chimie, Université de Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada

Received 1 May 1995; in revised form 11 August 1995

Contents

SSDI 0010-8545(95)01225-7

Abstract

This review will examine the accumulated structural and spectroscopic data, and particularly the metal–metal distances and the metal–metal frequencies, for various binuclear complexes, and occasionally other polynuclear clusters, in order to design reparameterized Herschbach–Laurie relationships (H–L) applicable to Cr, Mo, W, Re and Ir. This review will also compare these H–L equations ($r(M_2) = -b \ln F(M_2) + a$, where $F(M_2)$ is the M_2 force constant) with those that are already published on Rh, Pd, Pt, Ag, Au and Hg, and present some applications. Attempts to correlate the H–L parameters (slopes and intercepts) with the dissociation energy of the dinuclear "naked" dimer ($M_2(g)$) and the atomic radii are made, and, finally, interesting observations are presented regarding the design of relationships for heteronuclear systems. In these cases, the slopes and intercepts are taken as simple averages of those of the homonuclear designed equations. The agreements between the calculated and the experimental $F(M_2)$ are particularly good.

Keywords: Herschbach–Laurie relationships; Metal–metal bond lengths; Force constants; Metal–metal stretching frequencies

1. Introduction

Our research group recently published a series of articles that reported new empirical relationships relating the M–M separations ($r(M_2)$ in ångströms) with the M_2 force constants ($F(M_2)$ in millidynes per ångström) for M = Rh, Pd, Ag, Pt, Au and Hg for bi- and polynuclear complexes [1–5]. The equations proved to be particularly useful when estimating $r(M_2)$ for compounds with known geometry and well-interpreted vibrational spectra, particularly for the M–M and M–L stretching frequencies. These equations can also be used to extract a $F(M_2)$ value when $r(M_2)$ is known. Furthermore, $F(M_2)$ can be obtained conveniently in situations when $r(M_2)$ is very large, i.e. where $F(M_2)$ is difficult to calculate with precision even with force-field calculations.

The purpose of this review is to compile literature data on M_2 systems where M = Cr, Mo, W, Re, and Ir in order to obtain reparameterized H–L equations applied to these metals. Some applications of these equations will be provided. These new equations will allow us to compare the variation of the equation parameters as a function of the row number (i.e. Cr, Mo, W) and as a function of the position on a same-row element (i.e. W, Re, Ir, Pt, Au, Hg). This review is not a survey of $r(M_2)$, $\nu(M_2)$ and $F(M_2)$ for selected metals. Many reviews and books already exist and are referred to throughout this review (Refs. [6–10]). Some interesting predictions will be made on the basis of these equations, particularly for the $Re_2(g)$ and $Re_2^-(g)$ molecules, for which virtually nothing is known. In the Re_2 molecule, the $r(Re_2)$ distance is evaluated at 2.05 ± 0.05 Å, which is perfectly consistent with a diatomic molecule exhibiting a quintuple bond. This quintuple bond is predictable from the s^2d^5 electronic configuration of the Re atom in the gas phase. Finally, approximated equations for Fe_2, Ru_2 and Os_2, and for some mixed metal dimers, will be presented.

2. Historical background

Empirical relationships relating atom–atom bond lengths or separations with atom–atom force constants or stretching frequencies have been designed by a number of authors for quite some time now. One of the very first was Morse's in 1929. His empirical law applied to diatomic molecules and was $r^3 \nu = 3000A$, where r is the diatomic distance (in ångströms), ν is the stretching frequency (in centimeters^{-1}) and A is a constant [11]. In 1934, Badger pointed out that this expression was not very reliable except for a limited number of diatomic molecules [12]. He proposed a new empirical law which has the form $F(r-d_{ij})^3 = 1.86 \times 10^5$, where F is the force constant given in dynes per centimetre, r is given in ångströms, and d_{ij} is an empirical parameter characteristic of all diatomic molecules made up of one element in the ith row and one in the jth row of the periodic system. He modified his relationships in 1935 to include applications for polyatomic molecules which adopt the form $r = (C_{ij}/F)^{1/3} + d_{ij}$ where the 1.86×10^5 constant becomes C_{ij}, another parameter which also depends upon the row of the targeted elements in the bond [13]. During this period, two other rules were reported (Clark's rule [14] and Allen and Longair's rule [15]), but Badger's rule remained the fundamental empirical method because it gave more satisfactory results and could be applied to different excited states.

In 1961, Herschbach and Laurie noticed that Badger's rule was not providing satisfactory results for heavier elements, and reported a new equation: $r = b_{ij} \log F + a_{ij}$ again with a_{ij} and b_{ij} as empirical parameters associated with the ith and the jth row elements [16]. This rule gave satisfactory results for heavier element molecules in the ground and excited electronic and ionic states, but Badger's rule was still somewhat better for lighter elements. Finally in 1987, Woodruff et al. reported a new form of relations ($r = a + be(-F/c)$), where a, b and c are parameters adjusted for the ith row element with both atoms belonging to this same row) which improved both H–L and Badger's rules [17]. More satisfactory results were obtained with the addition of an extra adjustable parameter.

The evolution of the mathematical form of these rules followed a simple series of improvements between the calculated and experimental results. The basis of these rules is that the only variable on the empirical parameter is still the row in which the element belongs. The weakness of this approach is that it ignores the effective charge effect of lighter and heavier elements belonging to the same row. If only one element is used to design such relationships, the number of protons remains constant.

In the past, the number of homonuclear compounds using the same metal for the design of empirical relationships (particularly transition metals for this review), for which $r(M_2)$ exhibits a wide range of distances and are fully characterized by X-ray crystallography and Raman spectroscopy, was extremely limited. Authors were naturally attracted by the option of using data belonging to the same rows. For many elements this situation has now changed, and the design of reparameterized rules applied to specific elements is now possible. The question is: which mathematical form should be used? Woodruff's rule has a major problem for $r(M_2)$ values approaching and exceeding the sum of the a and b parameters, since the function is a convergent one. On the other hand, the H–L form is not $r(M_2)$-limited, and has been successfully used even at $r(M_2)$ values located at about 4.4 Å, a value that is far above the sum of the Van der Waals radii (r_{vdw}) of the investigated metal systems. Furthermore, the comparison of the published reparameterizd H–L equations [1–5] and Woodruff's rules with the experimental $r(M_2)$ data for a same M always favored the H–L results. In the following sections, different d-block M_2 systems will be reviewed, and new reparameterized H–L equations will be reported.

3. Reparameterized H–L equations

A large part of the third d-block transition-metal systems is left out of this review. In these cases the quantity of data is far too small to design empirical relations. Ordinarily at least nine to sixteen data points were used for the relation design [1–5].

3.1. *The Cr_2 systems*

Exceptionally in this case, only five data points were collected in the literature [6,7,18–26] and are summarized in Table 1. These systems allow an interesting comparison of the *a* and *b* parameters for Cr, Mo and W in Section 5. The design of an acceptable reparameterized H–L equation applied to Cr_2 systems is possible because the spread of the $r(Cr_2)$ data is wide, and the Cr_2 complexes exhibit bond orders from 0 to 6 (Fig. 1). The equation is:

$$r(Cr_2) = -0.746 \ln F(Cr_2) + 2.50 \qquad (1)$$

where *r* is in ångströms and *F* in millidynes per Ångströms. The correlation coefficient is 0.96 (Fig. 1). Interesting applications and predictions of this equation can be presented. For instance, the organometallic $Cp_2Cr_2(CO)_6$ dimer exhibits a very weak

Table 1
Structural and spectroscopic data for Cr_2 systems

Complexes	$r(Cr_2)$ (Å)	$\nu(Cr_2)$ (cm^{-1})	$F(Cr_2)$ (mdyn $Å^{-1}$)	Bond order
$Cp_2Cr_2(CO_6)$	3.28[18]	—	—	1
$Cr_2Cl_9^{3-}$	3.12[6]	161[7]	0.40	1
$Cr_2(CO)_{10}^{2-}$	2.97[19]	160[20]	0.60[20]	1
$Cr_2(O_2CCH_3)_4 \cdot 2H_2O$	2.836[21]	215 ± 15[21]	0.71	1
$Cp_2Cr_2(CO)_4$	2.23[22]	—	—	3
$Cr_2(CH_3)_8^{4-}$	1.980[23]	—	—	4
$Cr_2(mph)_4$	1.889[24]	340[24]	1.77	4
$Cr_2(g)$; Σ_g^+	1.68 ± 1[25]	427.5[26]	2.80	6
Cr_3(matrix); C_{2v} (apex angle = 60°)	—	$\nu_1 = 313$[26] $\nu_2 = 123$ $\nu_3 = 226$	1.09[26]	?

[a] $F(Cr_2)$ calculated using the diatomic harmonic oscillator unless stated otherwise.

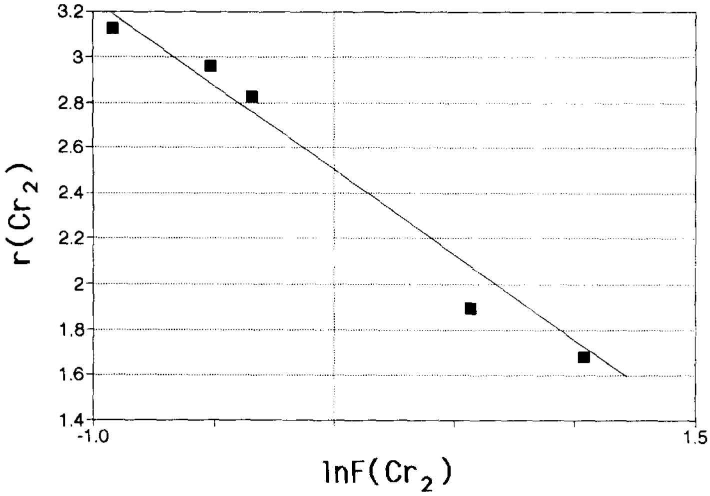

Fig. 1. Graph of ln $F(Cr_2)$ vs. $r(Cr_2)$. The data are from Table 1.

