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# Equilibrium studies on metal–metal bond dissociation in the $[(C_5Me_5)Cr(CO)_3]_2$ dimer by use of NMR spectroscopy

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## Abstract

The thermodynamics of metal–metal bond dissociation in the $[(C_5Me_5)Cr(CO)_3]_2$ dimer was studied by variable-temperature proton NMR study in toluene-$d_8$. Dissociation constants and proton isotropic shifts at various temperatures were obtained. Application of the van 't Hoff equation gives the following thermodynamic parameters: $\Delta H = 18.3$ ($\pm 0.6$) kcal mol$^{-1}$; $\Delta S = 54.8$ ($\pm 2.2$) cal mol$^{-1}$ K$^{-1}$ ($\Delta G = 1.9$ kcal mol$^{-1}$ at 300 K). These parameters were compared with those of the $[(C_5H_5)Cr(CO)_3]_2$ dimer. The most likely spin delocalization mechanism for the methyl protons is believed to be a combination of $\sigma$ and $\pi$ spin delocalization. The ESR spectrum in toluene ($g_0 = 2.004 \pm 0.001$) at or below 273 K is consistent with a non-degenerate ground state of the monomer.

## Introduction

The dimeric $[CpCr(CO)_3]_2$ ($Cp = \eta^5$-$C_5H_5$) (**1**) species has been extensively studied. Reactivity investigations [1–6] supported by spectral [7,8] and electrochemical [8] studies provide ample evidence for a very facile reversible thermal dissociation in solution as shown in equation 1:

$$[CpCr(CO)_3]_2 \rightleftharpoons 2[CpCr(CO)_3] \qquad (1)$$

The extreme weakness of the Cr–Cr bond was confirmed by calorimetric measurements [9] and very recently by equilibrium studies via UV and IR spectral measurements which indicate a 10% dissociation in a 10 m*M* solution at 298 K [10].

The $[Cp^\star Cr(CO)_3]_2$ ($Cp^\star = \eta^5$-$C_5Me_5$) dimer (**2**), the permethyl analogue of (**1**), was recently synthesised by Baird [11] and ourselves [12] via different methods and both the reactivity and the spectral data [11] indicate extensive dissociation in solution, in agreement with a Cr–Cr bond which at 3.310 Å [11,12] is longer than that in (**1**). It was desirable to compare the extent of this dissociation with that of (**1**) in solution. Here we describe a quantitative NMR spectra investigation with this particular objective and report on the ESR spectral characteristics of the monomeric species.

## Experimental

All samples were prepared in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train. NMR spectra were recorded on a JEOL FX 100 100 MHz spectrometer, the probe temperature of which was measured using a chromel–alumel thermocouple. ESR spectra were measured on a Bruker B-R 70 Spectrometer (23 cm magnet), the field determined with the aid of an NMR oscillator, and the *g*-value calibrated with DPPH.

The complex **2** was obtained from the reaction of $K[Cp^\star Cr(CO)_3]$ with $Fe^{3+}$ ions in an acidic medium as described [12,13]. Toluene-$d_8$ was dried over sodium benzophenone and vacuum-transferred before use. Benzonitrile (from B.D.H Ltd) was dried over calcium hydride, and distilled over $P_2O_5$ at reduced pressure.

Approximately 15 m$M$ stock solutions of **2** were prepared in toluene-$d_8$ and aliquots were appropriately diluted to provide samples of concentrations from 1.36 m$M$ to 13 m$M$ for $^1H$ NMR measurements in sealed 5 mm NMR tubes. The probe temperature was raised stepwise from 183 K and the samples were monitored continually during measurement to check for probable decomposition; indicated by the appearance of $\delta(CH_3)$ at 1.73 (30 ° C) pertaining to the decarbonylated product, $[Cp^\star Cr(CO)_2]_2$ [14].

