Indian Journal of Chemistry
Vol. 46A, January 2007, pp. 33-38

Force constant calculations for $Hg[Co(CO)_4]_2$ from the CO-factored force field

Cemal Kaya* & Duran Karakaş
Department of Chemistry, Cumhuriyet University, 58140 Sivas, Turkey
Email:kaya@cumhuriyet.edu.tr

Received 12 June 2006; revised 23 November 2006

An analytical approach to solve the CO-factored force fields of $Hg[Co(CO)_4]_2$ belonging to D_{3d} point group is described here. The approach leads to relationships which allow direct calculation of carbonyl stretching force constants and CO-CO interaction constants from C-O stretching frequencies of an all $^{12}C^{16}O$ molecule. The force constants calculated by these relationships have been found to be in excellent agreement with those obtained from the Cosβ parameter method. In addition, carbonyl stretching frequencies of the mono ^{13}CO substituted derivatives of $Hg[Co(CO)_4]_2$ have been estimated. The results exhibit agreement between calculated and observed frequencies, showing thereby that the analytical approach presented here gives a valid solution to the CO-factored force field of the molecule under study.

Both the vibrational[1-3] and X-ray crystallographic[4-6] data show that the compound $Hg[Co(CO)_4]_2$ has a geometry consistent with the D_{3d} symmetry. For this molecule, under the D_{3d} local symmetry of the carbonyls, group theory predicts six carbonyl stretching modes ($2a_{1g}+e_g+2a_{2u}+e_u$). The a_{1g} and e_g modes are Raman-active; the a_{2u} and e_u modes are infrared-active[7]. On the basis of the CO-factored force field[8-10], the molecule has two carbonyl stretching force constants (k_1 and k_2) and six CO-CO interaction constants (k_c, k_c', k_t, k_m, p and q) (Fig. 1). Since these are eight force constants to be calculated and only six observable C-O stretching modes, the CO-factored force field for $Hg[Co(CO)_4]_2$ is not yet fully determined.

The first attempt to overcome this problem was made by Bor[11]. In his Cosβ parameter method[12-13], all eight force constants are expressed as a function of only one parameter (Cosβ). This parameter depends on both the declination angle of equatorial ligands and the intensity ratio of two absorption bands belonging to the same symmetry species. The method, therefore, has a difficulty in obtaining a suitable range for Cosβ. In the application of the Cosβ parameter method to $Hg[Co(CO)_4]_2$, Bor made use of isotopic data to calculate the value of Cosβ[11].

Another attempt, based on Cosβ parameter method, to determine force constants for $Hg[Co(CO)_4]_2$ was made by Ernstbrunner and Killner[14]. Here, infrared and Raman modes were treated separately and two different parameters were defined as $Cos\beta_g$ and $Cos\beta_u$. These parameters were determined from the intensity ratios of the two absorption bands belonging to the same symmetry species ($2a_{1g}+2a_{2u}$).

In our previous work on solving the CO-factored force fields of complexes of the types *cis*-$L_2M(CO)_4$ (ref. 15), $M(CO)_4$ with C_{3v} symmetry (ref. 16), $LM(CO)_5$ (ref. 17) and $Fe(CO)_5$ (ref. 18), we have developed some analytical approaches which allow a direct calculation of carbonyl stretching and CO-CO interaction force constants from C-O stretching frequencies of the all-$^{12}C^{16}O$ molecule. Of the complexes mentioned above, pentacarbonyliron is closely related to $Hg[Co(CO)_4]_2$ because the cobalt atoms are in trigonal bipyramidal coordination. In the present paper, we aim to obtain a valid solution for the CO-factored force field of $Hg[Co(CO)_4]_2$ by using an analytical approach similar to that used in the case of $Fe(CO)_5$.

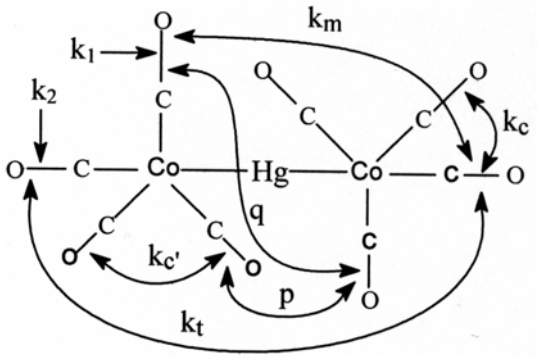

Fig. 1—Definition of CO-factored force constants for $Hg[Co(CO)_4]_2$.

