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Determination of metal–metal bond energies in $[CpCr(CO)_2L]_2$ complexes [L = CO, $P(OMe)_3$] by NMR

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Abstract

A variable-temperature proton NMR study of the dimer–monomer equilibrium in the $[CpCr(CO)_2L]_2$ complexes [(**1**), L = CO; (**2**), L = $P(OMe)_3$] and application of van't Hoff's equation gave the following thermodynamic parameters: **1**, $\Delta H = 21.3 \pm 0.7$ kcal mol^{-1}, $\Delta S = 50.7 \pm 2.2$ cal mol^{-1} K^{-1} and $\Delta G_{300} = 6.1$ kcal mol $^{-1}$; **2**, $\Delta H = 18.8 \pm 0.4$ kcal mol^{-1}, $\Delta S = 69.0 \pm 1.5$ cal mol^{-1} K^{-1} and $\Delta G_{300} = -1.9$ kcal mol^{-1}.

Introduction

Despite the wide occurrence of the metal–metal bond in organometallic complexes of the transition elements [1] and the extensive studies on its reactivity [2] in the last couple of decades, data on metal–metal bond dissociation energies remain scarce. Undoubtedly this is partly due to the limitations of the available methods and the difficulty of obtaining reliable measurements therefrom. Until recently the methods employed have made use of gas phase studies, e.g. for $Mn_2(CO)_{10}$ and $Co_2(CO)_{10}$ [3] and mass spectrometry, e.g. for $M_2(CO)_{10}$ (M = Mn, Tc, Re and M_2 = MnRe) [3–5], and $Co_2(CO)_8$ [3,6]. Thermodynamic activation parameters for the homolytic dissociation of M–M bonded dimers

$$M\text{–}M \rightleftharpoons 2M\bullet \qquad (1)$$

have been measured via kinetic studies of (a) their substitution and decomposition reactions, e.g. for $[CpFe(CO)_2]_2$ [7] and (b) recombination of the radicals initiated by flash photolysis, e.g. for $Mn_2(CO)_{10}$ [8]. Where the equilibrium as represented by eq. 1 is well-established, more recent work has reported the use of ESR, e.g. for $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ [9]. We have successfully applied exchange average NMR data to detemine the bond dissociation energy of $[Cp^\star Cr(CO)_3]_2$ ($Cp^\star = \eta^5\text{-}C_5Me_5$) [10]. Because the dissociation enthalpy so obtained (18.3 ± 0.6 kcal mol^{-1}) was, contrary to expectation, higher than that reported by McLain for $[CpCr(CO)_3]_2$ (15.8 kcal mol^{-1}) [11], we now apply this method to the latter complex and also to $[CpCr(CO)_2\{P(OMe)_3\}]_2$ (**2**) to demonstrate the general applicability of the method

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to dimers which dissociate into paramagnetic monomeric species detectable in the ^{1}H NMR spectrum.

Experimental

All sample preparations were performed 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.

The complexes **1** and **2** were prepared as described [12,13]. All solvents, including toluene-d_8 were dried and distilled over sodium benzophenone before use.

Stock solutions of the complexes, ca. 20 m*M* for **1** and ca. 50 m*M* for **2**, were prepared in toluene-d_8, and aliquots appropriately diluted to provide samples of a range of concentrations (as given in Table 1) in 5 mm NMR tubes. The samples were sealed and ^{1}H NMR spectra initially recorded at 277 K for **1** and 200 K for **2**, followed by stepwise increases of probe temperature. The samples were continually monitored during measurements to check for decomposition.

Treatment of NMR data

As was shown earlier [10], the observed proton NMR isotropic shift, Δ_{obs}, of the cyclopentadienyl ring protons (defined as $\Delta_{obs} = \delta_{obs} - \delta(M_2)$ where δ_{obs} is the observed chemical shift and $\delta(M_2)$ is the chemical shift of the dimer) is related to K_{dis}, the dissociation constant, Δ, the isotropic shift of the ring protons and $[M_2{}^\circ]$, the intial concentration of the dimer by eq. 2:

$$\Delta_{obs} = \frac{2\Delta}{1.5 + \left(0.25 + 4[M_2{}^\circ]K_{dis}^{-1}\right)^{1/2}} \qquad (2)$$

Taking $\delta(M_2)$ values for **1** and **2** as 3.97 and 4.78 ppm (measured at 178 K) respectively, the equation is treated by a Simplex program to obtain K_{dis} and Δ.