### *Treatment of NMR data*

The observed proton NMR isotropic shifts ($\Delta_{obs}$) of the methyl protons of the $Cp^\star$ group defined as

$$\Delta_{obs} = \delta_{obs} - \delta_{M_2}$$

where $\delta_{obs}$ is the observed chemical shift and $\delta_{M_2}$ is the chemical shift of the dimer, are treated according to the dimer–monomer equilibrium, i.e.

$$M_2 \rightleftharpoons 2M \tag{2}$$

Starting from the dissociation constant expression, $K_{dis}$, where

$$K_{dis} = \frac{[M]^2}{[M_2]} \tag{3}$$

it can be shown that

$$K_{dis} = \frac{4\alpha^2[M_2{}^0]}{1-\alpha} \tag{4}$$

where $\alpha$ is the degree of dissociation and $[M_2{}^0]$ is the initial concentration of the dimer. Since the exchange is rapid in the temperature range studied (indicated by a single averaged line), it can also be shown that

$$\alpha = \frac{\Delta_{obs}}{2\,\Delta - \Delta_{obs}} \tag{5}$$

where $\Delta$, the isotropic shift of the methyl protons is defined as

$$\Delta = \delta_M - \delta_{M_2}$$

Substituting eq. 5 into eq. 4 gives

$$\Delta_{obs} = \frac{2\,\Delta}{1.5 + (0.25 + 4[M_2{}^0]K_{dis}^{-1})^{1/2}} \tag{6}$$

Equation 6 is then subjected to a Simplex program [15] to obtain $K_{dis}$ and $\Delta$. The initial concentration of the dimer, $[M_2{}^0]$ was corrected for solvent density changes at various temperatures.

## Results and discussion

### *NMR Studies*

As observed by Baird [11], solutions of **2** sealed under rigorous exclusion of air were found to be indefinitely stable at ambient temperature in the absence of light. Hence, in order to avoid complications from decarbonylation which might arise on heating [11], spectral measurements were initially recorded at 183 K, followed by stepwise increases of the probe temperature. Any decomposition was detectable from the appearance of the methyl resonance ($\delta$ 1.73 at ca. 303 K) of the decarbonylated product, $[Cp^\star Cr(CO)_2]_2$. In most cases, the extent of decomposition was found to be negligible, $\leq 5\%$, as shown in Fig. 1, at the end of the final measurement at 348 K. However, if more than 5% decomposition was detected, the result was discarded and the experiment repeated.

The temperature-dependent proton NMR spectral changes of a 13 m*M* solution in toluene-$d_8$ is illustrated in Fig. 1 and the variation with temperature of the $Cp^\star$ resonance of 13 m*M* and 1.36 m*M* solutions is depicted in Fig. 2. It is observed that at 183 K, $\delta(Cp^\star)$ occurs as a sharp singlet signal at 1.53 ppm, attributed to the dimeric species **2**. As the temperature is raised, the line-width broadens and the signal shifts to lower field with a reversal at ca. 323 K and 293 K for the 13 m*M* and 1.36 m*M* solutions respectively (Fig. 2). The turnover point temperature increases with concentration. The apparent Curie-law behaviour at high temperature is due to the extensive dissociation of the dimer which gives the paramagnetic monomer—with the apparent inverse temperature dependence of the isotropic shift. At low temperature, the extent of dissociation decreases and hence the diamagnetic dimer contribution becomes more important as reflected in the upfield shift toward the position of the diamagnetic resonance signal.

$$\underset{(2)}{[Cp^* Cr(CO)_3]_2} \rightleftharpoons 2[Cp^* Cr(CO)_3] \tag{7}$$

At a given temperature, the observed isotropic shifts $\Delta_{obs}$ move upfield with increasing concentration, which indicates that there is a higher concentration of dimer in the solution, as reflected in eq. 7. The fit of the concentration-dependent isotropic shifts to the dimer–monomer equilibrium is good at all the temperatures chosen for study. Table 1 allows comparison of $\Delta_{obs}$ values with the expected isotropic shifts based on the best-fit parameters at 303 K. The good fit between the concentration and the observed isotropic shift to the dissociation equilibrium lends further support to the above explanation.