Theoretical

The secular equations for $Hg[Co(CO)_4]_2$ with D_{3d} symmetry, derived employing an energy-factored force field, are given elsewhere[11]. These are presented in Table 1. When these equations were rearranged so that six of the eight constants are expressed in terms of the two remaining and the observed frequencies, the following relations are obtained:

$$k_1=\frac{1}{12\mu}\left[(\lambda_1+\lambda_2+4\lambda_3)+(\lambda_1'+\lambda_2'+4\lambda_3')+(\beta+\beta')\right] \quad \ldots (1)$$

$$k_2=\frac{1}{4\mu}\left[(\lambda_1+\lambda_2)+(\lambda_1'+\lambda_2')-(\beta+\beta')\right] \quad \ldots (2)$$

$$k_c'=\frac{1}{12\mu}\left[(\lambda_1+\lambda_2-2\lambda_3)+(\lambda_1'+\lambda_2'-2\lambda_3')+(\beta+\beta')\right] \quad \ldots (3)$$

$$k_t=\frac{1}{4\mu}\left[(\lambda_1+\lambda_2)-(\lambda_1'+\lambda_2')-(\beta-\beta')\right] \quad \ldots (4)$$

$$p=\frac{1}{12\mu}\times\left[(\lambda_1+\lambda_2-2\lambda_3)-(\lambda_1'+\lambda_2'-2\lambda_3')+(\beta-\beta')\right] \quad \ldots (5)$$

$$q=\frac{1}{12\mu}\times\left[(\lambda_1+\lambda_2+4\lambda_3)-(\lambda_1'+\lambda_2'+4\lambda_3')+(\beta-\beta')\right] \quad \ldots (6)$$

where,

$$\beta=\sqrt{(\lambda_1-\lambda_2)^2-12\mu^2(k_c+k_m)^2} \quad \ldots (7)$$

$$\beta'=\sqrt{(\lambda_1'-\lambda_2')^2-12\mu^2(k_c-k_m)^2} \quad \ldots (8)$$

From Eqs (1)-(8), one can conclude that the solution of the secular equations for the molecule under study is reduced to the problem of finding the values of k_c and k_m. In order to determine the values of these constants, we have employed some substitutions, similar to those in our previous paper[18], two for infrared modes and two for Raman modes.

For infrared modes:

$$k_1+2k_c'+2p+q=\delta_1(k_c+k_m) \quad \ldots (9)$$

$$k_2+k_t=\delta_2(k_c+k_m) \quad \ldots (10)$$

For Raman modes:

$$k_1+2k_c'-2p-q=\delta_3(k_c-k_m) \quad \ldots (11)$$

$$k_2-k_t=\delta_4(k_c-k_m) \quad \ldots (12)$$

With these substitutions, the following relations are obtained from the secular determinants given in Table 1:

$$\lambda_1=\frac{\mu}{2}[(\delta_1+\delta_2)+\sqrt{(\delta_1-\delta_2)^2+12}](k_c+k_m) \quad \ldots (13)$$

$$\lambda_2=\frac{\mu}{2}[(\delta_1+\delta_2)-\sqrt{(\delta_1-\delta_2)^2+12}](k_c+k_m) \quad \ldots (14)$$

$$\lambda_1'=\frac{\mu}{2}[(\delta_3+\delta_4)+\sqrt{(\delta_3-\delta_4)^2+12}](k_c-k_m) \quad \ldots (15)$$

$$\lambda_2'=\frac{\mu}{2}[(\delta_3+\delta_4)-\sqrt{(\delta_3-\delta_4)^2+12}](k_c-k_m) \quad \ldots (16)$$

where $\lambda_1,\lambda_2,\lambda_1',\lambda_2'$ are the λ parameters of a_{1g} and a_{2u} modes. λ_1 and λ_1' denote the modes at the higher frequency, and λ_2 and λ_2' the modes at the lower frequency. From Eqs (13)-(16) for both (k_c+k_m) and (k_c-k_m) two relations are obtained:

