Relationships between Metal–Metal Force Constants and Metal–Metal Separations. 3.[1] Binuclear Rhodium Complexes

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Introduction

There exists numerous types of empirical equations relating atom–atom distances (r) and atom–atom force constants (F)[3]. Harvey *et al.* recently proposed[1] using reparametrized Herschbach and Laurie type (H–L) relationships[3b] ($r = a + b(\log F)$) applicable to each individual element. There would be two advantges. First, these equations do not exhibit mathematical limitations due to convergence for small F values (see Woodruff's rules);[3c,d] second, the equations are more accurate in most cases.[1] Two important features have been observed: these relationships exhibit linearity above the sum of the van der Waals radii (r_{vdW}), and both slopes (b) and intercepts (a) are element-dependent. It was not possible to adequately correlate these empirical parameters with any property related to the elements, as the number of investigated elements so far (3) is too limited. We now wish to report the H–L relationship for Rh_2 systems, determined by measuring $\nu(Rh_2)$ (from which $F(Rh_2)$ values have been extracted) from complexes of known metal–metal separations ($d(Rh_2)$) and with the help of some literature data. The two key features are the design of a relatively accurate empirical relationship for $d(Rh_2)$ values >3 Å and the estimation of the a and b values which provide a better rationalization of the element dependence of the parameters.

Experimental Section

Materials. $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$,[4a] $Rh_2(dppm)_2(CO)_3$,[4b] $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$,[4c] $Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$,[4d] $Rh_2(PN)_2(\mu\text{-}CO)(BH_4)_2$,[4d] $Rh_6(CO)_7(PPh_3)_9$,[4e] $[Rh_2(dppm)_2(CO)_2(\mu\text{-}CH_3OH)]\ (CF_3SO_3)$,[4f] and $Rh_2(dppm)_2(CO)_2Cl_2$[4g] (dppm = $((C_6H_5)_2P)_2CH_2$; PN = $(C_6H_5)_2P(C_5H_4N)$) were prepared according to literature procedures.

Instruments. The Raman spectra were measured on two different spectrometers. The first one was a Bruker IFS 66/CS FT-IR spectrometer coupled with an FRA 106 FT-Raman module using a Nd:YAG laser (1064-nm excitation) and a Notch filter (cutoff ~60 cm^{-1}). The spectra were acquired using 200–300 scans and a 4-cm^{-1} resolution. The laser power applied at the sample was typically 100 mW. The second instrument was an ISA Raman spectrometer equipped with a U-1000 Jobin-Yvon 1.0-m double monochromator using the 514.5-nm green line of a Spectra-Physics argon ion laser for excitation. For each sample, one scan was acquired using the 32× microscope objective, 1 s/point, 1 point/cm^{-1}, no smoothing, and typically 10–30-mW laser power at the sample.

Results

The $\nu(Rh_2)$ Assignment. It has long been known that the assignment of the $\nu(Rh_2)$ mode to the Rh_2 species has been the subject of great controversy,[5] ever since the first reports of the Raman spectra (in 1973) of the $Rh_2(O_2CCH_3)_4L_2$ complexes.[6] It is only since 1986 that two independent research groups, Clark *et al.*[7] and Woodruff *et al.*,[3c] have correctly assigned $\nu(Rh_2)$, using isotopic effects and UV–visible resonance Raman and polarized light methods, respectively. Part of the problem came from the occasional lack of dominating intensity of the $\nu(Rh_2)$ mode in comparison with some low-frequency modes such as ν(Rh–O) and ν(Rh–L). Woodruff *et al.*[3c,d] have proposed an empirical relationship relating the bond distance ($d(M_2)$ in Å) and the force constant $F(M_2)$ in mdyn Å^{-1}) for the 4d elements (which was subsequently modified):[8]