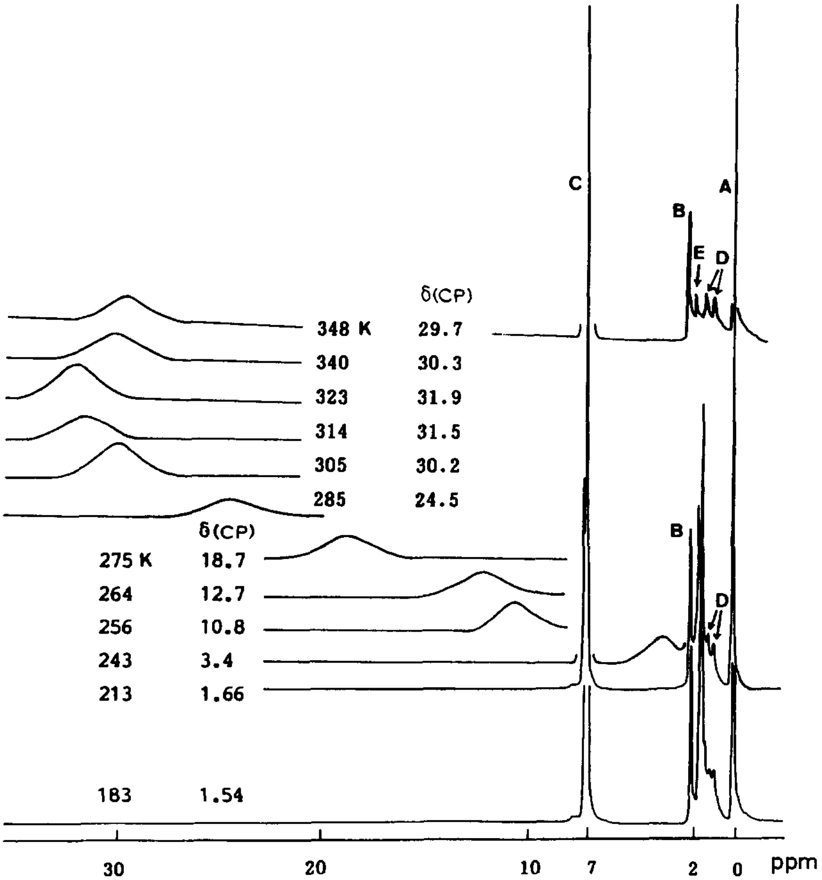

Fig. 1. Proton NMR spectral variation of a 13 m*M* solution of $[Cp^{\star}Cr(CO)_3]_2$, in toluene-$d_8$, with temperature. Resonance peaks: A, $\delta(CH_3)_4Si$; B and C, $\delta(C_6D_5CHD_2)$ and δ(aromatics) of solvent; D, δ 1.27 and 0.90 (hexanes in solvent); E, δ 1.73 ($CH_3$ resonance of $[Cp^{\star}Cr(CO)_2]_2$.

The calculated dissociation constants and the isotropic shifts at various temperatures are summarised in Table 2. As expected, the dissociation constant decreases with decreasing temperature. Application of the van 't Hoff equation gives the following thermodynamic parameters: $\Delta H = 18.3$ ($\pm 0.6$) kcal $mol^{-1}$; $\Delta S = 54.8$ ($\pm 2.2$) cal $mol^{-1}$ $K^{-1}$ ($\Delta G = 1.9$ kcal $mol^{-1}$ at 300 K).

Consonant with the demands of $\Delta H$ versus metal–metal bond length correlations, the dissociation enthalpy agrees very well with that of the Cp analogue ($21.3 \pm 0.7$ kcal $mol^{-1}$) determined by a similar NMR investigation [16]. McLain recently reported a $\Delta H$ value of $15.8 \pm 0.4$ kcal $mol^{-1}$ for the Cp complex from a UV spectrophotometric determination [10]. However, discrepancies in metal–metal bond energies determined by different methods are not uncommon [17]. These results indicate that **2** dissociates to an extent of 63% in a 10 m*M* solution at 298 K compared with 10% for the Cp analogue (**1**) [10].