Table 1— Secular equations for $Hg[Co(CO)_4]_2$ with D_{3d} symmetry

Symmetry	λ parameters	Secular equations [a]
$a_{1g}^{(1)}$	λ_1	$\begin{vmatrix} \mu(k_1+2k_c'+2p+q)-\lambda & \mu(k_c+k_m) \\ \mu(k_c+k_m) & \mu(k_2+k_t)-\lambda \end{vmatrix}=0$
$a_{1g}^{(2)}$	λ_2	
e_g	λ_3	$\mu(k_1-k_c'+q-p)-\lambda=0$
$a_{2u}^{(1)}$	λ_1'	$\begin{vmatrix} \mu(k_1+2k_c'-2p-q)-\lambda & \mu(k_c-k_m) \\ \mu(k_c-k_m) & \mu(k_2-k_t)-\lambda \end{vmatrix}=0$
$a_{2u}^{(2)}$	λ_2'	
e_u	λ_3'	$\mu(k_1-k_c'-q+p)-\lambda=0$

[a]The various k are defined in Fig. 1; μ represents the reciprocal of the CO group; $\lambda=4\pi^2c^2\nu^2$ where ν is the frequency in cm^{-1}.

$$k_c + k_m = \frac{\lambda_1 + \lambda_2}{\mu(\delta_1 + \delta_2)} \quad \ldots (17)$$

$$k_c + k_m = \frac{\lambda_1 - \lambda_2}{\mu\sqrt{(\delta_1 - \delta_2)^2 + 12}} \quad \ldots (18)$$

$$k_c - k_m = \frac{\lambda_1' + \lambda_2'}{\mu(\delta_3 + \delta_4)} \quad \ldots (19)$$

$$k_c - k_m = \frac{\lambda_1' - \lambda_2'}{\mu\sqrt{(\delta_3 - \delta_4)^2 + 12}} \quad \ldots (20)$$

Combining Eqs (17) and (18), we get:

$$\frac{\sqrt{(\delta_1 - \delta_2)^2 + 12}}{\delta_1 + \delta_2} - \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} = 0 \quad \ldots (21)$$

From Eqs (19) and (20), a similar equation is obtained:

$$\frac{\sqrt{(\delta_3 - \delta_4)^2 + 12}}{\delta_3 + \delta_4} - \frac{\lambda_1' - \lambda_2'}{\lambda_1' + \lambda_2'} = 0 \quad \ldots (22)$$

Eqs (21) and (22) enable us to conclude that the determination of k_c and k_m is reduced to the problem of finding the values of δ_1, δ_2, δ_3 and δ_4 which satisfy them. For a given molecule, the left-hand sides of these equations have two variables, and may be therefore regarded as the function of δ_1 and δ_2 for Eq. (21), and δ_3 and δ_4 for Eq. (22), which are represented by $f(\delta_1, \delta_2)$ and $f(\delta_3, \delta_4)$, respectively. When the function $f(\delta_1, \delta_2)$ is plotted against δ_2 for various values of δ_1, such as δ_1', δ_1'', δ_1''', the curves shown in Fig. 2 are obtained. The graphs of the function $f(\delta_3, \delta_4)$ versus δ_4 for various values of δ_3 are the similar to those of $f(\delta_1, \delta_2)$.

As can be seen from Fig. 2, one of the solutions of Eq. (21) or Eq. (22) corresponds to the point at which the δ_2-axis [δ_4-axis for Eq. (22)] is tangential to the curve obtained for $\delta_1 = \delta_1''$ [$\delta_3 = \delta_3''$ for Eq. (22)]. The curve considered has a minimum at the point and we make use of the partial derivatives of the functions for obtaining the solution mentioned. With the use of $\frac{\partial f(\delta_1, \delta_2)}{\partial \delta_2} = 0$, $f(\delta_1, \delta_2) = 0$, $\frac{\partial f(\delta_3, \delta_4)}{\partial \delta_4} = 0$ and $f(\delta_3, \delta_4) = 0$, we get:

$$\delta_1 = \frac{2\sqrt{3}\sqrt{\lambda_1 \lambda_2}}{\lambda_1 - \lambda_2} \quad \ldots (23)$$

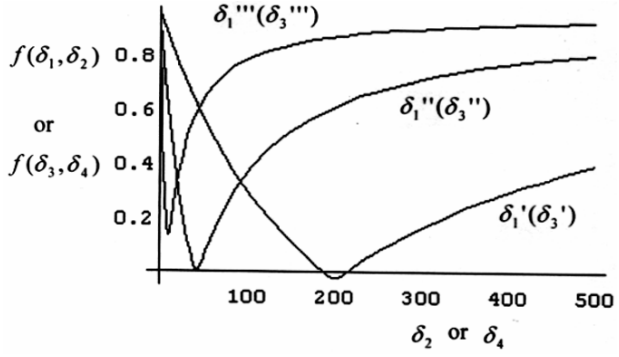

Fig. 2—Model graphs of the function $f(\delta_1, \delta_2)$ vs. δ_2 or the function $f(\delta_3, \delta_4)$ versus $\delta 4$.