$$d(4d) = 1.82 + 1.46 \exp(-F/2.61) \qquad (1)$$

In this work the $\nu(Rh_2)$ assignments are made on the basis of frequency range, relative intensity, and change in relative intensity with laser excitation. We have accumulated the spectroscopic and structural data from the literature for a number of polynuclear Rh complexes (Table 1). The investigated Rh–dppm and Rh–PN complexes (except one) exhibit a Rh–Rh single bond where $d(Rh_2)$ ranges from 2.612 to 2.757 Å (see Table 1 for details). Typically, the frequency window for $\nu(Rh_2)$ in Rh–Rh single-bonded complexes ranges from 286–314 cm^{-1} (data for strong bonds found for the $Rh_2(O_2CCH_3)_4L_2$ complexes)[3c] to 130 cm^{-1} (datum from $Rh_2(b)_4Cl_2^{2+}$; b = $CN(CH_2)_3NC$).[9] In the latter case, coupling of ν(Rh–Cl) with $\nu(Rh_2)$ for linear X–M–M–X systems decreases $\nu(Rh_2)$ significantly. Interestingly, the polynuclear Rh–carbonyl complexes $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ exhibit d(Rh–Rh) values between 2.7 and 2.8 Å[10,11] (similar to investigated complexes), and their totally symmetric $\nu(Rh_2)$ modes have been located at 219 and 199 cm^{-1}, respectively.[12,13] Using this literature comparison, we expect $\nu(Rh_2)$ in the 200–286-cm^{-1} range.

Figure 1 compares the FT-Raman spectra (1064-nm excitation) of solid $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$, $Rh_2(dppm)_2(CO)_2Cl_2$, and $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$, in the low-frequency range. The second complex does not have a Rh–Rh bond. The higher intensity band located at 225 cm^{-1} in $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$ is reasonably assigned to ν(Rh–Rh) (the 162 ± 3 cm^{-1} peak is common to all the compounds). Similarly, ν(Rh–Rh) is found at 223 and 221 cm^{-1} for $Rh_2(dppm)_2(\mu\text{-}CO)(CO)_2$ and $Rh_2(dppm)_2(\mu\text{-}CO)$-

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Table 1. Spectroscopic and Structural Data for Polynuclear Rh Complexes[a]

no.	complex	d(Rh–Rh)/Å	ν(Rh–Rh)/cm^{-1}	F(Rh–Rh)/mdyn Å^{-1} [b]	bond order
1	$Rh_2(O_2CCH_3)_4L_2$	2.41 ± 0.03[c]	286–314[d]	2.60[d]	1
2	$Rh_2(PN)_2(\mu\text{-}CO)Cl_2$	2.612(1)[e]	233[f]	1.65	1
3	$Rh_2(PN)_2(\mu\text{-}CO)(BH_4)_2$	2.639(5)[e]	223[f]	1.51	1
4	$Rh_2(dppm)_2(CO)_3$	2.739(1)[g]	223[f]	1.51	1
5	$Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$	2.757(1)[h]	225[f]	1.54	1
	$Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$	?	221[f]	1.48	1
6	$Rh_6(CO)_7(PPh_3)_9$	2.79 ± 0.04[i]	202, 156, 115[f,j]	~1.1 ± 0.1[f]	1
7	$Rh_6(CO)_{16}$	2.776[l]	199 (R), 172 (R)[m] 165.5 (IR)[n]	0.83[n]	1
8	$Rh_4(CO)_{12}$	2.73 ± 0.02[o]	219, 170, 125[p]	1.03[p]	1
9	$Rh_2(b)_4Cl_2^{2+}$	2.837[q]	130[r]	0.948[r]	1
10	$Rh_2(TMB)_4Cl_2^{2+}$	2.770[s]	155[r]	1.141[r]	1
11	$Rh_2(dppm)_2(CO)_2(\mu\text{-}CH_3CO)^+$	2.952[t]	~120[f]	~0.44	0
12	$Rh_2(dppm)_2(CO)_2Cl_2$	3.2386[u]	94[f]	0.27	0
13	$Rh_2(b)_4^{2+}$	3.243[v]	79[w]	0.19[w]	0
14	$Rh_2(TMB)_4^{2+}$	3.262[x]	76[x]	0.175	0
15	$[Rh_2(CNC_6H_5)_4]_2^{2+}$	3.193[y]	60[w]	0.11	0