The $\Delta G$ value obtained is much smaller than that reported for the Cp analogue (4.6 kcal $mol^{-1}$ at 300 K) [10]. This is consistent with the presence of a bulkier $Cp^{\star}$ ring which would facilitate the dissociation of the Cr–Cr bond. The larger $\Delta S$ value

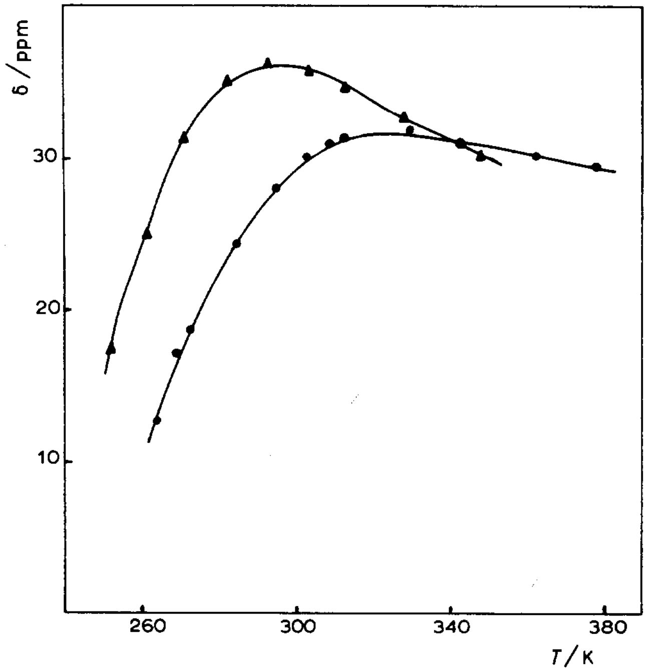

Fig. 2. Temperature dependence of chemical shifts for 13 mM (●) and 1.36 mM (▲) solutions in toluene-$d_8$.

in the permethyl analogue as compared with 37.1 cal $mol^{-1}$ $K^{-1}$ in the Cp complex [10], and with 30 cal $mol^{-1}$ $K^{-1}$ in $[(\eta^3\text{-}C_3H_5)Fe(CO)_2]_2$ [18], reflects the greater relief of the steric strain of the bulky Cp* ring on dissociation into a monomer. This result is in accord with the apparent absence of *anti* and *gauche* dimer equilibrium in $[Cp^{\star}Cr(CO)_3]_2$ from our NMR study at various temperatures. It is very likely that only the *anti* rotamer exists in solution due to the steric hindrance of the bulky Cp* ring.

Table 1

Comparison of the observed and calculated isotropic shifts at 303 K in toluene-$d_8$ based on the best-fit parameters: $\Delta = -35.6$ ppm, $K_{dis} = 7.43 \times 10^{-2}$

| Concentration/mM | $\Delta_{obs}$/ppm | $\Delta_{cal.}$/ppm |
|---|---|---|
| 1.2 | −34.54 | −34.50 |
| 1.34 | −34.19 | −34.39 |
| 2.42 | −33.72 | −33.59 |
| 3.92 | −32.61 | −32.63 |
| 5.80 | −31.82 | −31.60 |
| 8.48 | −30.41 | −30.38 |
| 9.57 | −29.85 | −29.94 |
| 10.54 | −29.65 | −29.58 |
| 11.30 | −29.14 | −29.30 |

Table 2

Dissociation constants and proton isotropic shifts at various temperatures

| Temperature (K) | $K_{dis}/M$ [a] | $\Delta$/ppm [a] |
|---|---|---|
| 247 | $7.48\times10^{-5}$ | $-68$ |
| 252 | $1.36\times10^{-4}$ | $-67$ |
| 261.5 | $4.24\times10^{-4}$ | $-62$ |
| 271.5 | $1.63\times10^{-3}$ | $-52$ |
| 274.5 | $1.89\times10^{-3}$ | $-53$ |
| 282.5 | $6.55\times10^{-3}$ | $-44$ |
| 292.7 | $2.1\times10^{-2}$ | $-39$ |
| 303.5 | $7.43\times10^{-2}$ | $-36$ |
| 313.5 | $2.08\times10^{-1}$ | $-34$ |
| 328 [b] | – | $-31.1$ |
| 348.4 [b] | – | $-28.7$ |
| 363.6 [b] | – | $-26.4$ |

