Journal of Organometallic Chemistry, 255 (1983) 327–334
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

EVIDENCE FOR A NEGATIVE CHARGE ON HYDROGEN FOR SOME METAL CARBONYL HYDRIDES

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(Received April 22nd, 1983)

Summary

Because of the acidity of hydrogen on several metal carbonyl hydrides, it has been presumed that the hydrogen bears a positive charge in the molecule. Matrix isolation studies have led to the characterization of neutral metal carbonyl fragments either directly from hydrogen loss from the related hydride or by independent routes. A comparison of the energy factored force fields of the fragment with those of the hydride containing molecule supports the conclusion that the hydrogen does bear a negative charge in spite of the acidity of the molecule in polar solvents. The acidity of the hydrides is less a function of the charge on hydrogen than a reflection of the weakness of the metal–hydrogen bond.

Introduction

Chen et al. recently published X-ray photoelectron spectra of $HCo(CO)_4$, $HMn(CO)_5$ and $H_2Fe(CO)_4$ from which they estimated that the hydrogen in each of the complexes bore a partial negative charge [1]. This revelation has not had as large an impact as one might expect. These hydrides, as well as most other transition metal hydrides, exhibit Bronsted-Lowry acidic behavior in polar media which has suggested to some that the hydrogen should bear a positive charge in the molecule. $HCo(CO)_4$, in particular, is as strong an acid in water as HCl, while $HMn(CO)_5$ and $H_2Fe(CO)_4$ have pK_a values around 7 [2]. Imjanitov and Rudkovskij referred to hydrides as electrophiles and correlated catalytic behavior in hydroformylation reactions with acidity [3]. Husebye et al. went so far as to refer to $HCo(CO)_4$ as hydrogen tetracarbonylcobaltate(−I) even in non-polar solvents [4]. More recently, Pez et al. imply that the hydrogen of $HCo(CO)_4$ bore a partial positive charge because of the acidity of the molecule in polar solvents [5]. Nishihara et al. attempted to compare the ability of mineral acids and acidic hydrides to protonate coordinated dinitrogen in methanol solution, implying that the mechanism for the reactions were similar [6]. On the other hand, Labinger and Komadina have attempted to use the reductions of ketones by hydrides as a kinetic measure of the

0022-328X/83/$03.00

negative charge on hydrogen [7]. The hydrides were increasingly active to the left of the periodic chart. $HReCp_2$ showed no reaction under the conditions of the comparison. A mechanism for the reactions has yet to be established. Granting that the reaction is initiated by electrophilic attack at the carbonyl carbon, their results still cannot be interpreted as showing the Group VII and Group VIII hydrides are positively charged, but may imply they are just less negatively charged. Bodnar et al., for instance, described the reactions of $HFeCp(PPh_3)CO$ with coordinated olefins as nucleophilic attack [8]. The reactions of certain activated olefins and $HMCp(CO)_3$ ($M = Mo$, W) [9], for which there are analoguous reactions of $HCo(CO)_4$ and $HMn(CO)_5$ [10], appear to proceed via nucleophilic attack by the hydride ligand on carbon. Finally, Trogler was able to abstract the hydrogen of $HMn(CO)_5$ using a strong acid, the type of behavior one expects from a negatively charged hydrogen [11]. Similar behavior is not observed for $HCo(CO)_4$, however [12]. Richmond et al. have claimed to have formed adducts of some hydrides with Lewis acids of the type BX_3 or AlX_3 [13]. $HCo(CO)_4$ notably failed to react with BCl_3 and followed a different reaction course with $AlBr_3$.