Cr–Cr bond where the $r(Cr_2)$ value is 3.28 Å [18]: a value that is well above the sum of the covalent radii (2.58 Å). The dimer is further held together by bridging CO ligands. The $\nu(Cr_2)$ value in this case is not known. To predict this value, $F(Cr_2)$ must be known. Eq. (1) computes a $F(Cr_2)$ of 0.35 mdyn $Å^{-1}$. Such a value would place these interactions in the weakly interacting categories despite the odd-electron electronic configuration at each metal center. On the other hand, the multiply bonded $Cp_2Cr_2(CO)_4$ exhibits a $r(Cr_2)$ of 2.23 Å [22], and Eq. (1) predicts that $F(Cr_2)$ is 1.44 mdyn $Å^{-1}$. In the two later cases, $F(Cr_2)$ values are readily extracted from a simple equation despite their "complicated" structures. Moskovitz et al. [26] measured the three $\nu(Cr_2)$ frequencies of the Cr_3 molecule isolated in Ar matrices. They evaluated $F(Cr_2)$ to be 1.09 mdyn $Å^{-1}$. By applying Eq. (1), $r(Cr_2)$ in this case would be 2.44 Å.

3.2. The Mo_2 systems

These systems contain a wealth of structural and spectroscopic data [6,8,9,17,19,20,27–39], particularly with the $Mo\overset{4}{-}Mo$ quadruple bond [9] (Table 2). A graph of $r(Mo_2)$ vs. ln $F(Mo_2)$ also provides a line (Fig. 2), with an equation according to:

$$r(Mo_2) = -0.538 \ln F(Mo_2) + 2.87 \qquad (2)$$

with 27 data points used and a σ of 0.96. It is interesting that the Mo(m) and $Mo_6(Cl_{14})^{2-}$ data points fall on the line (Fig. 2). Most of the data points are within about 0.1 Å from the line.

Table 2
Structural and spectroscopic data for Mo_2 systems

Complexes	$r(Mo_2)$ (Å)	$\nu(Mo_2)$ (cm^{-1})	$F(Mo_2)$ (mdyn $Å^{-1}$)	Bond order
$Mo_2Cp_2(CO)_6$	3.235[27]	124[28]	0.435	1
$[Mo_2(CO)_{10}](Et_4N)_2$	3.123[19]	138[20]	0.680	1
$Mo_2Cp_2(CO)_4(HC{\equiv}CCH_2)^+$	3.015[28]	180[28]	0.917	1
$[Mo_2(S_2)_6](NH_4)_2$	2.82(1)[29]	219[30]	1.358	1
Mo(m)	2.7251[17]	—	1.28[17]	—
$Mo_6Cl_{14}{}^{2-}$	2.63[6]	220[8]	1.65[8]	1
$Mo_2Cp_2(CO)_4$	2.448[31]	228[28]	1.47	3
$Mo_2(NMe_2)_6$	2.214[32]	319[33]	2.88	3
$Cs_2[Mo_2(HPO_4)_4]\cdot 2H_2O$	2.223[35]	361[36]	3.69	3
$(PyH)_3Mo_2(HPO_4)Cl$	2.232[35]	358[37]	3.63	3
$K_3[Mo_2(SO_4)_4]$	2.167[34]	373, 385[9]	4.07 (average)	3.5
$Mo_2(CH_3)_8{}^{4-}$	2.147[9]	336[9]	3.20	4
$Mo_2Cl_4(PMe_3)_4$	2.130[9]	355[37]	3.57	4
$Mo_2Br_4(PMe_3)_4$	2.125[37]	352[37]	3.51	4
$Mo_2I_4(PMe_3)_4$	2.127[37]	343[37]	3.33	4
$K_4[Mo_2Cl_8]\cdot 2H_2O$	2.139[9]	345[9]	3.37	4
$[NH_4]_5[Mo_2Cl_8]Cl\cdot H_2O$	2.150[9]	378[9]	4.04	4
$[C_2H_{10}N_2]_2MoCl_8\cdot 2H_2O$	2.134[9]	348[9]	3.43	4
$[NH_4]_4[Mo_2Br_8]$	2.135[9]	336[38]	3.20	4
$K_4[Mo_2(SO_4)_4]$	2.110[9]	370[9]	3.88	4
$Mo_2[PhC(CPh)_2]_4$	2.090[9]	410[9]	4.76	4
$Mo_2(O_2CCF_3)_4$	2.090[9]	397[9]	4.46	4
$Mo_2(O_2CCH_3)_4$	2.0934[9]	406[9]	4.67	4
$Mo_2(O_2CH)_4$	2.091[9]	403[9]	4.60	4
$Mo_2[(CH_2)_2P(CH_3)_2]_4$	2.082[9]	388[9]	4.26	4
$Mo_2(mhp)_4$	2.065[9]	425[9]	5.10	4
$Mo_2(g)$	1.93[39]	477[39]	6.44	6

[a] Diatomic approximation, unless stated otherwise.

3.3. The Rh_2 systems

The reparameterized H–L equation for Rh_2 systems is:

$$r(Rh_2) = -0.287 \ln F(Rh_2) + 2.78 \qquad (3)$$

with $\sigma = 0.96$ for 14 data points [4]. This equation proved to be useful in evaluating $r(Rh_2)$ in an A-frame $Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$ complex: $r(Rh_2) = 2.65 \pm 0.10$ Å, establishing the presence of a Rh–Rh single bond [4]. In this work, cluster species ($Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, etc.) were also used in the design of such an equation. It was interesting to find that Rh_2 systems exhibiting a Rh–Rh bond order of zero still fell on the line, even when $r(Rh–Rh) > 4$ Å. No multiply bonded data were used. The $Rh_2(g)$ molecule exhibits a dissociation energy (D_e) of 282 ± 21 kJ mol^{-1} [40], which accounts for the cleavage of a Rh–Rh triple bond [41] according to recent theoretical

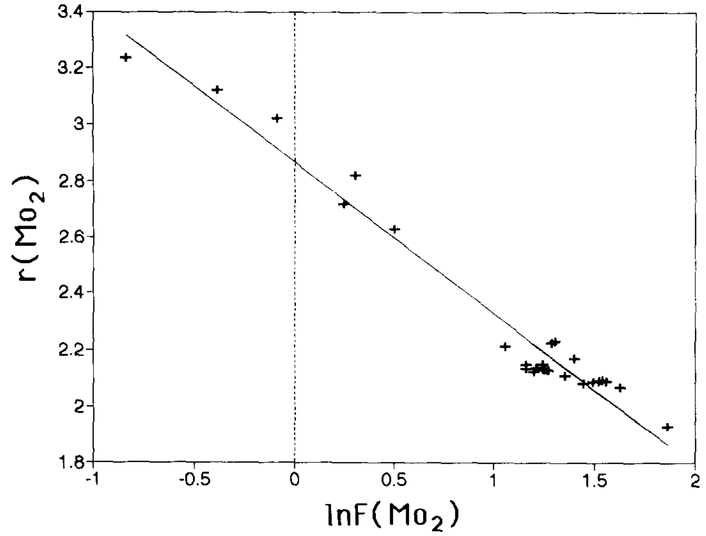

Fig. 2. Graph of+ln $F(Mo_2)$ vs. $r(Mo_2)$. The data are from Table 2.

calculations (ground state = $^5\Pi_g$). It would be useful if $\nu(Rh_2)$ could be obtained; $r(Rh_2)$ is not known in this case.

3.4. The Pd_2 systems

The reparameterized H–L equation designed for Pd_2 systems is:

$$r(Pd_2) = -0.387 \ln F(Pd_2) + 2.67 \tag{4}$$

with an impressive σ value of 0.99 for 12 data points [2]. The line was constructed with samples exhibiting a Pd–Pd bond order of 0 or 1, and the $r(Pd_2)$ data ranged from 2.4 to 4.4 Å. The empirical equation was used to estimate the Pd–Pd bond length in the d^9–d^9 $Pd_2(dmb)_2X_2$ complexes (X = Cl, Br) from vibrational data [42]. The calculated $r(Pd_2)$ value was 2.72 ± 0.05 Å and the result corroborated very well with the position of the $d\sigma \rightarrow d\sigma^*$ band in the UV–visible spectra [42] by comparison with literature data. The vibrational spectra for $Pd_3(dppm)_3CO^{2+}$ were recently presented and the a_1 and e ν(Pd–Pd) modes assigned [43], but no force-field calculations were performed, owing to the complexity of the molecule. By using $r(Pd_2)$ of 2.60 Å (average r(Pd–Pd) value for the $Pd_3(dppm)_3CO^{2+}$ [44]) and Eq. (4), a $F(Pd_2)$ value of 1.2 mdyn Å^{-1} is obtained and compares favorably with literature data of Pd_2 systems exhibiting similar $r(Pd_2)$ values [2].

3.5. The Ag_2 systems

The empirical relationship for Ag_2 systems is:

$$r(Ag_2) = -0.284 \ln F(Ag_2) + 2.53 \tag{5}$$

for nine data points ranging from 2.4 to 3.5 Å with $\sigma = 0.95$. The data set was mostly composed of d^{10} Ag^I species exhibiting only weak Ag–Ag interactions (bond-order zero). Many of the complexes used exhibited distorted tetrahedral structures around the Ag atoms which led to the problem of evaluating $F(Ag_2)$ accurately in the absence of appropriate force-field calculations. More importantly, for systems where the M–M interactions are very weak, force-field calculations generally failed to obtain an accurate $F(M_2)$value. One example of an application for Eq. (5) is the $Ag_2(dmpn)_2Br_2$ dimer ($r(Ag_2) = 3.60$ Å [1]) which exhibits a non-linear $(Br)_2$–Ag...Ag–$(Br)_2$–Ag... polymeric structure in the solid state [1]. $\nu(Ag_2)$ is found at 48 cm^{-1} but the evaluation of $F(Ag_2)$ is not simple in this case [1]. Eq. (5) predicts that $F(Ag_2) = 0.023$ mdyn $Å^{-1}$. This result compares particularly favorably with the Van der Waals molecule $Cd_2(g)$ in its various electronic states: $Cd_2(^1\Sigma g^+)$, $\nu(Cd_2) = 21$ cm^{-1}, $F(Cd_2) = 0.015$ mdyn $Å^{-1}$, $r(Cd_2) = 3.31$ Å; $Cd_2(^3\Sigma_u{}^+)$, $\nu(Cd_2) =$ 37 cm^{-1}, $F(Cd_2) = 0.045$ mdyn $Å^{-1}$, $r(Cd_2) = 3.05$ Å; $Cd_2(^1\Sigma_u{}^+)$, $\nu(Cd_2) = 39$ cm^{-1}, $F(Cd_2) = 0.050$ mdyn $Å^{-1}$, $r(Cd_2) = 3.00$ Å [45], with Cd being the Ag neighboring element in the periodic table.