[a] Error in $K_{dis}$ is $\leq \pm10\%$ while that of $\Delta$ is $\leq \pm5\%$. Negative sign indicates downfield shift. [b] At these high temperatures, $K_{dis}$ was not determined because of extensive dissociation resulting in small changes in $\Delta_{obs}$ with concentration. The observed isotropic shift of the solution at the extremely dilute concentration was taken to be the isotropic shift with an error of ±1 ppm at most.

### *Mechanism of spin delocalization*

By analogy with [CpCr(CO)$_3$], the ground state of [Cp*Cr(CO)$_3$] is expected to be $^2$A′, the result of Jahn–Teller distortion in the $t_{2g}^5$ manifold. For such an orbitally non-degenerate state, the proton isotropic shift originates mainly from the contact term. In order to explore the plausible modes of spin delocalization, it would be useful to compare the isotropic contact shift of the methyl protons with that of the ring protons in [CpCr(CO)$_3$]. As the latter value is not available in the literature, we estimated it from eq. 6 based on the value of $K_{dis}$ of [CpCr(CO)$_3$]$_2$ in toluene at 303 K [10] and the observed isotropic shifts in 13.0 m$M$ and 7.41 m$M$ solutions. The shift was found to be $-10.1$ ppm which is smaller than that of the methyl protons ($-36$ ppm).

Three plausible modes of spin delocalization in metallocenes have been suggested in the literature: (i) $\pi$ delocalization with spin polarization (Levy–Orgel) [19], (ii) $\sigma$ delocalization, and (iii) direct metal–hydrogen interaction [20].

In the first mode, the positive spin density is delocalized in the $\pi$-type ligand m.o.. The negative spin density reaches the ring hydrogens by means of a McConnell-type $\pi$–$\sigma$ exchange [21] and the positive spin density reaches the ring methyl hydrogens by means of hyperconjugation which predicts different directions of shift for both kinds of protons. Since this is contrary to what is observed in the present system, we can rule out this possibility. In (ii), the positive spin density is delocalized in the $\sigma$-type ligand m.o. and would predict downfield shift for both kinds of protons. However, a characteristic property of $\sigma$ delocalization is the attenuation of shift as the distance of hydrogen from the unpaired spin centre increases. This mechanism therefore predicts greater downfield shifts for the ring protons which again is contrary to what is observed. In (iii), the hydrogen atoms overlap directly with the metal $d$ orbital(s) containing the unpaired electron. This again can be ruled out because (a) the average distance between the methyl hydrogens and metal is > 3.5 Å which is too great for hyperconjugation to occur; and (b) it cannot

Table 3

Direction of contact shifts arising from the different delocalization mechanisms

| Mode of spin delocalization | Ring proton | Methyl proton |
|---|---|---|
| $\sigma$ | downfield (larger) | downfield (smaller) |
| $\pi$ | upfield | downfield |
| $\sigma + \pi$ | downfield (smaller) | downfield (larger) |

reconcile the smaller shift of the ring protons since it predicts a greater downfield shift because of the shorter metal–ring proton distance.

Hence, the most likely mechanism probably involves some combination of $\sigma$ and $\pi$ delocalization as this is consistent with the smaller contact shift in the ring protons due to the mutual cancellation of the $\sigma$ and $\pi$ delocalization and a larger contact shift in the methyl protons due to the mutual reinforcement of the two mechanisms. (See Table 3 for a summary of the above discussion.)