Calculations using a variety of techniques show the hydrogen to be negatively charged. Guest et al. calculate a small negative charge on the hydrogen of $HMn(CO)_5$ [14]. Grima et al. show a negative charge on the hydrogen of $HCo(CO)_4$ [15], as do Fonnesbeck et al. [16]. Elian and Hoffmann address the question of the charge on hydrogen for $HCo(CO)_4$, $HMn(CO)_5$ and $H_2Fe(CO)_4$ but avoid asserting one charge or the other, explicitly [17]. We infer from their arguments that the hydrogens of $HCo(CO)_4$ and $HMn(CO)_5$ are negative. The geometry of $H_2Fe(CO)_4$ is so different from the idealized geometries considered by the authors that it is impossible to predict a charge from their arguments. These arguments were structurally based and steric factors could not be ignored as would be required to make the analysis rigorous. Collman and Hegedus avoid claiming a negative charge on the hydrogen, although they do assert that the protonation of a metallate ion is oxidative addition because the change in the formal oxidation number of hydrogen goes from $+1$ to -1 [2]. Using this convention, however, does not imply the actual state of affairs.

Results and discussion

Infrared data obtained from matrix isolation experiments are also consistent with a negative charge on hydrogen for the three hydrides studied by Chen et al. although the degree of charge build up on the hydrogen cannot be quantified. Table 1 shows the force constants for the carbonyl stretching vibrations for each of the hydrides and the related neutral fragments, mostly derived from matrix isolation experiments. The force constants were either taken from the literature or calculated from published spectra [18]. Wherever possible the force field was determined using carbon-13 isotopically substituted molecules. The assumption of energy factoring of the carbonyl modes is not correct in molecules containing metal–hydrogen bonds, but the resulting error in still making the assumption is probably small. For example, Braterman et al. calculated a force field for $HRe(CO)_5$ including the metal–hydrogen stretching coordinate and again without that coordinate [19]. The only diagonal element of the force constant matrix which was greatly affected by the

TABLE 1

FORCE CONSTANTS AND STRUCTURES OF CARBONYL HYDRIDES AND RELATED FRAGMENTS

	k_{trans} [a]	k_{cis} [b]	Symmetry	[c]
$HMn(CO)_5$	16.50 [d]	16.99 [d]	C_{4v} [e]	94 [e]
	16.46 [f]	16.88 [f]		
$Mn(CO)_5$	16.04 [g]	16.51 [g]	C_{4v} [g]	98 [g]
$Mn_2(CO)_{10}$	16.31 [h]	16.50 [h]	D_{4d} [i]	94 [i]
$HCo(CO)_4$	17.51 [j]	16.96 [j]	C_{3v} [e]	100 [e]
$Co(CO)_4$	16.95 [k]	16.76 [k]	C_{3v} [k]	100 [k]
$H_2Fe(CO)_4$	17.46 [l]	17.11 [l]	C_{2v} [e]	96 [e]
				148
$Fe(CO)_4$	16.55 [m]	16.15 [m]	C_{2v} [m]	120 [m]
				145
$HRe(CO)_5$	16.34 [n]	16.96 [n]	C_{4v}	
	16.60 [f]	16.95 [f]		
$Re(CO)_5$	15.96 [o]	16.61 [o]	C_{4v}	
$Re_2(CO)_{10}$	16.20 [h]	16.61 [h]	D_{4d}	

[a] Carbonyl stretching force constant for CO *trans* to the hydride or the vacancy. Units are mdyne A^{-1}. [b] Carbonyl stretching force constant for CO *cis* to the hydride or the vacancy. Units are mdyne A^{-1}. [c] Angle between *cis* and *trans* carbonyl bond vectors except for iron complexes. Then, the angles are between bond vectors of carbonyl ligands which are equivalent. [d] Cotton-Kraihanzel fit argon data similar to that of ref. 34. [e] Gas phase electron diffraction data, ref. 35. [f] A full energy factored force field, ignoring the metal–hydrogen stretching coordinate, ref. 19. [g] A full energy factored force field, CO matrix data, ref. 36. [h] Fit of solution data, ref. 24. [i] Solid state X-ray determination, ref. 42. [j] A full energy factored force field, CO matrix data, ref. 37. [k] A full energy factored force field, CO matrix data, ref. 38. [l] A Cotton-Kraihanzel fit of the following 3 frequencies: 2122, 2052, and 2044 cm^{-1}. Based on argon matrix data from ref. 39. [m] A full energy factored force field, argon matrix data, ref. 40. [n] A full energy factored force field, including the metal–hydrogen stretching coordinate, ref. 19. [o] A full energy factored force field, derived from CO matrix data published in ref. 36 and 41.

interaction with the hydride was that of the *trans* carbonyl and then the change in value was less than 2%.