$$\delta_2 = \frac{\sqrt{3}(\lambda_1^2 + \lambda_2^2)}{(\lambda_1 - \lambda_2)\sqrt{\lambda_1 \lambda_2}} \quad \ldots (24)$$

$$\delta_3 = \frac{2\sqrt{3}\sqrt{\lambda_1' \lambda_2'}}{\lambda_1' - \lambda_2'} \quad \ldots (25)$$

$$\delta_4 = \frac{\sqrt{3}(\lambda_1'^2 + \lambda_2'^2)}{(\lambda_1' - \lambda_2')\sqrt{\lambda_1' \lambda_2'}} \quad \ldots (26)$$

Combining Eqs (17), (23) and (24), we get:

$$k_c + k_m = \frac{(\lambda_1 - \lambda_2)\sqrt{\lambda_1 \lambda_2}}{\sqrt{3}\mu(\lambda_1 + \lambda_2)} \quad \ldots (27)$$

Combining Eqs (19), (25) and (26) yields:

$$k_c - k_m = \frac{(\lambda_1' - \lambda_2')\sqrt{\lambda_1' \lambda_2'}}{\sqrt{3}\mu(\lambda_1' + \lambda_2')} \quad \ldots (28)$$

From Eqs (27) and (28), the following relations are obtained:

$$k_c = \frac{1}{2\sqrt{3}\mu}\left[\frac{(\lambda_1 - \lambda_2)\sqrt{\lambda_1 \lambda_2}}{\lambda_1 + \lambda_2} + \frac{(\lambda_1' - \lambda_2')\sqrt{\lambda_1' \lambda_2'}}{\lambda_1' + \lambda_2'}\right] \quad \ldots (29)$$

$$k_m = \frac{1}{2\sqrt{3}\mu}\left[\frac{(\lambda_1 - \lambda_2)\sqrt{\lambda_1 \lambda_2}}{\lambda_1 + \lambda_2} - \frac{(\lambda_1' - \lambda_2')\sqrt{\lambda_1' \lambda_2'}}{\lambda_1' + \lambda_2'}\right] \quad \ldots (30)$$

These equations show that k_c and k_m can be calculated from observed frequencies of the a_{1g} and a_{2u} modes. Once k_c and k_m have been determined, the other force constants (k_1, k_2, k_c', k_t, p and q) can be estimated from Eqs (1)-(6). On the other hand, inserting Eqs (27) and (28) into Eqs (7) and (8) gives the relations by which

Table 2 — CO-factored force constants[a] for $Hg[Co(CO)_4]_2$ calculated by two methods

Methods [b]	k_1	k_2	k_c	k_c'	k_t	k_m	p	q
A	16.477	17.032	0.282	0.292	0.114	0.040	0.071	-0.020
B	16.477	17.052	0.282	0.287	0.118	0.041	0.070	-0.022

[a]Force constants are given in mdyn/Å. [b]A and B, respectively, represent our method and the Cosβ parameter method[11].

Table 3 — Secular equations[a] for mono-^{13}CO substituted species of $Hg[Co(CO)_4]_2$ with D_{3d} symmetry

Equatorially substituted species

$$\begin{vmatrix} \mu^*k_1-\lambda & \sqrt{2}\mu k_c' & \mu q & \sqrt{2}\mu p & \mu k_c & \mu k_m \\ \sqrt{2}\mu^*k_c' & \mu(k_1+k_c')-\lambda & \sqrt{2}\mu p & \mu(q+p) & \sqrt{2}\mu k_c & \sqrt{2}\mu k_m \\ \mu^*q & \sqrt{2}\mu p & \mu k_1-\lambda & \sqrt{2}\mu k_c' & \mu k_m & \mu k_c \\ \sqrt{2}\mu^*p & \mu(q+p) & \sqrt{2}\mu k_c' & \mu(k_1+k_c')-\lambda & \sqrt{2}\mu k_m & \sqrt{2}\mu k_c \\ \mu^*k_c & \sqrt{2}\mu k_c & \mu k_m & \sqrt{2}\mu k_m & \mu k_2-\lambda & \mu k_t \\ \mu^*k_m & \sqrt{2}\mu k_m & \mu k_c & \sqrt{2}\mu k_c & \mu k_t & \mu k_2-\lambda \end{vmatrix} = 0 \qquad 6a'$$

$$\begin{vmatrix} \mu(k_1-k_c')-\lambda & \mu(q-p) \\ \mu(q-p) & \mu(k_1-k_c')-\lambda \end{vmatrix} = 0 \qquad 2a''$$