[a] b = $CNCH_2CH_2CH_2NC$; TMB = $(CH_3)_2(CN)CCH_2CH_2C(NC)(CH_3)_2$. [b] $F = \mu(\nu(2\pi)c)^2$, unless stated otherwise. [c] Average value taken from: Colton, F. A.; Felthouse, T. R.; Wlein, S. *Inorg. Chem.* **1981**, *20*, 3037 and references therein. Clark, R. J. H.; Hempleman, A. J.; Dawes, H. M.; Hursthouse, M. B.; Flint, C. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1775. [d] From ref 3c. [e] From ref 4a. [f] This work. [g] From ref 4b. [h] Distance found for $Rh_2(dppm)_2(\mu\text{-}CO)Br_2$.[4c] [i] Average value for $Rh_6(CO)_{12}(P(OPh)_3)_4$ in: Ciani, G.; Garlaschelli, L.; Manassero, M.; Sartarelli, U. Albano, V. G. *J. Organomet. Chem.* **1977**, *129*, C25. [j] These are the a_{1g}, t_{2g}, and e_g modes assuming an approximated O_h point group. [k] The unobserved t_{1u} mode is estimated to be 188 ± 15 cm^{-1} using the relation $\nu(a_{1g}):\nu(t_{2g}):\nu(e_g):\nu(t_{1u}) = 2:\sqrt{2}:1:\sqrt{3}$. From $\nu(t_{1u})$, F(Rh–Rh) is then extracted from $\mu(\nu(2\pi)c)^2$. [l] From ref 11. [m] From ref 13. [n] From: Cariati, F.; Valenti, V.; Barone, P. *Inorg. Chim. Acta* **1970**, *4*, 1327. [o] From ref 10. [p] Average value for the CO-bridged and unbridged Rh–Rh bonds from ref 12. [q] From: Mann, K. R.; Bell, R. A.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 2671. [r] From ref 9. The authors obtained the F values from the force field equations related to linear X–M–M–X systems. See: Herzberg G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945; p 181. [s] From Maverick, A. W. Ph.D. Thesis, California Institute of Technology, 1982. [t] From ref 4f. [u] From ref 4g. [v] From: Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. A.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462. [w] From ref 14c. [x] From ref 3c. [y] From ref 14b.

$(BH_4)_2$. For $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$, ν(Rh–Rh) is found at 233 cm^{-1} (Figure 1), which is consistent with the shorter Rh–Rh bond distances 2.612(1) Å.[4a] The ν(Rh–Rh) assignment for $Rh_2(dppm)_2(CO)_2Cl_2$ is interesting. According to literature results, resonance Raman spectroscopy has placed ν(Rh···Rh) in the 60–80-cm^{-1} range in the isocyanide d^8–d^8 complexes (see Table 1 for details). The FT-Raman spectra exhibit peaks at 81 cm^{-1} for $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$, 81 and 69 cm^{-1} for $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$, 85 and 62 cm^{-1} for $Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$, 73 cm^{-1} for $Rh_2(dppm)_3(\mu\text{-}CO)(CO)_2$, and 94 and 74 cm^{-1} for $Rh_2(dppm)_2(CO)_2Cl_2$. The micro-Raman spectrum preresonance effect from a 514.5-nm excitation of solid $Rh_2(dppm)_2(CO)_2Cl_2$ exhibits peaks at 374, 348, 140, 95, and 33 cm^{-1}. The 74-cm^{-1} peak is absent from the spectra and allows us to assign ν(Rh–Rh) at 94 cm^{-1}. The micro-Raman spectrum of $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$ exhibits two features at 322 and 234 cm^{-1}, which are the ν(Rh–Cl) and ν(Rh–Rh) modes. The Raman enhancement selectivity is consistent with the nature of the excited state involved in the preresonance effect (dσdσ^*)[9] and confirms our assignment for ν(Rh–Rh). For the other samples, the scattered intensity was too weak to differentiate noise from signal and they were not investigated further.

With respect to $Rh_6(CO)_7(PRh_3)_9$, the $\nu(Rh_2)$ assignments have been made on the basis of comparison with $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$.[12,13] There has been no other peak observed in the region of the $\nu(Rh_2)$ reported.

Discussion

Using these results along with the literature data (Table 1), a data bank of 14 points[14] has been created. As a result, a reparametrized H–L equation adapted for Rh has now been obtained as eq 2 with a correlation coefficient of 0.96. When the

$$d(Rh_2) = 2.78 - 0.287 \ln F(Rh_2) \qquad (2)$$

diatomic approximation is used for $Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$, for which $d(Rh_2)$ is not available, an F(Rh–Rh) value of 1.48 mdyn Å^{-1} is obtained. From eq 2, the estimated d(Rh_2) is 2.67 Å. The uncertainty is set at ~0.10 Å and is based upon the average of the maximum differences observed between the calculated and experimentally known d(Rh–Rh) values for singly bonded complexes. The largest differences are found for $Rh_2(dppm)_2(CO)_3$ (0.08 Å), $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$ (0.10 Å), $Rh_2(dppm)_2(CO)_2(\mu\text{-}CH_3CO)^+$ (–0.07 Å), and $Rh_2(O_2CCH_3)_4L_2$ (–0.09 Å), which represent uncertainties of ~3–4%. In three former cases, the diatomic approximation is very crude. Nonetheless, since the $\nu(Rh_2)$ values are the same for $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$, $Rh_2(dppm)_2(CO)_3$, and $Rh_2(dppm)_2(\mu\text{-}CO)(BH_4)_2$, it is only reasonable that the $r(Rh_2)$ values are nearly the same (within the experimental error) in all cases.