The table shows that the values of the carbonyl force constants of the hydride containing molecules are larger than the values for the same molecules without the hydrogen. This change in magnitude can be interpreted as an indication of a decrease in electron density on the metal as a hydrogen atom is attached and implies that the hydrogen atom acts as an electron withdrawing group, i.e. becomes negatively charged relative to the hydrogen atom. The carbonyl force constants have been used to indicate the relative electron density on a metal in this manner in a number of contexts [20]. Such a naive conclusion requires further analysis before the argument becomes compelling. For example, it might be proposed that the unpaired electrons of $Mn(CO)_5$, $Fe(CO)_4$ and $Co(CO)_4$ are delocalized into the π^* of CO, causing the carbon–oxygen bond to weaken. First, it should be pointed out that for these systems (d^7, d^8 and d^9) the $d\pi$ donor orbitals of the metals in both the metal carbonyl fragment and their corresponding hydride are filled. Also, with the exception of $Fe(CO)_4$, the structures of the fragments are not greatly perturbed by the hydrogen atom so that one would not expect gross differences in bonding interactions for steric reasons (see Table 1). The molecular orbitals containing the lone electron of $Mn(CO)_5$ and $Co(CO)_4$ have been characterized by ESR and are believed to be localized largely on the metal [21,22]. Elian and Hoffman have described these orbitals in great detail, especially that of $Mn(CO)_5$ [17], although they compute a percent metal character which is less than that which is derived from ESR measurements. Deduced from theory or experiment, the most important metal d orbital in the HOMO of the radicals, $Mn(CO)_5$ and $Co(CO)_4$, is the d_{z^2}. The calculations of Elian and Hoffmann shows some participation of the metal $4p_z$ in the HOMO as well. This $4p_z$ participation gives the orbital "weak" π bonding ability with respect to the basal carbonyls. One wonders whether changes in hybridization as this HOMO is used in bonding with hydrogen might reduce the amount of back-bonding to carbon monoxide without any real charge transfer, or even with transfer of charge from hydrogen to carbon. The orbital is, however, predominately a σ orbital and it need not rehybridize in order to form a bond with H or another metal carbonyl radical. Thus, calculations of $Mn_2(CO)_{10}$ show 35% carbonyl $\pi^\star$ character in the same orbital which affords the metal–metal bond and a similar amount of carbonyl $\pi^\star$ character in the HOMO of $Mn(CO)_5$ [23]. It is interesting to note how similar the carbonyl force constants of the basal carbonyls of $Mn_2(CO)_{10}$ [24] are to those of $Mn(CO)_5$. (This agreement may be fortuitous because of the less determined nature of the $Mn_2(CO)_{10}$ force field.) Taken at face value, the comparison of force constants supports the view that the lone electron of $Mn(CO)_5$ need not be substantially more delocalized into the carbonyl π acceptor orbitals than for the σ-bonded complex, $Mn_2(CO)_{10}$. Presumably, were the hydrogen to bond to $Mn(CO)_5$ in the same fashion as $Mn(CO)_5$ and be partially negatively charged, then electron density would be shifted out of the carbonyls' $\pi^\star$ orbitals as it is fed out to the hydrogen. This draining of charge out of the carbonyl $\pi^\star$ orbital is possible because of the continuing $4p_z$ participation in the bonding orbital. The carbonyl force constant would therefore become greater. In addition, π dative bonding via the d_{xy}, d_{xz} and d_{yz} orbitals would also decrease as a result of the general stabilization of the d orbitals caused by less shielding as electrons are drawn away from the metal. A similar argument can be made for $HCo(CO)_4$ and $H_2Fe(CO)_4$. Arguing a positively charged hydrogen would lead to just the opposite result; the carbonyl modes should shift to lower energy as the metal carbonyl fragment attains a partial negative charge. The shift of the carbonyl modes upon the attainment of a full negative charge (anion formation) is to dramatically lower energies of several hundred wavenumbers [25–27]. Care must be exercised in making numerical comparisons of the frequency shifts as the anions are subject to ion pairing, solvent effects and are frequently of a different symmetry than the radical and hydride.