Axially substituted species

$$\begin{vmatrix} \mu(k_1+2k_c')-\lambda & \mu(q+2p) & \sqrt{3}\mu^*k_c & \sqrt{3}\mu k_m \\ \mu(q+2p) & \mu(k_1+2k_c')-\lambda & \sqrt{3}\mu^*k_m & \sqrt{3}\mu k_c \\ \sqrt{3}\mu k_c & \sqrt{3}\mu k_m & \mu^*k_2-\lambda & \mu k_t \\ \sqrt{3}\mu k_m & \sqrt{3}\mu k_c & \mu^*k_t & \mu k_2-\lambda \end{vmatrix} = 0 \qquad 4a_1$$

$$\begin{vmatrix} \mu(k_1-k_c')-\lambda & \mu(q-p) \\ \mu(q-p) & \mu(k_1-k_c')-\lambda \end{vmatrix} = 0 \qquad 2e$$

[a]μ and μ^* denote the reciprocal of the reduced mass of $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively.

β and β' can be calculated from frequencies of the a_{1g} and a_{2u} modes:

$$\beta = \frac{(\lambda_1-\lambda_2)^2}{\lambda_1+\lambda_2} \qquad \ldots (31)$$

$$\beta' = \frac{(\lambda_1'-\lambda_2')^2}{\lambda_1'+\lambda_2'} \qquad \ldots (32)$$

Results and Discussion

Equations (1)-(6) show that the determination of CO-factored force constants for $Hg[Co(CO)_4]_2$ with D_{3d} symmetry from frequencies of fundamental modes leads to an algebraic system which consists of six equations in eight unknowns. It is mathematically evident for such a system that an infinite number of solutions will be possible. In fact, the solution corresponding to Eqs (29) and (30) is the only one possible solution of the algebraic system.

In order to test the validity of the solution found here, Eqs (1)-(6), (29) and (30) were first used to calculate force constants of $Hg[Co(CO)_4]_2$ and then compared with those determined from the Cosβ parameter method[11]. The infrared-active[1,3,6] and Raman-active[2,11,14,19] C-O stretching frequencies of $Hg[Co(CO)_4]_2$ were reported by many authors. In our calculations, we have used the frequencies given in

ref. [11], $a_{1g}^{(1)}$=2094.6, $a_{1g}^{(2)}$=2027.5, e_g=1996.0, $a_{2u}^{(1)}$=2072.3, $a_{2u}^{(2)}$=2021.7 and e_u=2007.3 cm^{-1}. Our results, together with those obtained from the Cosβ parameter method, are given in Table 2.

The table reveals that there exists a very good agreement between the force constants calculated by the two methods. It should also be noted that the presented method utilizes only frequencies of the fundamental modes whereas the application of the Cosβ parameter method[12] needs to use frequencies of isotopically enriched species for finding value of Cosβ and therefore the present method is easier to apply than the Cosβ parameter method.

As a further check upon the validity of the solution presented here, the force constants calculated from Eqs (1)-(6), (29) and (30) were employed to predict C-O stretching frequencies of isotopically enriched species of $Hg[Co(CO)_4]_2$, and the results obtained were compared with observed isotopic frequencies. The reliability of such a comparison is based on the assumption that the force constants remain unchanged on isotopic substitution[20]. This also means that C-O stretching frequencies of isotopically substituted species can be determined by using the force constants of all-$^{12}C^{16}O$ molecule. For such a comparison, we have made use of ^{13}CO-substituted species since the CO-factored force field works best for $^{13}C^{16}O$-substitution[21,22]. The ^{13}CO enriched $Hg[Co(CO)_4]_2$ was prepared and its some isotopic frequencies (2092.2, 2026.0 and 1963.7 cm^{-1}) were reported by Bor[11]. In order to calculate these frequencies, the secular equations for mono-^{13}CO substituted species of $Hg[Co(CO)_4]_2$ were derived by procedures given in Ref.[20] and are presented in Table 3.