3.6. The W_2 systems

Like the Cr_2 complexes, the number of data points available is small and the disparity between them is limited. For the most part, data for quadruply bonded species have been accumulated (Table 3). The equation is:

$$r(W_2) = -0.471 \ln F(W_2) + 2.93 \qquad (6)$$

with $\sigma = 0.99$ for eight data points ranging from 2.16 to about 3.1 Å (Fig. 3). The data for triply bridged $W_2Cl_9{}^{3-}$ and the triply bonded $W_2(NMe_2)_6$ [9] ($r(W_2) =$ 2.292 ± 0.002 Å, and $\nu(W_2) = 213$ and 332 cm^{-1} (!)) were not used for the design of this equation. In the former complex, there are some difficulties evaluating $F(W_2)$, in part due to the heavy coupling between the δ(WClW) modes and $\nu(W_2)$. In the second complex, two $\nu(W_2)$ values have been reported, and isotopic substitution experiments were not successful in making a secure assignment [9]. By using Eq. (6) and $r(W_2) = 2.292$ Å, a F value for $W_2(N(CH_3)_2)_6$ of 3.88 mdyn $Å^{-1}$ is obtained. Then using the diatomic approximation, the back-calculated $\nu(W_2)$ is 267 cm^{-1}! It was concluded that in the $W_2(N(CH_3)_2)_6$ molecule there is *considerable mixing* of the W–W stretching coordinate with other internal coordinates, such as W–N stretching and $N(CH_3)_2$ rocking modes. In these two complexes, the points fall far from the line, worsening σ (the correlation coefficient).

3.7. The Re_2 systems

This series is interesting because data for complexes exhibiting bond orders going from 1 to 4 are available (see Table 4 [9,10,50,52–56]). First, one has to point out

---

[1] The force constant F is given in millidynes per ångström, and referred to once in the text in dynes per centimeter. The IUPAC units are newtons per meter.

Table 3
Structural and spectroscopic data for W_2 systems

Complexes	$r(W_2)$ (Å)	$\nu(W_2)$ (cm^{-1})	$F(W_2)$ (mdyn $Å^{-1}$)	Bond order
$W_2(CO)_{10}^{2-}$	~3.1[b]	111[20]	0.73[20]	1
W(m)	2.7409[46]	—	1.46[51]	—
$W_2Cl_9^{3-}$	2.41[6]	139[7]	1.15[7]	3
$W_2Cl_4(PR_3)_4$[c]	2.262[9]	260±10[9]	3.67	4
$W_2(TFA)_4 \cdot 2PPh_3$	2.242[29]	280[47]	4.25[d]	4
$W_2(O_2C\text{-t-Bu})_4 \cdot 2Ph_3$	2.218[48]	287[48]	4.47[d]	4
$W_2(TFA)_4$-	2.209[47]	310[47]	5.21	4
$W_2(O_2C\text{-}t\text{-Bu})_4$	2.189[49][e]	313[48]	5.31	4
$W_2(mhp)_4$	2.161[9]	284[9]	4.71	4

[a] $F(W_2)=\mu[2\pi c\,\nu(W_2)]^2$, unless stated otherwise

[b] Because $r(M_2)$ is about the same in the $M_2(CO)_{10}$ complexes (M = Mn, Tc, Re) [50], it is assumed that $r(Mo_2)$ ~ $r(W_2)$ in the $W_2(CO)_{10}^{2-}$ complex.

[c] R = Me for $r(W_2)$ and R = *t*-Bu for $\nu(W_2)$

[d] The presence of PPh_3 at the axial position is ignored, but the data points fit on the line.

[e] *R* = *Et* for $r(W_2)$ instead of *t*-Bu.

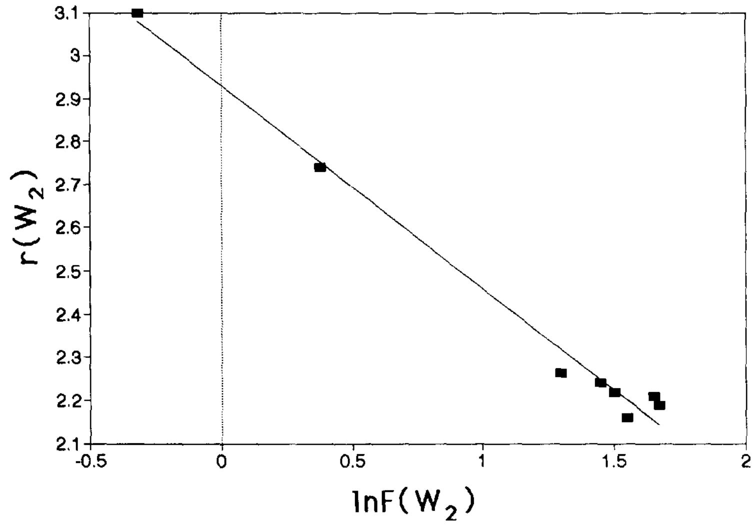

Fig. 3. Graph of + ln $F(W_2)$ vs. $r(W_2)$. The data are from Table 3, but the data for $W_2Cl_9^{3-}$ were not used (see text).

that there has been some controversy over the $\nu(Re_2)$ assignment for $Re_2(CO)_{10}$. Although it is still accepted that $\nu(Re_2)$ is 120 cm^{-1} [8], Spiro et al. [57] have shown that the $Re_2(CO)_8X_2$ (X = Cl, Br; bond-order 0, $r(Re_2) = 3.8$ Å) Raman spectra also exhibited a strong Raman at 125 cm^{-1} where $\nu(Re_2)$ appears in the $Re_2(CO)_{10}$ spectra. Adams et al. have reassigned $\nu(Re_2)$ to 110 cm^{-1} based upon polarized

Table 4
Structural and spectroscopic data for Re_2 systems

Complexes	$r(Re_2)$ (Å)	$\nu(Re_2)$ (cm^{-1})	$F(Re_2)$ (mdyn $Å^{-1}$)	Bond order
$Re_2(CO_6(CN\text{-}2,6\text{-}(Me)_2\text{-}C_6H_3)_4$	3.079[52]	106.5[52]	0.62^b	1
$Re_2(CO)_7(CNCH_2C_6H_5)_3$	3.049[52]	106[52]	0.72^b	1
$Re_2(CO)_8(CN\text{-}2,6\text{-}(Me)_2\text{-}C_6H_3)_2$	3.048[52]	113[52]	0.70^b	1
$Re_2(CO)_9(CN\text{-}t\text{-}Bu)$	3.048[52]	101[52]	0.72^b	1
$Re_2(CO)_{10}$	3.041[50]	110.7[60]	0.78^b	1
$Re_2OCl_5(O_2CEt)(PPh_3)_2$	2.522[53]	216[55]	2.56	~2
$Re_2OCl_3(O_2CEt)(PPh_3)_2$	2.514[54]	216[55]	2.56	~2
Re_3Cl_9	2.48[9, 55]	252.4[10]	2.29^c	2
Re_3Br_9	2.48[9, 55]	254[55]	2.36^c	2
$Re_2Cl_5(2,5\text{-dth})_2$	2.293[56]	267[55]	3.92	3
$Re_2Cl_6(PEt_3)_2{}^d$	2.222[9]	278[55]	4.25	4
$Re_2Cl_8{}^{2-}$	2.222[9]	276.2[10]	4.19	4
$Re_2Br_8{}^{2-}$	2.228[9]	272.6[10]	4.08	4
$Re_2(O_2CCH_3)_2Cl_4$	2.209[9]	279[55]	4.28	4
$Re_2(g)$	?	340±20[61]	6.4	?
$Re_{2-}(g)$	?	320±15[61]	5.6	?

[a] $F(Re_2) = \mu[2\pi c\nu(Re_2)]^2$, unless stated otherwise.
[b] $F(Re_2)$ is evaluated using the X-M-M-X equations: $\lambda_1 + \lambda_2 - \lambda_3 = 1/2F/m$, where $\lambda_i = (2\pi c\nu_i)^2$ with $\nu_1 = \nu(Re_2)$, ν_2), $\nu_2 = \nu_{sym}(Re\text{–}CO)$ and $\nu_3 = \nu_{assym}(Re\text{–}CO)$ available in Ref. [52].
[c] $F(Re_2) = 3(2\pi c\nu(Re_2)_{a1})^2\ m$.
[d] For $\nu(Re_2)$, R = Pr instead of Et.

Raman spectra of a single crystal [58,59]. Butler et al. have also adopted this assignment [60], particularly when they observe that the strong 120 cm^{-1} feature did not follow a correlation with $r(Re_2)$ for various $Re_2(CO)_{10}$-substituted derivatives [52]. $\nu(Re_2)$ is now reassigned to about 110 cm^{-1}, and the strong 120 cm^{-1} feature is δ(CReC), according to Adams's [58,59] polarization results. The empirical relationship for Re_2 systems is (Fig. 4):

$$r(Re_2) = -0.458 \ln F(Re_2) + 2.89 \tag{7}$$

with 14 data points ranging from 2.21 Å to 3.08 Å, and an excellent σ value of 0.99 (Fig. 4).