Although the major contributor to the shifts of CO frequencies will be due to π-bonding effects [2], changes in σ-bonding between the metal and carbon monoxide may also cause a shift of the carbonyl modes as the radical bonds with a hydrogen atom. If hydrogen withdraws electron density off the metal, then the metal should be a better σ acceptor as compared to the radical. The behavior of the carbonyl mode as CO forms a σ complex with BH_3 [2] suggests that increased σ-bonding will result in a blue shift in the carbonyl modes as hydrogen atoms are attached to the radical. This is the same direction of shift as we expect with decreased π-bonding. In conclusion, one can rationalize the observed shifts in the carbonyl force constants as a result of the hydrogen acting as an electron withdrawing group both by π- and σ-based arguments.

All the carbonyls, *trans* to the hydrogen as well as *cis* to the hydrogen, are affected by the attachment of the hydrogen atom. Because the interaction between the hydride and the *trans* carbonyl has been ignored in the force fields, one must be careful in interpreting the decline in the force constant of the *trans* carbonyl as the hydrogen is removed. However, it is apparent from $HRe(CO)_5$ that the magnitude of change in the stretching force constant for the *trans* carbonyl should not be credited to just the interaction between carbonyl and hydride stretches. The values of the force constant of the *cis* carbonyls suffer from none of these ambiguities. Because the structure of the hydrides and their related fragments are so similar, one really need only relate the changes in frequency of correlated infrared absorptions to come to the same conclusion. In each case, the carbonyl bands of the hydride containing molecules appear at higher frequency than those of their related fragments.

The acidity of $HCo(CO)_4$ is not so much a consequence of the partial charge on hydrogen as it is a reflection of the weakness of the metal–hydrogen bond. An analogous situation has been summarized by Cotton and Wilkinson for the hydrohalic acids [28]. HI, the strongest acid in that series, has the weakest H–X bond and is presumably less polar than the other hydrogen halides. The acidity of these molecules was summarized in a cycle which corresponds to the one shown below.

$$HCo(CO)_4(aq) \rightarrow H^+(aq) + Co(CO)_4^-(aq) \qquad \text{(net)}$$

$$HCo(CO)_4(aq) \rightarrow HCo(CO)_4(g) \qquad (1)$$

$$HCo(CO)_4(g) \rightarrow H(g) + Co(CO)_4(g) \qquad (2)$$

$$H(g) \rightarrow H^+(g) + e^- \qquad (3)$$

$$Co(CO)_4(g) \xrightarrow{e^-} Co(CO)_4^-(g) \qquad (4)$$

$$H^+(g) \rightarrow H^+(aq) \qquad (5)$$

$$Co(CO)_4^-(g) \rightarrow Co(CO)_4^-(aq) \qquad (6)$$

Although all the pertinent data are not known for the above reactions, reactions 3, 5 and probably 6 will not cause the dissociation constant of $HCo(CO)_4$ to differ from those of other carbonyl hydrides. The hydration energy of the metallate anions will not vary greatly among the metallate ions of like charge and these energies will be small when compared to the hydration energies of monoatomic, negatively charged ions. The solvation energy (eq. 1) of the hydride is probably not large; oddly, for being a strong acid, $HCo(CO)_4$ is quite insoluble in water [29]. The breaking of the M–H bond is clearly key to the acidity of $HCo(CO)_4$ as compared to other hydrides, as is the solvation of the hydrogen ion key to the overall exothermicity of the process. The cobalt–hydrogen bond energy has been estimated to be on the order of 58 kcal mol^{-1}. That of $HMn(CO)_5$ is around 64 kcal mol^{-1} [30]. Other things being equal, this difference in bond energies nearly accounts for the weaker acidity of $HMn(CO)_5$. It is a lack of knowledge of the electron affinity of the metal carbonyl fragments which stymies a more rigorous analysis.