Table 1

Comparison between the observed and calculated isotropic shifts in toluene-d_8 based on the best-fit parameters:

$[CpCr(CO)_3]_2$			$[CpCr(CO)_2\{P(OMe)_3\}]_2$		
Concentration/m*M*	Δ_{obs}/ppm	Δ_{cal}/ppm	Concentration/m*M*	Δ_{obs}/ppm	Δ_{cal}/ppm
0.511	−8.03	−8.03	2.27	−14.84	−15.06
0.729	−7.06	−6.95	3.02	−14.77	−14.83
0.96	−5.98	−6.18	8.25	−13.76	−13.59
1.058	−6.11	−5.93	16.53	−12.84	−12.32
1.860	−4.45	−4.64	22.78	−11.68	−11.64
6.495	−2.59	−2.62	25.87	−11.32	−11.36
8.74	−2.29	−2.27	40.65	−10.27	−10.31
13.08	−1.94	−1.88	45.09	−9.79	−10.06
17.39	−1.74	−1.64	54.32	−9.46	−9.61
$\Delta = -31.8$ ppm; $K_{dis} = 4.98 \times 10^{-5}$ $T = 303$ K			$\Delta = -15.9$ ppm; $K_{dis} = 7.15 \times 10^{-2}$ $T = 253.1$ K		

The initial concentration of the dimer was corrected for solvent density changes at various temperatures.

Results and discussion

The temperature-dependent proton NMR spectra of solutions in toluene-d_8 of **1** (17.4 m*M*) and **2** (37.9 m*M*) are illustrated in Fig. 1. It is observed that in both cases, the Cp resonance occurs as a sharp singlet at low temperatures (< 277 K for **1** and < 200 K for **2**). The limiting value of the chemical shift of this sharp signal at low temperature is attributable to the diamagnetic dimeric species $[CpCr(CO)_2L_2]_2$.

$$[CpCr(CO)_2L]_2 \rightleftharpoons 2CpCr(CO)_2L\cdot \qquad (3)$$

(**1**: L = CO; **2**: L = P(OMe)$_3$)

As the temperature is raised this peak shifts to a lower field with a reversal observed for **2** at 283 K, but not observed for **1** up to 348 K. For **1** line-width broadening occurs with rise of temperature, as well as decrease of concentration, as expected from the accuring paramagnetic monomeric species produced in the dissociation equilibrium 3. For example, the line-width ($\nu_{1/2}$) of the 17.4 m*M* solution of (**1**) (δ(Cp) 4.68) at 277 K broadens from 6 to 89 Hz at 348 K and to 32 Hz on dilution to 3.88 m*M*. For **2**, at a given temperature ($\leqslant 273$ K), dilution has a