It is particularly interesting to note that the H–L equation for Rh_2 system, eq 2, fits data that are "far" from the investigated $r(Rh_2)$ range. Unpublished data for a $Rh_2(dmb)_4^{2+}$ compound ($d(Rh_2)$ = 4.4 Å and $\nu(Rh_2)$ = 26 cm^{-1}; dmb = 1,8-diisocyano-*p*-methane) are available.[15] The diatomic model predicts that $F(Rh_2)$ = 0.02 mdyn Å^{-1}. Hence eq 2 computes a $d(Rh_2)$ value of 3.90 Å, which compares somewhat reasonably (9% error) with the experimental value, taking into account the very large uncertainty in the $F(Rh_2)$ datum. Linearity of the H–L equation up to values of 4.4 Å has already been observed for Pd_2 systems[1a] and indicates the directional situation of the d_{z^2}–d_{z^2} orbital interactions in the M–M bondings. Interestingly, eq 1 is not adequate for d(M–M) values exceeding 3.28 Å and also becomes inacurate for d(M–M) approaching this limit. Equation 2 (H–L equation) is a more interesting alternative in these cases.

The Rh, Pd, and Ag elements are neighbours in the periodic table. The most important H–L parameter is "*b*" (the slope). A high slope (in this case –0.387 found for the Pd_2 systems)[1b] indicates that the force constants are very sensitive to $d(M_2)$, which means that attractive interactions disappear quickly with the increase in $d(M_2)$. Such a diatomic molecule (Pd_2) should be easy to dissociate. Indeed the dissociation energy (E_{diss}) for the singly bonded Pd_2 molecule (in the ground state; $^1\Sigma_g^+$) is 105 ± 21 kJ/mol.[16] Consistent with this observation, the H–L slope value for the Ag_2 systems is lower (–0.284),[1a] and E_{diss} for the

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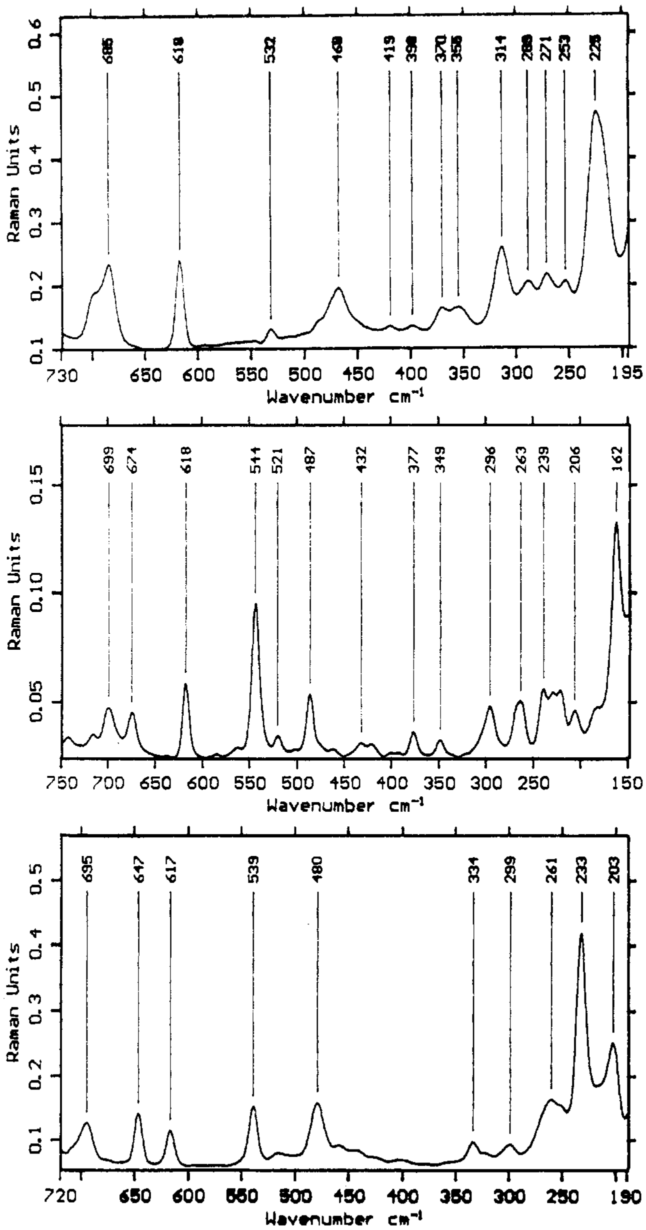