Leopold et al. have reported $\nu(Re_2)$ for $Re_2(g)$ and $Re_2{}^-(g)$ [60]. Surprisingly, nothing else is known about these dimers, as no experimental and no theoretical work has addressed the bonding scheme of these molecules. The diatomic approximation suggests that $F(Re_2) = 6.4$ and 5.6 mdyn $Å^{-1}$ (for $\nu(Re_2) = 340$ and 320 cm^{-1}) in the $Re_2(g)$ and $Re_2{}^-(g)$ compounds, respectively. Using Eq. (7), the calculated $r(Re_2)$ values are 2.04 and 2.10 Å, respectively. The estimated uncertainty is ±0.05 Å. A typical value for $r(W_2)$ and $r(Re_2)$ quadruple bond is 2.21±0.05 Å, and a sextuple bond is 1.93 Å (in Mo_2). The value of 2.04 Å for $Re_2(g)$ is clearly an intermediate value between bond orders of 4 and 6. Knowing that the electronic configuration for Re is s^2d^5, and adopting the typical MO diagram for diatomic molecules

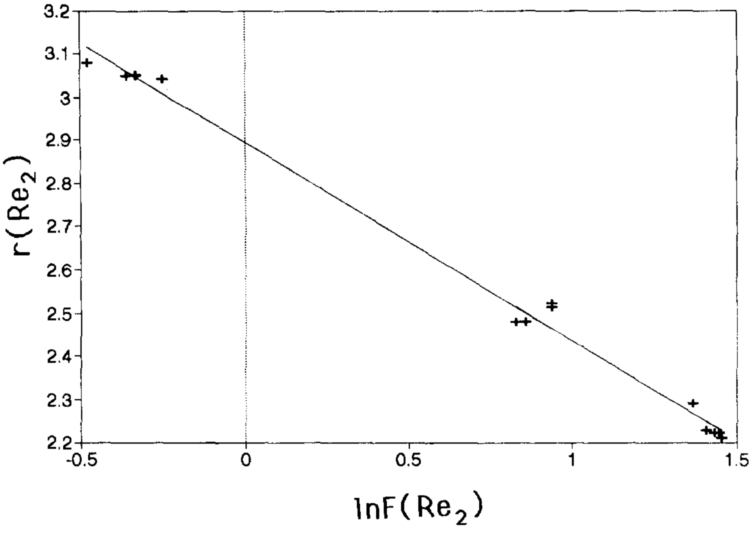

Fig. 4. Graph of+ln $F(\mathrm{Re_2})$ vs. $r(\mathrm{Re_2})$. The data are from Table 4.

($\mathrm{d}\sigma < \mathrm{d}\pi < \mathrm{d}\delta < \mathrm{d}\delta^* < \mathrm{d}\pi^*, \mathrm{d}\sigma^*$), theoretically Re_2 is expected to have a bond order of 5. When considering Re_2^-, the theoretical bond order is 4.5. The calculated $r(\mathrm{Re_2})$ increases to 2.10 Å but does not reach the lower $r(\mathrm{Re_2})$ limit typical of quadruply bonded species.

All these results suggest that the $Re_2(g)$ molecule is a rare example of dimers exhibiting a quintuple bond. There is no theoretical investigation on the Re_2 molecule, presumably because the problem is complex owing to the presence of the numerous spin states. For a compound like $Re_2(CO)_8Cl_2$ ($r(\mathrm{Re_2}) = 3.8$ Å [57]), Eq. (7) predicts that $F(\mathrm{Re_2})$ would be about 0.14 mdyn Å^{-1}. Using the diatomic approximation, $\nu(\mathrm{Re_2})$ would then appear in the 50 cm^{-1} range. In the spectra reported by Swanson et al. [57], an intense and broad band does appear in this range but no formal assignment can be provided at this time.

3.8. The Ir_2 systems

These systems also represent a family with fewer data points (Table 5, Refs. [8,62–70]). Nonetheless a reasonable reparameterized H–L line is obtained (Fig. 5):

$$r(\mathrm{Ir_2}) = -0.160 \ln F(\mathrm{Ir_2}) + 2.92 \tag{8}$$

(seven data points; $3.22 < r(\mathrm{Ir_2}) < 2.80$ Å; $\sigma = 0.99$). The bond orders are either 0 or 1, and again all the data points fall on the line (Fig. 5), except for one compound. This complex is the $Ir_4(CO)_{12}$ cluster ($r(\mathrm{Ir_2}) = 2.691$ Å [69]) and it was not used in the design. The Rh_4 and Rh_6 complexes were successfully used to design the H–L relationship for Rh_2 systems. This phenomenon is not easy to explain at this time,

Table 5
Spectroscopic and structural data for Ir_2 systems

Complexes	$r(Ir_2)$ (Å)	$\nu(Ir_2)$ (cm^{-1})	E(Ir) (mdyn $Å^{-1}$)	Bond order
$[Ir(\mu\text{-pz})(COD)]_2$	3.216[62]	58[63]	0.19	0
$Ir_2(tmb)_4^{2+}$	3.199[64]	53[64]	0.16	0
$Ir_2(\mu\text{-}3,4,5\text{-}(Me)_3pz)(COD)]_2$	3.096[65]	77[63]	0.34	0
$[Ir_2(\mu\text{-}3\text{-}CF_3\text{-}5\text{-Mepz})(COD)]_2$	3.066[66]	79[63]	0.36	0
$[Ir_2(\mu\text{-}3,5\text{-}(CF_3)_2pz)(COD)_2]$	3.073[66]	80[63]	0.37	0
$Ir_2(tmb)_4H_2^{2+}$	2.920[64]	136[64]	1.05	1
$Ir_2(tmb)_4I_2^{2+}$	2.803[67]	116[68]	2.09[68]	1
$Ir_4(CO)_{12}$	2.691[69]	207[8] 161 131	1.69[8]	1

[a] $F(Ir_2) = [2\pi\, c\, \nu(Ir_2)]^2\, \mu$ for binuclear species.

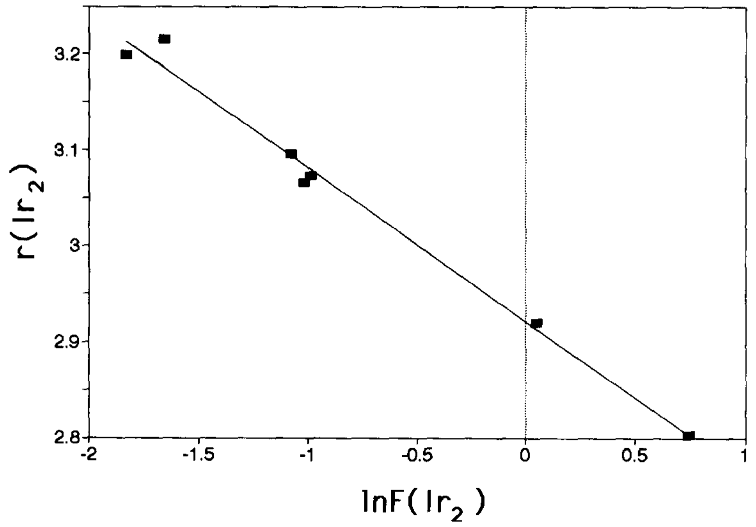

Fig. 5. Graph of+ln $F(Ir_2)$ vs. $r(Ir_2)$. The data are from Table 5, but the data for $Ir_4(CO)_{12}$ were not used (see text).

except that $r(Ir_2)$ appears to be somewhat short. Errors in $\nu(M_2)$ assignments (as in the $Re_2(CO)_{10}$ case), or in the evaluation of $F(Ir_2)$ are still possible.

3.9. The Pt_2 systems

The reported equation for Pt_2 systems is:

$$r(Pt_2) = -0.233 \ln F(Pt_2) + 2.86 \tag{9}$$

(16 data points, $2.58 < r(\mathrm{Pt_2}) < 3.4$ Å, $\sigma = 0.98$) [3]. Systems with bond orders of 0, 0.5 and 1 are used. $\mathrm{Pt_2}$ systems with bond orders of 0 are achieved with binuclear complexes where the two planar tetracoordinated d^8 or tricoordinated d^{10} metal centers are placed face-to-face with the use of bridging ligands, or by solid-state stacking. Systems with a bond order of one-half are the mixed valence (II, III) $\mathrm{Pt_2(pop)_4X^{4-}}$ complexes ($\mathrm{pop = P_2O_5H_2^{2-}}$, X = Cl, Br). One application of this equation would be the estimation of the $F(\mathrm{Pt_2})$ values in the well-known planar D_{2h} $\mathrm{Pt_2X_6^{2-}}$ compounds ($r(\mathrm{Pt_2}) = 3.418$ Å, X = Cl [70]; $r(\mathrm{Pt_2}) = 3.55$ Å, X = Br [71]) where the Pt–Pt interactions occur side-by-side as established by electronic spectroscopy [70]. For such distances, Eq. (9) computes F values of 0.082 and 0.045 mdyn Å^{-1} for X = Cl and Br, respectively. The $\nu(\mathrm{Pt_2})$ modes are expected to be mixed extensively with the Pt–X–Pt bending modes, and resemble the $\mathrm{Cr_2Cl_9^{3-}}$ [6,7] and $\mathrm{W_2Cl_9^{3-}}$ [6,7] systems, except that the $F(\mathrm{M_2})$ values in the Pt systems are much smaller.

3.10. The Au_2 systems

The reparameterized H–L relation for the $\mathrm{Au_2}$ system is:

$$r(\mathrm{Au_2}) = 0.290 \ln F(\mathrm{Au_2}) + 2.68 \qquad (10)$$

with $\sigma = 0.96$ for 11 data points ranging from 2.5 to 3.6 Å [1]. It was on the basis of this equation that the assignment for $\nu(\mathrm{Au_2})$ (at 185 cm^{-1} [72]) was argued in the dithiocarbamate complex $\mathrm{Au_2(S_2CNR_2)_2}$ where $r(\mathrm{Au_2})$ is 2.76 Å [73]. Clark et al. also argued this assignment [74], and suggested that $\nu(\mathrm{Au_2})$ should be found between 60 and 105 cm^{-1}. Eq. (10) predicts that $\nu(\mathrm{Au_2})$ should be found at about 114 cm^{-1} (based upon the X-ray $r(\mathrm{Au_2})$ value). The $\mathrm{Au_2(S_2CNR_2)_2}$ spectra need to be reinvestigated [72,74].