### *Temperature dependence of the isotropic shifts*

The plot of $\Delta$ vs $1/T$ is shown in Fig. 3. The non-linear plot is not that expected for an orbitally non-degenerate system in which Curie law is obeyed. As the isotropic shift of the methyl protons measures $A_{\mathrm{CH}_3}$, the hyperfine coupling constant, the non-linear behaviour implies that $A_{\mathrm{CH}_3}$ will be temperature dependent (Fig. 4). The temperature dependence of $A_{\mathrm{CH}_3}$ cannot be ascribed to the hindered rotation of the methyl group because the three protons are magnetically equivalent

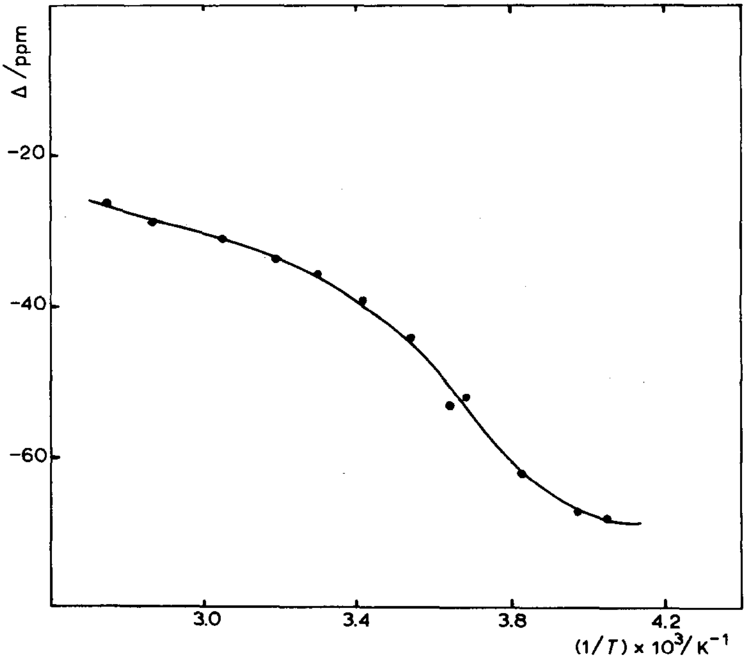

Fig. 3. Proton isotropic shifts of the methyl protons versus the reciprocal of temperature.

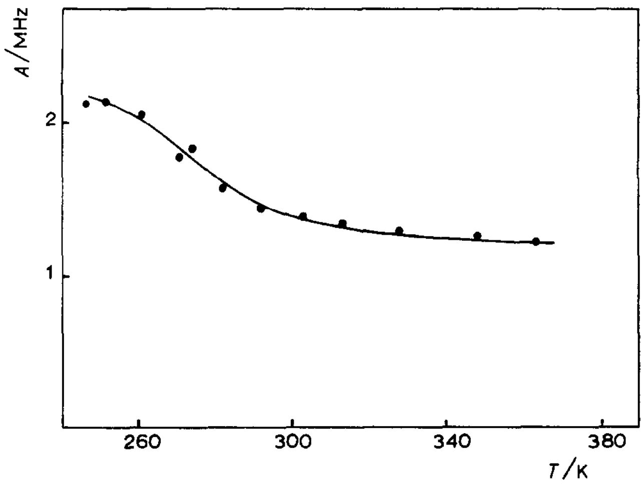

Fig. 4. Temperature dependence of the hyperfine coupling constants of the methyl protons.

[22*], and is probably due to a vibrational effect involving the motions of the chromium atom, the Cp★ ring and the three carbonyl groups [23]. In such a situation, the hyperfine splitting is given as

$$\bar{A} = \frac{A^0 + \sum_i A^i \exp(-\Delta E^i/kT)}{1 + \sum_i \exp(-\Delta E^i/kT)}$$

where $A^0$ is the splitting in the vibrational ground state, $A^i$ that in the $i$th vibrational state and $\Delta E^i$ is the energy difference between the ground and the $i$th states.