Figure 1. FT-Raman spectra of solid $Rh_2(dppm)_2(\mu\text{-}CO)Cl_2$ (top), $Rh_2(dppm)_2(CO)_2Cl_2$ (middle), and $Rh_2(PN)_2(\mu\text{-}CO)Cl_2$ (bottom).

singly bonded Ag_2 molecule is larger (159 ± 6 kJ/mol).[17] For the Rh_2 systems, the "*b*" value (−0.287) is very similar to that of the Ag_2 ones, which would, in principle, predict that $E_{diss}(Rh_2) \sim E_{diss}(Ag_2)$ for the hypothetical singly bonded Rh_2 molecule. Experimentally, E_{diss} for Rh_2 is 282 ± 21 kJ/mol[18] but accounts for the cleavage of a Rh–Rh triple bond.[19] If it is assumed that the ratio E_{diss} (triple bond)/E_{diss} (single bond) is transferable from one heavy element to another (in this case As_2; ~2.12),[20] one can estimate E_{diss}(single bond) for the Rh_2 molecule. Using 2.12 as the ratio, the estimated Rh–Rh E_{diss} is ~133 ± 16 kJ/mol, which is somewhat an intermediate value between 105 ± 21 (Ag_2) and 159 ± 6 kJ/mol (Pd_2). Considering the experimental uncertainties, $E_{diss}(Ag_2)$ could be taken as similar to this estimated $E_{diss}(Rh_2)$ for the singly bonded M_2 molecule. It is also interesting to note that $b = -0.290$ for the Au_2 systems[1a] (a value close to those for Ag_2 and Rh_2) and that $E_{diss}(Au_2) = 221 \pm 2$ kJ/mol.[21] In principle, we would have predicted that $E_{diss}(Au_2) \sim E_{diss}(Ag_2)$ on the basis of this slope argument, but experimentally $E_{diss}(Au_2) > E_{diss}(Ag_2)$ is observed. Relativistic effects clearly appear to play a role in this increased mutual attraction between the gold atoms.[22] Further studies of Ir_2, Pt_2, and Hg_2 systems are now in progress.

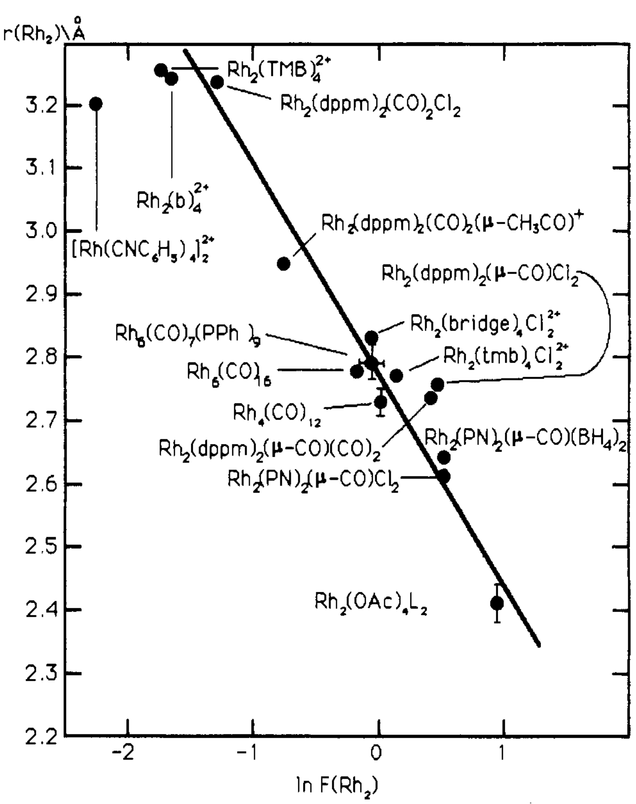

Figure 2. Graph of $r(Rh_2)$ vs ln $F(Rh_2)$. The datum for $[Rh(CNC_6H_5)_4]_2^{2+}$ is not included in the relationship (see text). The error bars for the $Rh_2(O_2CCH_3)_4L_2$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_7(PPh_3)_9$ data are related to the upper and lower values observed within the same family of complexes or within the same cluster. No other error bar appears in this graph simply because the error bars are smaller than the size of the point.

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