In conclusion, the hydrogen atom of these carbonyl hydrides must be considered negatively charged in the absence of strongly polarizing influences. The acidity of the hydrides in polar solvents does not result from the partial charge of the hydrogen atom on the molecule, but is better rationalized as a reflection of the weakness of the metal–hydrogen bond. Experimental data which has been correlated with the acidity of the hydride leads one to mistakenly consider the hydrogen as nucleophilic. It might be better to correlate such behavior with the strength of the metal–hydrogen bond. Even missing some of the thermochemical data, the Born cycle based model of hydride acidity does help to rationalize trends. The presence of a coordinated phosphine tends to reduce the acidity of the hydride and is also reputed to strengthen the metal–hydrogen bond [31]. The mechanism for proton dissociation may be quite complicated in contrast to other proton transfer reactions. Walker et al. noted that slow rates of reaction may reflect large activations due to structural rearrangements as well as charge relocation [32]. The catalytic enhancement which Imjanitov and Rudkovski [3] noted in hydroformylation reactions which correlated with the acidity of the hydride need not imply that the hydrides are acting as electrophiles. Such enhancement may simply result from a legitimate correlation with metal–hydrogen bond energies which parallels the acidity of the hydride. Ungvary and Marko have suggested that olefins may substitute at $Co(CO)_4$ during hydroformylation reactions [33]. They suggested that a hydrogen atom could then be transferred to the cobalt from $HCo(CO)_4$ which would be followed by olefin insertion into the new metal–hydrogen bond. It may also be possible under some conditions for the incoming hydrogen to add, as a nucleophile, directly to the coordinated olefin analogous to the reaction described by Bodnar et al. [8].

Experimental

The energy factored force field for $Re(CO)_5$ was obtained using published infrared data [36,41] using a computer program generously provided by Professor Donald J. Darensbourg. The following results were obtained:

	Observed (cm^{-1})	Calcd (cm^{-1})	Symmetry
$Re(^{12}CO)_5$	2099.0	2099.3	a_1
C_{4v}	1977.0	1976.7	a_1
	1995.5	1995.4	e
$Re(^{13}CO)_5$	1933.0	1932.9	a_1
C_{4v}	1951.0	1951.1	e
$Re(^{12}CO)_4(^{13}CO)$	2024.0	2023.9	a'
C_s			

The preceding observed frequencies were used to determine the factored force field of $Re(CO)_5$. Other reported frequencies were equally well fit, although problems were encountered in the fit of bands at 1957.5 and 1969.5 cm^{-1}. A number of intense bands of abundant molecules are present in the immediate vicinity of those positions as determined by calculation. What is observed is undoubtedly an envelope of several transitions which makes it less likely that the absorption maximum actually corresponds to a transition energy. The apparent resolution of the published spectra did not warrant attempts at more rigorous fitting, in our opinion. The calculated force constants are as follows:

k_{ax}	15.96 ± 0.03 mdyne A^{-1}
k_{eq}	16.61 ± 0.02
$k_{ax,eq}$	0.286 ± 0.000
$k_{eq,eq}(trans)$	0.529 ± 0.016
$k_{eq,eq}(cis)$	0.241 ± 0.022

The negligible error reported in $k_{ax,eq}$ is probably due to a strong negative correlation between k_{ax} and $k_{ax,eq}$. Error estimates assume the reported frequencies are accurate to ± 1 cm^{-1}.