## *ESR studies*

The ESR spectrum $[Cp^{\star}Cr(CO)_3]_2$ in toluene shows a single line at $g_0 = 2.004$ ($\pm 0.001$). The line-width is 2.7 gauss at 243 K and increases to 3.2 gauss at 273 K. The spectrum is hardly detectable at ambient temperature but is readily observed at or below 273 K. The single-line spectrum most probably arises from the monomer $[Cp^{\star}Cr(CO)_3]$ which can also be trapped by rapidly freezing the solution in liquid nitrogen. The proximity of the $g$ value to the free-electron value is consistent with a non-degenerate ground state of the monomer. It is of interest to note that the ESR spectrum of $[CpCr(CO)_3]$ is not observed at the ambient temperature but it can be observed for $[Cp^{\star}Cr(CO)_3]$. This may be attributed to the greater extent of Jahn–Teller distortion in the permethyl case (the Cp★ ligand being a better electron donor) which makes observation of the ESR spectrum at room temperature possible.

In benzonitrile, the spectrum is observable even at the ambient temperature. Its $g$-value of 2.023 ($\pm 0.001$) is similar to that of $[CpCr(CO)_3]_2$ in the same solvent ($g = 2.025$) which has been attributed to the solvent-substituted monomeric species

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* A reference number with an asterisk indicates a note in the list of references.

[$CpCr(CO)_2(C_6H_5CN)$] [24]. The large difference in the *g*-values in the toluene and benzonitrile tends to confirm this suggestion.

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## References

1 P. Hackett, P.S. O'Neil, and A.R. Manning, J. Chem. Soc., Dalton Trans., (1974) 1626.
2 L.Y. Goh, M.J. D'Aniello Jr., S. Slater, E.L. Muetterties, I. Tavanaiepour, M.I. Chang, M.F. Fredrich, and V.W. Day, Inorg. Chem., 18 (1979) 192.
3 L.Y. Goh, W. Chen, and E. Sinn, Organometallics, 7 (1988) 2020.
4 N.A. Cooley, K.A. Watson, S. Fortier, and M.C. Baird, Organometallics, 5 (1986) 2563.
5 N.A. Cooley, P.T.F. MacConnachie, and M.C. Baird, Polyhedron, 7 (1988) 1965.
6 L.Y. Goh, R.C.S. Wong, C.K. Chu, and T.W. Hambley, J. Chem. Soc., Dalton Trans., (1989) 1951.
7 R.D. Adams, D.E. Collins, and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.
8 T. Madach and H. Vahrenkamp, Z. Naturforsch., (a) 33b (1978) 1301; (b) 34b (1979) 573.
9 J.T. Landrum and C.D. Hoff, J. Organomet Chem., 282 (1985) 215.
10 S.J. McLain, J. Am. Chem. Soc., 110 (1988) 643.
11 T.J. Jaeger and M.C. Baird, Organometallics, 7 (1988) 2074.
12 L.Y. Goh, T.W. Hambley, D.J. Darensbourg, and J. Reibenspies, J. Organomet. Chem., 381 (1990) 349.
13 R. Birdwhistell, P. Hackett, and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
14 D.S. Ginley, C.R. Bock, and M.S. Wrighton, Inorg. Chim. Acta, 23 (1977) 85.
15 J.H. Noggle, Physical Chemistry On a Microcomputer, Little, Brown and Co., Boston, 1985.
16 L.Y. Goh and Y.Y. Lim, unpublished results.
17 A.R. Cutler and M. Rosenblum, J. Organomet. Chem., 120 (1976) 87, and references therein.
18 E.L. Muetterties, B.A. Sosinsky, and K.I. Zamaraev, J. Am. Chem. Soc., 976 (1975) 5299.
19 D.A. Levy and L.E. Orgel, Mol. Phys., 3 (1961) 583.
20 M.P. Fritz, H.J. Keller, and K.E. Schwarzhans, Z. Naturforsch., 23B (1968) 298.
21 H.N. McConnell, J. Chem. Phys., 24 (1956) 764.
22 We thank one of the referees for pointing this out to us.
23 H.R. Falle and G.R. Luckhurst, Mol. Phys., 10 (1966) 597.
24 J.R. Morton, K.F. Preston, N.A. Cooley, M.C. Baird, P.J. Krusic, and S.J. McLain, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 3535.