3.11. The Hg_2 systems

In a recent article, the equation for $\mathrm{Hg_2}$ systems has been reported [5]:

$$r(\mathrm{Hg_2}) = -0.24 \ln F(\mathrm{Hg_2}) + 2.69 \qquad (11)$$

($\sigma = 0.96$, 10 data points). The uncertainties are large (±0.16 Å) when compared to those of the $\mathrm{Pd_2}$ systems (±0.05 Å), but the equation allows the estimation of $F(\mathrm{Hg_2})$ in the d^{10}–d^{10} $\mathrm{[Hg_2(dppm)_2Cl_3]^+}$ cation ($r(\mathrm{Hg_2}) = 3.342$ Å, $F(\mathrm{Hg_2}) \approx 0.07$ mdyn Å^{-1}), and led to an interesting comparison. In the family of the d^{10}–d^{10} species having the "$\mathrm{M_2(dppm)_2}$" skeleton, $\mathrm{Pt_2(dppm)_3}$, $\mathrm{[Au_2(dppm)_2](PF_6)_2}$ and $\mathrm{[Hg_2(dppm)_2Cl_3]^+}$, the $r(\mathrm{M_2})$ values are 3.025 [75,76], 3.045 [1]) and 3.342 Å [5], and the $F(\mathrm{M_2})$ values are 0.60 [77], 0.28 [1] and about 0.07 mdyn Å^{-1} [5], respectively. This comparison indicates that the charge (promoting both metal orbital contractions and M–M repulsion) plays an important role in the M–M interactions.

4. The Fe_2, Ru_2 and Os_2 family

This series is addressed separately owing to the large uncertainties that their H–L reparameterized equations provide. In the Fe_2 cases, the problem is that $F(Fe_2)$ is difficult to determine reliably. For Ru_2 and Os_2 complexes, not enough data points are available.

Table 6 summarizes literature data for Fe_n systems ($n=2,3,4$) [8,78–90]. Spiro et al. [80,86] calculated $F(Fe_2)$ values for three complexes, $[FeCp(CO)_3]_4$ (1.3 mdyn Å^{-1}), $Fe_2(CO)_6S_2$ (1.3 mdyn Å^{-1}) and $Fe_2(t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)_2$ $(CO)_4$ (3.4 mdyn Å^{-1}), using the FG matrix method with the aid of Schachtschneider's programs GMAT and FPERT [91,92]. The $F(Fe_2)$ value calculated for the acetylene derivative (3.4 mdyn Å^{-1}) is too large to account for a Fe–Fe double bond. Data from Table 1 for Cr_2 systems exhibiting quadruple and sextuple bonds indicate that F should be smaller than 1.77 mdyn Å^{-1}. Further support for this observation is provided when comparing the quadruply bonded species in Tables 2 and 3. For the other two compounds that Spiro et al. [80,86] calculated $F(Fe_2)=1.3$ mdyn Å^{-1}, the data compare more reasonably with those for singly bonded complexes. When compared with Cr_2 systems exhibiting single bonds ($0.40 \leqslant F(Cr_2) \leqslant 0.71$ mdyn Å^{-1}, Table 1), the $F(Fe_2)$ calculations may once again appear to be a little large.

For all complexes presented in Table 6, the $F(Fe_2)$ values are estimated in the following ways. For $Fe_3(CO)_{12}$, $F=3(2\pi c\nu^2)/m(Fe)$, where $\nu=\nu(a_1)=240\ cm^{-1}$. In this case the $\nu(a_1)/\nu(e)$ ratio ($240/176=1.364$) is close to the theoretical value ($\sqrt{2}=$

Table 6
Spectroscopic and structural data for Fe_2, Fe_3 and Fe_4 systems

Complexes	$r(Fe_2)$ (Å)	$\nu(Fe_2)$ (cm^{-1})	$F(Fe_2)$ (mdyn Å^{-1})	Bond order
$Fe_3(CO)_{12}$	2.64^b[78]	240[8] 176	0.63^c	1
$Fe_2(CO)_6S_2$	2.55[79]	195[80]	0.63^d	1
$Fe_2Cp_2(CO)_4$	2.534[81] 2.531[82]	225[83]	0.83	1
$[FeCp(CO)]_4$	2.52[85]	214[86]	$0.82^{d,e}$	1
$Fe_2(CO)_9$	2.46[84]	260[8]	1.11	1
$Fe_2Cp_2(CO)_3$	2.265[87]^b	214[83]	1.63^g	2
$Fe_2(t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)_2(CO)_4$	2.215[88]	284[80]	1.33^h	2
Fe_2(g) ($^7\Delta_u$)	2.02[89]	199.6[90]	1.48	3

[a] Calculated using the diatomic approximation unless stated otherwise.

[b] Average value.

[c] $F=3\ (2\pi\ c\ \nu)^2\ m(Fe)$; $\nu=\nu(a_1)=240\ cm^{-1}$.

[d] Spiro and Kubas [80] calculated $F(Fe_2)$ to be 1.3 mdyn Å^{-1}.

[e] $F=4\ (2\pi\ c\ \nu)^2\ m(FeCp)$

[f] $r(Fe_2)$ for $Fe_2\ Cp_2{}^*(CO)_3$. It is safely assumed that $r(Fe_2)$ is not greatly affected by the substitution of Cp by Cp*.

[g] Because of the linear Cp–Fe=Fe–Cp structure, $m(Fe)$ is replaced by $m(FeCp)$.

[h] Spiro and Terzis [86] calculated the unreasonable value of 3.4 mdyn Å^{-1} (see text).

1.414) for an equilateral triangular structure and indicates that the coupling between the a_1 and e modes is small. The presence of the CO groups, both axial and equatorial, is ignored; the CO groups are not located parallel to the Fe nuclear displacements. A value of 0.63 mdyn Å^{-1} is calculated and is consistent with the expected trend $F(3d)<F(4d)<F(5d)$: 0.63, 0.82 and 0.91 mdyn Å^{-1} for the $M_3(CO)_{12}$ complexes where M = Fe, Ru and Os, respectively [93]. For $[FeCp(CO)]_4$, if the equation $F=4(2\pi cv)^2/m$, where $v=v(a_1)=21.4$ cm^{-1} and $m=m(Fe)+m(Cp)$ is applied, $F(Fe_2)$ is 0.82 mdyn Å^{-1}. In this case the Cp groups are located in line with the a_1 motions. Details on the $F(Fe_2)$ calculations are provided in the footnotes of Table 6. A reasonable correlation between $r(Fe_2)$ and $F(Fe_2)$ is observed (Table 6 and Fig. 6), except for the triply bonded $Fe_2(g)$ dimer. This observation is not understood at this point. By excluding this latter datum, the equation of the line is

$$r(Fe_2) = -0.39 \ln F(Fe_2) + 2.43 \qquad (12)$$

In this case it is highly recommended that the $F(Fe_2)$ values be re-examined.

For the Ru and Os systems ($n=2, 3$), Table 7 summarizes the data [93–111], and Figs. 7 and 8 show $r(M_2)$ vs. $+\ln F(M_2)$ for M = Ru, Os, respectively. The equations for the lines are:

$$r(Ru_2) = -0.45 \ln F(Ru_2) + 2.81 \qquad (13)$$

$$r(Os_2) = -0.53 \ln F(Os_2) + 2.90 \qquad (14)$$

There is still a good correlation between $r(M_2)$ and $F(M_2)$, except that the number of data points is small (six for Ru, and four for Os). In one case, the $F(Os_2)$ value

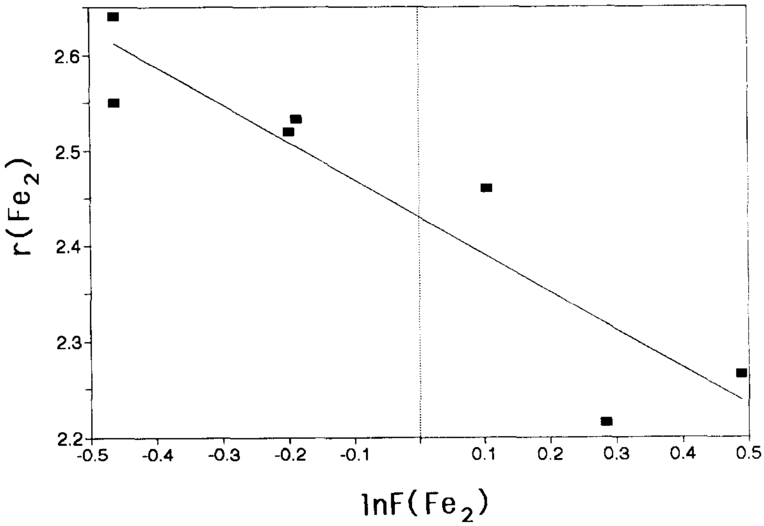

Fig. 6. Graph of $+\ln F(Fe_2)$ vs. $r(Fe_2)$. The data are from Table 6, but the data for $Fe_2(g)$ ($^7\Delta_u$) were not used (see text).

Table 7
Spectroscopic and structural data for Ru_2 and Ru_3 and Os_2, Os_3 systems

Compounds	$r(M_2)$ (Å)	$\nu(M_2)$ (cm^{-1})	$F(M_2)$ (mdyn $Å^{-1}$)	Bond order
$Ru_3(CO)_{12}$	2.85[94]	185 (a_1)[94] 149 (^{e})	0.82[93, 95]	1
$Ru_2Cp_2(CO)_4$ bridged	2.735[96]	221[7]	1.46	1
non-bridged	2.821^e	180[7]	0.97	1
$Ru_2(TTP)_2$	2.41[97]	285[98]	2.42	2
$\{Ru_2(O_2CCH_3)_4Cl\}_n$	2.286[99]	327.3[100]	2.94^b	2.5
$\{Ru_2(O_2CC_3H_7)_4Cl\}_n$	2.281[101]	330.8[100]	3.15^b	2.5
$Os_3(CO)_{12}$	2.89[6]	158 (a_1)[95] 117 (e)	0.91[93, 95]	1
$Os_3(CO)_{12}I_2$(linear)	2.935[102]	97 sym [103] 153 asym	0.96^c	1
$Os_3(\mu\text{-OMe})_2(CO)_{10}$ (bent)	2.82[104]	172 ν_1[103] 136 ν_3 119 ν_2	1.30^d	1
$Os_2(O_2CCH_3)_4Cl_2$	2.31[105]	229[106]	2.94	3
$\{[Os(OEP)]_2\}^{2+}$	?	266[107]	3.79[107]	3

[a] Diatomic approximation unless stated otherwise.

[b] Calculated using equations relating $F(M_2)$ and $\nu(M_2)$ in MMX systems [108]. In these cases, the ν(Ru–Cl) values were from Ref. [100].