The spectrum of $H_2Fe(CO)_4$ [39] was fit with a Cotton-Kraihanzel force field [18b]. In argon matrices three features appear with maximum intensity at 2121.8, 2051.8, and 2044.3 cm^{-1}. The latter two are split but it is impossible to assign a cause, be it two nearly degenerate fundamentals or site effects. The frequencies which were used in the calculation were of the most intense peak in each of the split bands. This allowed the determination of three force constants and led to a predicted spectrum which matched the input frequencies within ±0.1 cm^{-1}. The fourth fundamental, a_1 in character, was calculated to be at 2056.9 cm^{-1}, the position of which corresponds to a shoulder on the band at 2052 cm^{-1}. The diagonal force constant corresponding to a CO *trans* to hydrogen is 17.11 ± 0.03 mdyne A^{-1} and the other diagonal element was 17.46 ± 0.02 mdyne A^{-1}. The interaction force constant has the value of 0.231 ± 0.007 mdyne A^{-1}.

The infrared spectrum of $HMn(CO)_5$ in argon matrices was also fit with a Cotton-Kraihanzel force field [18b]. The infrared spectrum of $HMn(CO)_5$ has already appeared in the literature but accurate frequencies were not reported [34]. The spectrum of $HMn(CO)_5$ was measured in argon at a concentration of 1/1000 in argon. (Equipment and procedures were similar to those reported in ref. 37.) Bands appear at 2123.0, 2011.5 and 2019.2 cm^{-1}, the latter showing a weaker shoulder at 2017.5 cm^{-1}. This feature was shown not to be a fundamental of the molecule by its failure to attenuate and grow upon photolysis and photobleaching to the same extent as the other bands of $HMn(CO)_5$. A fit of the band positions was successful to within ±0.2 cm^{-1}. The force constants were 16.50 ± 0.03, 16.99 ± 0.02 and 0.263 ± 0.006 mdyne A^{-1} for the axial, equatorial and interaction force constants, respectively.

The use of the Cotton-Kraihanzel approximation is justified because of the relatively large changes which are observed in the force constants upon attachment of the hydrogen atom. Although more accurate fittings of the spectra may eventually be possible, it is improbable that the diagonal elements of the force constant matrix of the metal carbonyl fragments will ever exceed the corresponding elements of the hydride. The fit of $HMn(CO)_5$ produced by a Cotton-Kraihanzel force field agrees quite favorably with that obtained by a more accurate procedure [19]. Also, the fact that these data were derived largely from argon matrices does not limit our conclusions to matrix conditions. The matrix spectra of metal carbonyls resemble the spectra obtained from non-polar solutions to a high degree. Were it possible to measure the fragment spectra in fluid media under more normal conditions, we believe the same conclusions would be justified.