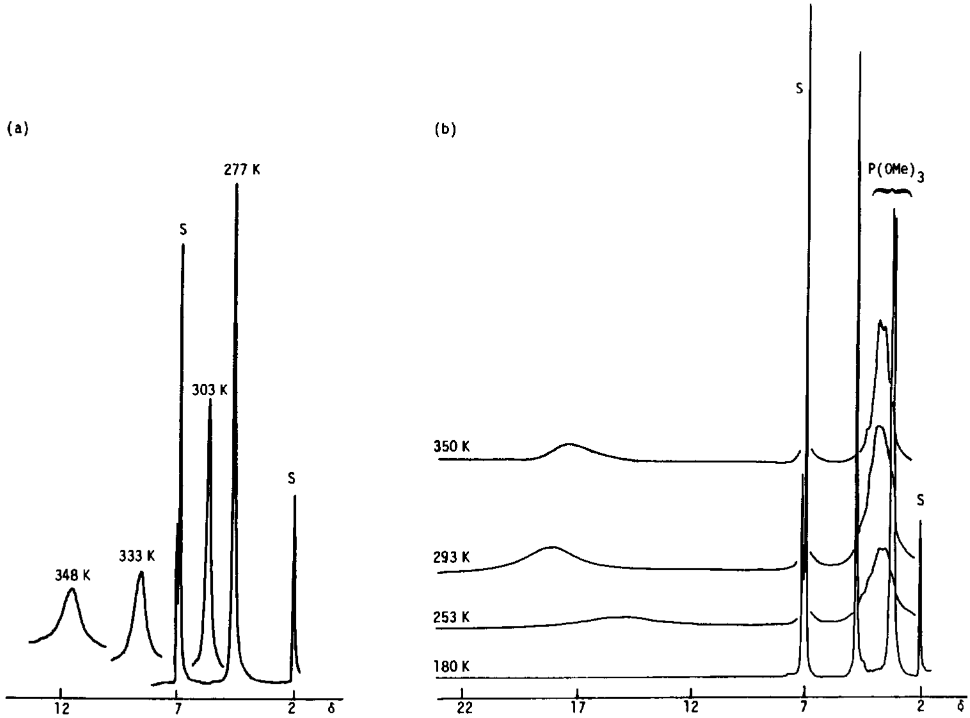

Fig. 1. Temperature-dependent proton NMR spectra in toluene-d_8, showing (a) the Cp resonance of a 17.4 m*M* solution of $[CpCr(CO)_3]_2$ (**1**) and (b) the Cp and CH_3 resonances of a 37.9 m*M* solution of $[CpCr(CO)_2\{P(OMe)_3\}]_2$ (**2**). S, solvent peaks in toluene-d_8.

Table 2

Dissociation constants and proton isotropic shifts [a] at various temperatures

$[CpCr(CO)_3]_2$			$[CpCr(CO)_2\{P(OMe)_3\}]_2$		
T/K	K_{dis}/M	Δ/ppm	T/K	K_{dis}/M	Δ/ppm
298	2.78×10^{-5}	-34.1	242.5	1.37×10^{-2}	-18.6
303	4.98×10^{-5}	-31.8	248	3.00×10^{-2}	-17.3
310.5	1.08×10^{-4}	-28.4	253.1	7.15×10^{-2}	-15.9
318	2.25×10^{-4}	-25.6	258	1.41×10^{-1}	-15.3
333	1.27×10^{-3}	-20.2	263.3	2.92×10^{-1}	-14.8

[a] Error in K_{dis} is $\leqslant 10\%$ while that of Δ is $\leqslant 5\%$. Negative sign indicates downfield shift.

similar effect on the line-width as **1** but the temperature effect is different. The line-width of the 37.9 mM solution broadens from 5 Hz at 179 K to 320 Hz at 263 K but decreases thereafter when the temperature is raised above 278 K. The reason for this reversal in line-width for **2** most probably lies in its large dissociation constant (estimated to be approximately 1.9 at 278 K from the data given in Table 2 discussed below), resulting in an almost complete conversion to the monomer radical at 278 K. Any further increase in temperature will therefore only have a negligible effect on the radical concentration, but will decrease the viscosity of the solvent with a concomitant decrease in line-width. In addition, the increase in the rate of exchange at the higher temperature will also decrease the line-width. The methyl resonance of the phosphite ligand in the 37.9 mM solution of **2** is observed as a sharp resolved doublet (δ 3.25, $J = 11$ Hz) at 179 K broadening to an unresolved peak (δ 3.72, $\nu_{1/2}$ ca. 120 Hz) at 263 K, above which line-width decreases like the Cp resonance.