[c] Hartley et al. [103] calculated $F(Os_2)=1.7$ mdyn $Å^{-1}$ based on the incorrect structure where they assumed that the I–Os–Os–Os–I was linear. In fact, the X-ray structure showed [102] that the I atoms are perpendicular to the M–M bonds. This value has been recalculated using $\lambda_1\ \lambda_3=\{3m(Os)/[m(Os)]^3\}\cdot[F(Os_2)]^2$ from Ref. [109], $\lambda_i=(2\pi\ c\ \nu_i)^2$.

[d] Calculated from $\lambda_3=(1+2\sin^2\alpha)\ F(Os_2)/m(Os)$ in Ref. [110] for acrylic structures; $\lambda_3=(2\pi\ c\ \gamma_3)^2$; $\gamma_3=136\ cm^{-1}$ [102] $\alpha=33°$ (half of 66° from the X-ray Os–Os–Os angle).

[e] The non-bridged $Cp_2Ru_2(CO)_4$ has never been characterized by X-ray crystallography. In the literature a 1,1′-bis(cyclopentadienyl) tetracarbonyldiruthenium (I) exists and is non-bridged ($r(Ru_2)=2.821$ Å). This datum was used instead, from Ref. [111].

has been recalculated ($Os_3(CO)_{12}I_2$). Originally it was assumed that this structure contained a linear I–Os–Os–Os–I unit [103]. Nine years later, the X-ray structure was reported, which consisted of a linear Os_3 unit where the I ligands were placed in the equatorial positions, not the axial [102].

Recently Woodruff et al. reported the Raman spectra of a series of $\{Os_2(OEP)_2\}^n$ complexes ($n=0$, $+1$, $+2$) [107]: for example, in the case where $n=+2$, $\nu(Os{\equiv}Os)=266\ cm^{-1}$, and $F(Os_2)=3.79$ mdyn $Å^{-1}$. In applying Eq. (14), one calculated $r(Os_2)=2.18$ Å, which is consistent with the multiply bonded nature of the complex, but could appear slightly too short when comparing the Re_2 data (Table 4). Clearly, more data points are needed in order to appropriately design reliable reparameterized H–L relationships in these cases.

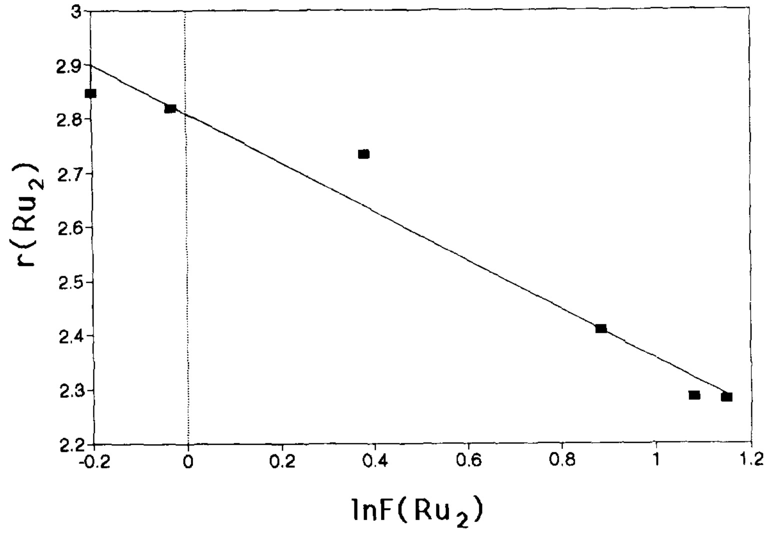

Fig. 7. Graph of+ln $F(Ru_2)$ vs. $r(Ru_2)$. The data are from Table 7.

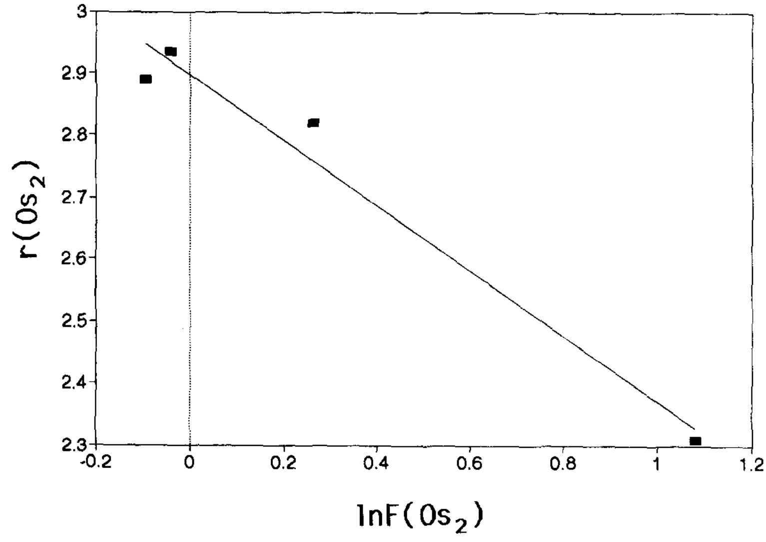

Fig. 8. Graph of+ln $F(Os_2)$ vs. $r(Os_2)$. The data are from Table 7.

5. Discussion

5.1. Periodicity in the H–L parameters

The reparameterized H–L parameters (slopes and intercepts) are listed in Table 8. Consider individual rows (3d, 4d, and 5d). Only one element is available on the 3d

Table 8
Comparison of the reparametrized H–L parameters

Element	H–L slope[a] (Å)	H–L intercept[a] (Å)	σ[b]	No. of data points	Refs.
Cr	−0.746 (0.08)	2.50 (0.14)	0.96	5	This work
Fe[c]	−0.39 (0.7)	2.43 (0.07)	0.85	7	This work
Mo	−0.538 (0.021)	2.87 (0.07)	0.96	26	This work
Ru[c]	−0.45 (0.04)	2.81 (0.06)	0.96	6	This work
Rh	−0.287 (0.019)	2.78 (0.06)	0.96	14	[4]
Pd	−0.387 (0.013)	2.67 (0.07)	0.99	12	[2]
Ag	−0.284 (0.025)	2.53 (0.08)	0.95	9	[2]
W	−0.439 (0.020)	2.87 (0.03)	0.99	7	This work
Re	−0.455 (0.012)	2.90 (0.03)	0.99	13	This work
Os[c]	−0.53 (0.07)	2.90 (0.06)	0.97	4	This work
Ir	−0.160 (0.008)	2.92 (0.02)	0.99	11	This work
Pt	−0.223 (0.009)	2.86 (0.04)	0.98	16	[3]
Au	−0.290 (0.019)	2.68 (0.07)	0.96	11	[1]
Hg	−0.249 (0.009)	2.68 (0.09)	0.97	11	[5]

[a] The values in parentheses are the standard deviations.
[b] Correlation coefficients.
[c] The parameters are considered uncertain (see text).

row element (Cr). If one also considers Fe (slope = −0.39, intercept = 2.43 Å), one can see that slope(Cr) > slope(Fe), and intercept (Cr) > intercept (Fe). By making the same comparison with the 4d elements; slopes: Mo > "Ru" > Rh > Ag. Pd is an exception. Finally, for the 5d elements the intercepts are not as strongly dependent on the atomic number of the elements between W and Ir: W ≈ Re ≈ "Os" ≈ Ir (i.e. $2.87 < \text{intercept} < 2.92 \pm 0.03$ Å), but decrease again between Ir and Hg: Ir > Pt > Au = Hg. From these comparisons, the intercepts (position where $F(M_2) = 1$ mdyn Å^{-1} for all elements) are clearly dependent upon the atomic radii, which decrease with the atomic number [112]. For the 5d elements, the slopes fluctuate greatly along the row: W (−0.439), Re(−0.455), "Os"(−0.53), Ir (−0.160), Pt (−0.223), Au (−0.290), Hg (−0.249).

However, the slopes appeared to decrease with the atomic number along the 3d and 4d row elements, the tendency is observed for the 5d row element as well, but local increases are noticed. Going from 3d→4d→5d, the intercepts increase in all cases (except for Mo and W: Mo ≈ W), again indicating that the atomic radii increase with the row number. Similarly, the slopes generally decrease (or stay about the same in one case: Ag and Au) from the 3d→4d→5d elements. The exception is the Fe, Ru and Os family, for which a slight increase is noticed. In these cases, the lack of accuracy in the $F(M_2)$ calculations and the limited number of data points preclude the accurate estimation of the slopes (and perhaps intercept as well).

5.2. *Correlation with the dissociation energy*

Recently an attempt was made to correlate the slopes of the reparameterized H–L equations with some physical or theoretical properties of the M atom or one of its simple molecules [3]. One correlation was invoked using the bond energy dissociations (E_{Diss}) of the "naked" dinuclear M_2 species [3]. All the data for E_{Diss} can be found in Ref. [113], and are compared with the H–L slopes in Table 9. Generally, on a same-row element the large slopes are associated with low E_{Diss}. The comparison should include elements where the bond order of the M_2 molecules is the same. For instance, for Pd and Ag, the slopes are −0.387 and −0.284, and the E_{Diss} are 105 and 159 kJ mol^{-1} respectively. This trend is also true for Pt and Au, Cr and Mo, and Fe and Rh (even though the two latter comparisons include elements from different rows in the periodic table). No comparison is possible for Hg; the Hg_2 molecule has a very small E_{Diss} (7.5 kJ mol^{-1}) and exhibits a bond order of zero. One interesting case is Ir. The slope (−0.160) is the smallest observed, but E_{Diss} for Ir_2 does not exist. Instead E_{Diss} data for Ir M molecules are compared (M = La, Th, Y). The bond order is not known in these cases, but the E_{Diss} values are the largest in this series, consistent with the low slope. Finally, it is interesting to note that E_{Diss} for Mn_2 is very small (42 ± 29 kJ mol^{-1}). On the basis of these observations, it would not be surprising to obtain a large slope in a reparameterized H–L equation, if such an equation could be designed.