References

1 H-W. Chen, W.L. Jolly, J. Kopf and T.H. Lee, J. Am. Chem. Soc., 101 (1979) 2607.

2 J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1980.

3 N.S. Imjanitov and D.M. Rudkovskij, J. Prak. Chem., 311 (1969) 712.

4 S. Husebye, H.B. Jonassen and D.W. Moore, Acta Chem. Scand., 18 (1964) 1581.

5 G.P. Pez, R.A. Grey and J.J. Corsi, J. Am. Chem. Soc., 103 (1981) 7528.

6 H. Nishihara, T. Mori, Y. Tsurita, K. Nakano, T. Saito and Y. Sasaki, J. Am. Chem. Soc., 104 (1982) 4367.
7 J.A. Labinger and K.H. Komadina, J. Organomet. Chem., 155 (1978) C25.
8 T. Bodnar, S.J. LaCroce and A.R. Cutler, J. Am. Chem. Soc., 102 (1980) 3292.
9 R.L. Sweany, D.S. Comberrel, M.F. Dombourian and N.A. Peters, J. Organomet. Chem., 216 (1981) 57.
10 R.L. Sweany and J. Halpern, J. Am. Chem. Soc., 99 (1977) 8335, and, for example, J.A. Roth and M. Orchin, J. Organomet. Chem., 182 (1979) 299.
11 W.C. Trogler, J. Am. Chem. Soc., 101 (1979) 6459.
12 Y. Matsui and M. Orchin, J. Organomet. Chem., 236 (1982) 381.
13 T.G. Richmond, F. Basolo and D.F. Shriver, Organometallics, 1 (1982) 1624.
14 M.F. Guest, M.B. Hall and I.H. Hillier, Mol. Phys., 25 (1973) 629.
15 J.Ph. Grima, F. Choplin and G. Kaufmann, J. Organomet. Chem., 129 (1977) 221.
16 N. Fonnesbeck, J. Hjortkjaer and H. Johansen, Int. J. Quantum Chem., 12 (1977) Suppl. 2, 95.
17 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
18 J.K. Burdett, M. Poliakoff, J.A. Timney and J.J. Turner, Inorg. Chem., 17 (1978) 948, and C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533.
19 P.S. Braterman, R.W. Harrill and H.D. Kaesz, J. Am. Chem. Soc., 89 (1967) 2851.
20 See for example C.A. Tolman, Chem. Rev., 77 (1977) 313 and ref. 2.
21 L.A. Hanlan, H. Huber, E.P. Kundig, B.R. McGarvey and G.A. Ozin, J. Am. Chem. Soc., 97 (1975) 7054.
22 J.A. Howard, J.R. Morton and K.F. Preston, Chem. Phys. Lett., 83 (1981) 226, and M.C.R. Symons and R.L. Sweany, Organometallics, 1 (1982) 834.
23 W. Heijser, E.J. Baerends and P. Ros, Disc. Faraday Soc. (Symp.), 14 (1980) 211.
24 The force constants are a result of a less determined solution of the energy factored normal coordinate analysis of solution data. G. Sbrignadello, G. Battiston and G. Bor, Inorg. Chim. Acta, 14 (1975) 69.
25 P.S. Braterman and A.E. Leslie, J. Organomet. Chem., 214 (1981) C45.
26 C.D. Pribulla and T.L. Brown, J. Organomet. Chem., 71 (1974) 415.
27 M.Y. Darensbourg, D.J. Darensbourg and H.L.C. Barros, Inorg. Chem., 17 (1978) 297.
28 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, A Comprehensive Text, Wiley, New York, 1966.
29 Aqeous solubility is 5.6×10^{-2} M at 25°C. H.W. Sternberg, I. Wender, R.A. Friedel and M. Orchin, J. Am. Chem. Soc., 75 (1953) 2717.
30 J.W. Rathke and H.M. Feder, J. Am. Chem. Soc., 100 (1978) 3623.
31 D.R. Kidd and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 4095, and B.H. Byers and T.L. Brown, J. Am. Chem. Soc., 97 (1975) 947.
32 H.W. Walker, C.T. Kresge, P.C. Ford and R.G. Pearson, J. Am. Chem. Soc., 101 (1979) 7428.
33 F. Ungvary and L. Marko, J. Organomet. Chem., 219 (1981) 397.
34 A.J. Rest and J.J. Turner, J. Chem. Soc., Chem. Commun., (1969) 375.
35 E.A. McNeill and F.R. Scholer, J. Am. Chem. Soc., 99 (1977) 6243.
36 S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, J. Am. Chem. Soc., 103 (1981) 7515.
37 R.L. Sweany, Inorg. Chem., 21 (1982) 752.
38 O. Crichton, M. Poliakoff, A.J. Rest and J.J. Turner, J. Chem. Soc., Dalton Trans., (1973) 1321.
39 R.L. Sweany, J. Am. Chem. Soc., 103 (1981) 2410.
40 M. Poliakoff and J.J. Turner, J. Chem. Soc., Dalton Trans., (1974) 2276, and M. Poliakoff, Chem. Phys. Letts 78 (1981) 1.
41 H. Huber, E.P. Kundig and G.A. Ozin, J. Am. Chem. Soc., 96 (1974) 5585.
42 M. Martin, B. Rees and A. Mischler, Acta Cryst., B38 (1982) 6.