Since there are two different sets of CO groups, two mono-^{13}CO substituted species of $Hg[Co(CO)_4]_2$ are expected. The radially substituted derivative belongs to the C_s point group and for which group theory predicts eight C-O stretching modes (6a'+2a"), all being infrared active. The a" modes coincide with the e_g and e_u modes of the parent all-$^{12}C^{16}O$ molecule. On the other hand, the axially substituted derivative belongs to the C_{3v} point group and its observable C-O stretching modes have symmetry species $4a_1$ and 2e, the latter ones coinciding again with the parent e_g and e_u.

With the use of the secular equations given in Table 3 and the force constants calculated by Eqs (1)-(6), (29) and (30), the isotopic frequencies of mono-^{13}CO substituted species of $Hg[Co(CO)_4]_2$ were estimated. The results obtained are given in Table 4, together with observed frequencies of the species. It can be seen from the table that a rather good fit between observed and calculated frequencies was obtained.

Table 4—Observed[11] and calculated frequencies for mono-^{13}CO substituted species of $Hg[Co(CO)_4]_2$

Species	Frequencies (cm^{-1})		Assignment
	Obs.	Calc.	
Equatorially substituted	2092.2	2092.1	a'
	—	2069.6	a'
	2026.0	2026.3	a'
	—	2019.9	a'
	—	2002.2	a'
	1963.7	1964.2	a'
	2007.3	2007.3	a"
	1996.0	1996.0	a"
Axially substituted	—	2089.0	a_1
	2063.0[a]	2063.3	a_1
	—	2024.8	a_1
	—	1993.2	a_1
	2007.3	2007.3	e
	1996.0	1996.0	e

[a]The frequency taken from ref. 14.

Conclusions

Tables 2 and 4 show that the analytical approach employed here leads to a valid solution for the CO-factored force field of $Hg[Co(CO)_4]_2$ with D_{3d} symmetry. The relations obtained make it easy to calculate force constants, allowing direct calculation of them from fundamental C-O stretching frequencies of the all-$^{12}C^{16}O$ molecule. From the excellent agreement between observed and calculated frequencies of ^{13}CO-enriched species (Table 4), one can conclude that the method presented here may be employed to analyze isotopic spectra of $Hg[Co(CO)_4]_2$.

References

1 Bor G & Marko L, *Spectrochim Acta*, 16 (1960) 1105.
2 Stammereich H, Kawai K, Sala O & Krumholz P, *J Chem Phys*, 35 (1961) 2175.
3 Noack K, *Helv Chim Acta*, 47 (1964) 1555.
4 Sheldrick G M & Simpson R N F, *Chem Commun*, (1967) 1015.
5 Sheldrick G M & Simpson R N F, *J Chem Soc A*, (1968) 1005.
6 Lee B, Burlitch J M & Hoard J L, *J Am Chem Soc*, 89 (1967) 8362.
7 Bower L M & Stiddard M H B, *J Organometal Chem*, 13 (1968) 235.

8 Cotton F A & Kraihanzel C K, *J Am Chem Soc*, 84 (1962) 4432.
9 Haines L M & Sitiddard M H B, *Adv Inorg Chem Radiochem* , 12 (1969) 53.
10 Braterman P S, *Metal Carbonyl Spectra* (Academic Press, London) 1975.
11 Bor G, *Inorg Chim Acta*, 3 (1969) 196.
12 Bor G, *Inorg Chim Acta*, 1 (1967) 81.
13 Bor G, *Inorg Chim Acta*, 3 (1969) 191.
14 Ernstbrunner E E & Kilner M, *J C S Dalton*, (1975) 2598.
15 Kaya C, *Spectrochim Acta Part A*, 50 (1994) 1101.
16 Kaya C, *J Organometal Chem*, 575 (1999) 209.
17 Karakaş D & Kaya C, *J Organometal Chem*, 640 (2002) 37.
18 Zengin N & Kaya C, *J Organometal Chem*, 658 (2002) 176.
19 Ziegler R J, Burtlich J M, Hayes S E & Risen W M, *Inorg Chem*, 11 (1972) 702.
20 Wilson (Jr) E B, Decius J C & Cross P C, *Molecular Vibrations* (Mc Graw-Hill, New York) 1955.
21 Burdett J K, Poliakoff M, Timney J A & Turner J J, *Inorg Chem*, 17 (1978) 948.
22 Jones L H, *Inorg Chem*, 15 (1976) 1244.