5.3. The heteronuclear systems

The task of designing relations for heteronuclear systems appears practically impossible owing to problems of synthesis. This short section is concerned with some

Table 9
Comparison of the H–L slopes with E_{Diss} (M_2)

Element	Slope	$E_{\mathrm{Diss}}(M_2)$ (kJ mol^{-1})	Bond order
Cr	−0.746	151 ± 21	6
Fe	−0.39	100 ± 21	3
Mo	−0.538	404 ± 20	6
Ru	−0.45	—	—
Rh	−0.287	281.6 ± 20.9	3
Pd	−0.387	105 ± 21	1
Ag	−0.284	159.0 ± 6.3	1
W	−0.439	—	—
Re	−0.455	—	—
Os	−0.53	—	—
Ir	−0.160	—	—
Pt	−0.223	3.58 ± 1.5	1
Au	−0.290	221.3 ± 2.1	1
Hg	−0.249	7.5 ± 1	0
Selected molecules	—	$E_{\mathrm{Diss}}(M_2)$ (kJ mol^{-1})	Bond order
IrLa		573 ± 12	?
IrTh		570.7 ± 42	?
IrY		452.8 ± 16	?
Mn_2		42 ± 29	1

Table 10
Spectroscopic and structural data for heteronuclear systems

	r(MM′) (Å)	ν(MM′) (cm^{-1})	F(MM′) (mdyn $Å^{-1}$)	Eq. no.	r(MM′) (Å) calc.
$CrMo(O_2CCM_3)_4$	2.050(1)[9]	393[9]	3.07(dia.)	(15)	1.99
$MoW(mhp)_4$	2.091(1)[9]	384[9]	5.55(dia.)	(16)	2.03
$[(OC)_5CrRe(CO)_5]^-$	2.9–3.1	146[7]	0.67[7]	(17)	2.98
$[(OC)_5MoRe(CO)_5]^-$	2.9–3.1	130[7]	0.72[7]	(18)	3.04
$[(OC)_5WRe(CO)_5]^-$	2.9–3.1	109[7]	0.74[7]	(19)	3.05
$Re(CO)_5$-$FeCp(CO)_2$	2.888(1)[115]	170–175[116]	0.76(dia.)	(20)	2.80
$FeRh(C_7H_7)(CO)_5$	2.76[b]	172±2[7]	0.63(dia.)	(21)	2.79

[a] dia. = diatomic approximation
[b] In Ref. [114], in Refs. 2 and 3

interesting observations which helped to design such relationships. Without any scientific grounds, one can consider averaging both the slopes and intercepts of both homonuclear equations. For the following examples, new (but "synthetic") equations are designed:

$$r(\mathrm{CrMo}) = -0.642 \ln F(\mathrm{CrMo}) + 2.69 \qquad (15)$$

$$r(\mathrm{MoW}) = -0.505 \ln F(\mathrm{MoW}) + 2.90 \qquad (16)$$

$$r(\mathrm{CrRe}) = -0.694 \ln F(\mathrm{CrRe}) + 2.70 \qquad (17)$$

$$r(\mathrm{MoRe}) = -0.498 \ln F(\mathrm{MoRe}) + 2.88 \qquad (18)$$

$$r(\mathrm{WRe}) = -0.465 \ln F(\mathrm{WRe}) + 2.91 \qquad (19)$$

$$r(\mathrm{FeRe}) = -0.45 \ln F(\mathrm{FeRe}) + 2.66 \qquad (20)$$

$$r(\mathrm{FeRh}) = -0.39 \ln F(\mathrm{FeRh}) + 2.61 \qquad (21)$$

The literature data are listed in Table 10, for which both ν(MM′) and r(MM′) are known [7,9,115,116]. The exceptions are the $[ReM(CO)_{10}]$ complexes (M = Cr, Mo, Re), for which it is safe to assume that r(MM′) will be about 2.9–3.1 Å by comparison with the isoelectronic and isostructural $Cr_2(CO)_{10}^{2-}$ (2.97 Å, [19]), $Mo_2(CO)_{10}^{2-}$ (3.12 Å, [19]), $Mn_2(CO)_{10}$ (2.9038 Å, [50]), $Re_2(CO)_{10}$ (3.0413 Å [50]), and $Tc_2(CO)_{10}$ complexes (3.036 Å, [117]). The applications of Eqs. (15)–(21) work reasonably well (Table 10). The calculated r(MM′) data are between 0.09 to 0.06 Å shorter for three data than those of the X-ray results, and 0.03 Å longer for one datum, and may indicate that assuming a simple average of the slopes and intercepts is inappropriate. Nonetheless, this approach demonstrates that the design of such equations is possible. Again, more data points are needed.

Acknowledgements

Some of our research work involved the design and the use of some of these relationships, which were funded by the Natural Sciences and Engineering Research Council (NSERC), the Fond Concerté pour l'Avancement de la Recherche (FCAR), and the Government of Quebec (Affaires Internationales; Quebec/US collaborative grant, ref. 4). PDH is also grateful to R. Provencher, J. Gagnon, D. Fortin and M. Drouin for technical assistance.

Abbreviations

dmpm	bis(dimethylphosphino)methane
dppm	bis(diphenylphosphino)methane
dmb	1,8-diisocyano-*p*-menthane
mhp	2-methyl-6-hydroxypyridine
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
TFA	trifluoroacetates
TTP	tetraphenylporphyrin
OEP	2,3,7,8,12,13,17,18-octaethylphorphyrin dianion
dth	dithiahexane
Pz	pyrazole
tmb	2,5-dimethyl-2,5-diisocyanohexane
COD	5-cyclooctadiene

Note on the error bars

The uncertainties on the distance data are usually those provided by the X-ray crystallography. No error bar is added to the graphs, since for most data points the error bar is smaller than the point itself. The uncertainties in the force-constant data are those calculated for vibrational frequencies with uncertainties of ± 1 cm^{-1} (or smaller when decimal points are used). For large force constants, the error bar is again smaller than the points on the graph. For smaller force constants, the equations used to extract these data are approximations. The application of the error bars would be somewhat meaningless. For consistency, no error bar is provided. The readers can easily estimate these if desired.

References

[1] D. Perreault, M. Drouin, A. Michel, V.M. Miskowski, W.P. Schaefer and P.D. Harvey, Inorg. Chem., 31 (1992) 695.

[2] D. Perreault, M. Drouin, A. Michel, P.D. Harvey, Inorg. Chem., 32 (1993) 1903.
[3] P.D. Harvey, K.D. Truong, K.T. Aye and A.D. Bandrauk, Inorg. Chem., 33 (1994) 2347.
[4] P.D. Harvey, F. Shafiq and R. Eisenberg, Inorg. Chem., 33 (1994) 3424.
[5] P.D. Harvey, K.T. Aye, E. Isabel, K. Hierso, I. Lognot, Y. Mugnier and F. Rochon, Inorg. Chem., 33 (1994) 5981.
[6] M.C. Baird, Metal–Metal Bonds in Transition Metal Compounds, in F.A. Cotton (ed.), Progress in Inorganic Chemistry, Vol. 9, Interscience, New York, 1968.
[7] D.F. Shriver and C.B. Cooper III, Adv. Infrared Raman Spectrosc., 6 (1980) 127.
[8] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 4th Edn., 1986, pp. 329–338.
[9] F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, Wiley, New York, 1982, pp. 89, 427, etc.
[10] R.J.H. Clark, Struct. Bondings, 36 (1978) 1.
[11] P.M. Morse, Phys. Rev., 34 (1929) 57.
[12] R.M. Badger, J. Chem. Phys., 2 (1934) 128.
[13] R.M. Badger, J. Chem. Phys., 3 (1935) 710.
[14] C.H. Clark, Phil. Mag., 18 (1934) 459.
[15] H.S. Allen and A.K. Longair, Nature, 135 (1935) 764.
[16] D.R. Herschbach and V.W. Laurie, J. Chem. Phys., 35 (1961) 458.
[17] V.M. Miskowski, R.F. Dallinger, G.G. Christoph, D.E. Morris, G.H. Spies and W.H. Woodruff, Inorg. Chem., 26 (1987) 2127.
[18] R.D. Adams, D.M. Collins and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.
[19] L.B. Handy, J.K. Ruff and L.F. Dahl, J. Am. Chem. Soc., 92 (1970) 7312.
[20] S. Onaka, C.B. Cooper III and D.F. Shriver, Inorg. Chim. Acta, 37, (1979) L467.
[21] S.F. Rice, R.G. Wilson and E.I. Solomon, Inorg. Chem., 19 (1980) 3425.
[22] M.D. Curtis and W.M. Butler, J. Organomet. Chem., 155 (1978) 131.
[23] A.P. Sattelberger and J.P. Fackler, J. Am. Chem. Soc., 99 (1977) 1258.
[24] M.C. Manning and W.C. Trogler, J. Am. Chem. Soc., 105 (1983) 5311.
[25] V.E. Bondybey and J.H. English, Chem. Phys. Lett., 94 (1985) 443.
[26] D.P. DiLella, W. Limm, R.H. Lipson, M. Moskovitz and K.V. Taylor, J. Chem. Phys., 77 (1982) 5263.
[27] R.D. Adams, D.M. Collins and F.A. Cotton, Inorg. Chem., 13 (1974) 1086.
[28] C. Cordier, Ph.D. Thesis, Université Paris VI, 1991.
[29] J.P. Wignacourt, M. Drache, J.S. Swinnea, H. Steinfin, A. Lorriaux-Rubbens and F. Wallart, Can. J. Chem., (1991), also included in Ref. [25].
[30] A. Lorriaux-Rubberns, F. Wallart, J.P. Wignacourt and M. Drache, in R.J.H. Clark and D.A. Long (eds.), Eleventh Int. Conf. on Raman Spectra, Wiley, 1969, p. 20.8.
[31] R.J. Klingler, W. Butler and M.D. Curtis, J. Am. Chem. Soc., 100 (1978) 5034.
[32] M.H. Chisholm, F.A. Cotton, B.A. Frenz and L.W. Shive, J. Chem. Soc., Chem. Comm. (1974) 480.
[33] M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive and B.R. Stults, J. Am. Chem. Soc., 98 (1976) 4469.
[34] F.A. Cotton, B.A. Frenz, E. Pedersen and T.R. Webb, Inorg. Chem., 14 (1975) 391.
[35] A. Bino and F.A. Cotton, Inorg. Chem., 18 (1979) 3562.
[36] M.D. Hopkins, V.M. Miskowski and H.B. Gray, J. Am. Chem. Soc., 108 (1986) 959.
[37] M.D. Hopkins, W.P. Schaefer, M.F. Bronikowski, W.H. Woodruff, V.M. Miskowski, R.F. Dallinger and H.B. Gray, J. Am. Chem. Soc., 109 (1987) 408.
[38] R.J.H. Clark and N.R. D'Urso, J. Am. Chem. Soc., 10 (1978) 3088.
[39] Y.M. Efremov, A.N. Samoïlova, V.B. Kozhukhovsky and L.V. Gurvich, J. Mol. Spect., 73 (1978) 430.
[40] K.A. Gingerich, Faraday Discuss., 14 (1980) 109.
[41] A. Goursot, I. Rapai, D.R. Salahub, J. Am. Chem. Soc., 114 (1992) 7452.
[42] P.D. Harvey and Z. Murtaza, Inorg. Chem., 32 (1993) 4721.
[43] P.D. Harvey, S.M. Hubig and T. Ziegler, Inorg. Chem., 33 (1994) 3700.

[44] R. Provencher, K.T. Aye, M. Drouin, J. Gagnon, N. Boudreault and P.D. Harvey, Inorg. Chem., 33 (1994) 3689.
[45] C. Bousquet, J. Phys. B: Mol. Phys., 20 (1987) 2217.
[46] R.C. Weast and S.M. Selby, Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, OH, 48th edn., 1968, p. F-146.
[47] D.J. Santure, K.W. McLaughlin, J.C. Huffman and A.P. Sattelberger, Inorg. Chem., 22 (1983) 1877.
[48] D.J. Santure, J.C. Huffman and A.P. Sattelberger, Inorg. Chem., 24 (1985) 371.
[49] M.H. Chisholm, J.C. Huffman and H.T. Chiu, Polyhedron, 3 (1984) 759.
[50] M.R. Churchill, K.N. Amoh and H.J. Wasserman, Inorg. Chem. 20 (1981) 1609.
[51] W.H. Woodruff, personal communication.
[52] P.D. Harvey, I.S. Butler, G.W. Harris and N.J. Coville, Inorg. Chem., 25 (1986) 3608, and references cited therein.
[53] F.A. Cotton and B.M. Foxman, Inorg. Chem., 7 (1968) 1784.
[54] F.A. Cotton, R. Eiss and B.M. Foxman, Inorg. Chem., 8 (1969) 950.
[55] J.S. Filippo Jr. and H.J. Sniadoch, Inorg. Chem., 12 (1973) 2326.
[56] M.J. Bennett, F.A. Cotton and R.A. Walton, Proc. R. Soc. Lond. A., 303 (1968) 175.
[57] B.I. Swanson, J.J. Rafalko, D.S. Shriver, J. San Filippo Jr., and T.G. Spiro, Inorg. Chem., 14 (1975) 1737.
[58] D.M. Adams, M.A. Hooper and A. Squire, J. Chem. Soc. A, (1971) 71.
[59] D.M. Adams, M.A. Hooper and A. Squire, J. Chem. Soc., Chem. Commun. (1970) 1188.
[60] P.D. Harvey and I.S. Butler, Can. J. Chem., 63 (1985) 1510.
[61] D.G. Leopold, T.M. Miller and W.C. Lineberger, J. Am. Chem. Soc., 108 (1986) 178.
[62] A.W. Coleman, D.T. Eadie, S.R. Stobart, M.J. Zaworotko and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 922.
[63] J.L. Marshall, Ph.D. Thesis, California Institute of Technology, Pasadena, 1986.
[64] D.C. Smith, Ph.D. Thesis, California Institute of Technology, Pasadena, 1989.
[65] G.W. Bushnell, D.O.K. Ejldsted, S.R. Stobart, M.J. Zamorotko, S.A.R. Knox and K.A. Macpherson, Organometallics, 4 (1985) 1107.
[66] K.A. Beveridge, G.W. Bushnell, S.R. Stobart, J.L. Atwood and M.J. Zaworotko, Organometallics, 2 (1983) 1447.
[67] T.P. Smith, Ph.D. Thesis, California Institute of Technology, Pasadena, 1982.
[68] V.M. Miskowski, J.P. Smith, T.M. Loehr and H.B. Gray, J. Am. Chem. Soc., 107 (1985) 7925.
[69] J.P. Hutchinson and M.R. Churchill, Inorg. Chem., 17 (1978) 3528.
[70] C.D. Cowman, J.C. Thibeault, R.J. Ziolo and H.B. Gray, J. Am. Chem. Soc., 98 (1976) 3209.
[71] N.C. Stephenson, Acta Cryst., 17 (1964) 587.
[72] F.J. Farrell and T.G. Spiro, Inorg. Chem., 10 (1971) 1606.
[73] S. Åkerstrom, Ark. Kemi., 14 (1959) 387.
[74] R.H.J. Clark, J.H. Tocker, J.P. Fackler Jr., R. Neira, H.M. Murray and H. Knackel, J. Organomet. Chem., 303 (1986) 437.
[75] L.J. Manojlovic-Muir and K.W. Muir, J. Chem. Soc., Chem. Commun. (1982) 1155.
[76] L.J. Manojlovic-Muir, K.W. Muir, M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, J. Chem. Soc., Dalton Trans. (1985) 1955.
[77] P.D. Harvey and H.B. Gray, J. Am. Chem. Soc., 110 (1988) 2145.
[78] C.H. Wei and L.F. Dahl, J. Am. Chem. Soc., 91 (1969) 1351.
[79] C.W. Wei and L.F. Dahl, Inorg. Chem., 4 (1965) 1.
[80] G.J. Kubas and T.G. Spiro, Inorg. Chem., 8 (1973) 1797.
[81] R.F. Bryan and P.T. Greene, J. Chem. Soc. A (1979) 3064.
[82] R.F. Bryan, P.T. Greene, M.J. Newlands and D.S. Fields, J. Chem. Soc. A (1970) 3068.
[83] M. Vitale, K.K. Lee, C.F. Hemann, R. Hille, T.L. Gustafson and B.E. Bursten, J. Am. Chem. Soc., 117 (1995) 2286.
[84] K.F. Purcell and J.C. Kotz, Inorganic Chemistry, Saunders, Philadelphia, PA, 1977, p. 859.
[85] M.A. Newmann, L.F. Dahl and R.B. King, cited by B.R. Penfold, Perpect. Struct. Chem., 2 (1968) 109.
[86] A. Terzis and T.G. Spiro, Chem. Commun. (1970) 1160.

[87] J.P. Blaha, B.E. Bursten, J.C. Bewan, R.B. Frankel, C.L. Randolph, B.A. Wilson and M.S. Wrighton, J. Am. Chem. Soc., 107 (1985) 4561.
[88] K. Nicholas, L.S. Bray, R.E. Davis and R. Pettit, Chem. Commun (1971) 608.
[89] H. Purdum, P.A. Montano, G.K. Shenoy and T. Morrison, Phys. Rev., 1325 (1982) 4412.
[90] C. Cossé, M. Fouassier, T. Mejean, M. Tranquille, D.P. Dilella and M. Moskovits, J. Chem. Phys., 73 (1980) 6076.
[91] E.B. Wilson, J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw–Hill, New York, 1955.
[92] J.H. Schachtschneider, Technical Reports No. 231-64 and 57-65, 1964–1965 (Shell Development Co., Emeryville, CA).
[93] I.A. Oxton, Inorg. Chem., 19 (1980) 2825.
[94] R. Mason and A.I.M. Rae, J. Chem. Soc. A (1968) 778.
[95] C.O. Quicksall and T.G. Spiro, Inorg. Chem., 7 (1968) 2365.
[96] O.S. Mills and J.P. Nice, J. Organomet. Chem., 9 (1967) 339.
[97] J.P. Collman, C.E. Barnes, P.N. Swepston and J.A. Ibers, J. Am. Chem. Soc., 106 (1984) 3500.
[98] C.D. Tait, J.M. Garner, J.P. Collman, A.P. Sattelberger and W.H. Woodruff, J. Am. Chem. Soc., 111 (1989) 7806.
[99] A. Bino, F.A. Cotton and T.R. Felthouse, Inorg. Chem., 18 (1979) 2599.
[100] R.J.H. Clark and M.L. Franks, J. Chem. Soc., Dalton Trans. (1976) 1925.
[101] M.J. Bennett, K.G. Caulton and F.A. Cotton, Inorg. Chem., 8 (1969) 1.
[102] N. Cook, L. Smart and P. Woodward, J. Chem. Soc., Dalton Trans. (1977) 1744.
[103] D. Hartley, P.A. Kilty and M.J. Ware, Chem. Commun. (1968) 493.
[104] V.F. Allen, R. Mason and P.B. Hitchcock, J. Organomet. Chem., 140 (1977) 297.
[105] F.A. Cotton, A.R. Chakravorty, D.A. Tocher and T.A. Stehenson, Inorg. Chim. Acta, 87 (1984) 115.
[106] R.J.H. Clark, A.J. Hempleman and D.A. Tocher, J. Am. Chem. Soc., 110 (1988) 5968.
[107] C.D. Tait, J.M. Garner, J.P. Collman, A.P. Sattelberger and W.H. Woodruff, J. Am. Chem. Soc., 111 (1989) 9072.
[108] G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra, Van Nostrand Reinhold, New York, 1945, p. 172.
[109] Ref. [108], p. 173.
[110] Ref. [108], p. 169.
[111] K.P.C. Vollhardt and T.W. Weidman, J. Am. Chem. Soc., 105 (1993) 1676.
[112] F.A. Cotton, G. Wilkinson and P.L. Gaus, Basic Inorganic Chemistry, Wiley, New York, 3rd Edn., 1995, p. 61.
[113] M. Moskovitz (ed.), Metal Clusters, Wiley, New York, 1986, pp. 136–138.
[114] S. Saunders and H.J. Bernstein, Inorg. Chem., 13 (1974) 2274.
[115] P. Johnston, C.A. Dickson, A.J. Markell, L. Denner, J.C.A. Boeyens and N.J. Coville, Inorg. Chim. Acta, 144 (1988) 185.
[116] P.D. Harvey, P. Johnston and N.J. Coville, Can. J. Chem., 72 (1994) 2176.
[117] M.F. Bailey and L.F. Dahl, Inorg. Chem., 4 (1965) 1140.