At a given temperature, the observed increase in the isotropic shift with a decrease in concentration is a reflection of the dissociation equilibrium 3. The fit of the concentration dependent shifts to the equilibrium using eq. 2 is good at all the temperatures reported here. A comparison of Δ_{obs} with the calculated isotropic shift based on the best-fit equation at a given temperature is given in Table 1 and the calculated K_{dis} and the isotropic shifts for the various temperatures are summarized in Table 2. A striking feature is that the K_{dis} value of **2** is much larger than that of **1**. This large difference necessitates the use of very different ranges of temperatures for their measurements in order to cover the largest possible range of the dissociation equilibrium for a meaningful estimate of K_{dis}.

The thermodynamic parameters for the dissociation of **1** and **2** in toluene which are obtained from the application of van't Hoff equation are listed in Table 3. It is to be noted that the values of ΔH (21.3 ± 0.7 kcal mol^{-1}) and ΔS (50.7 ± 2.2 cal

Table 3

Thermodynamic parameters for the homolytic dissociation equilibria and the Cr–Cr bond distances

	ΔH/kcal mol^{-1}	ΔS/cal mol^{-1} K^{-1}	ΔG_{300}/kcal mol^{-1}	d(Cr–Cr)/Å
$[CpCr(CO)_3]_2$	21.3 ± 0.7	50.7 ± 2.2	6.1	3.281 [a]
$[CpCr(CO)_2\{P(OMe)_3\}]_2$	18.8 ± 0.4	69.0 ± 1.5	-1.9	3.343 [b]
$[Cp^{\star}Cr(CO)_3]_2$	18.3 ± 0.6	54.8 ± 2.2	1.9	3.310 [c,d]

[a] Ref. 15. [b] Ref. 13. [c] T.J. Jaeger and M.C. Baird, *Organometallics*, 7 (1988) 2074. [d] L.Y. Goh, T.W. Hambley, D.J. Darensbourg, J. Reibenspies, *J. Organomet. Chem.*, 381 (1990) 349.

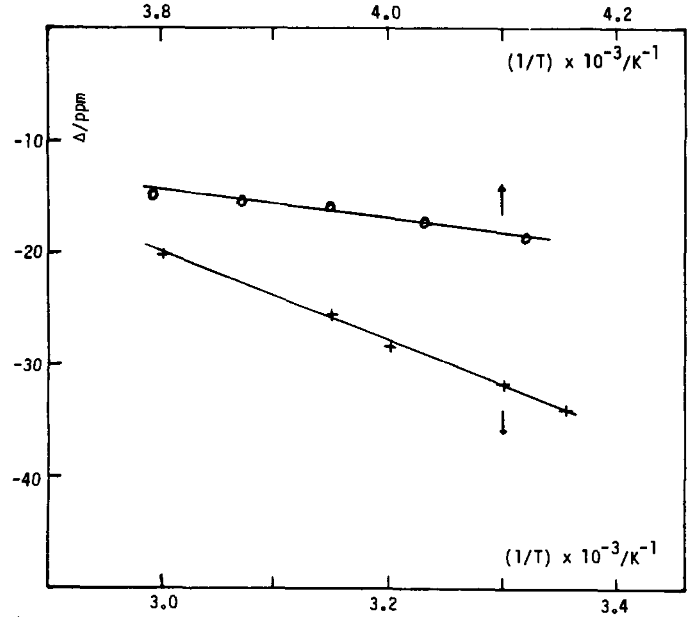

Fig. 2. Proton isotropic shifts of the Cp protons versus the reciprocal of temperature. +, $[CpCr(CO)_3]_2$ (1) and o, $[CpCr(CO)_2\{P(OMe)_3\}]_2$ (2).

mol^{-1} K^{-1}) obtained for **1** differ considerably from those reported in the literature, i.e. 15.8 kcal mol^{-1} and 37.1 cal mol^{-1} K^{-1} respectively [11]. However, our results for the three complexes, viz. **1**, **2** and $[Cp^{\star}Cr(CO)_3]_2$ are self-consistent and give a logical correlation between ΔH values versus M–M bond length and steric interaction in the dimers. Within experimental error, the ΔH value of the trimethyl phosphite derivative is similar to that of $[Cp^{\star}Cr(CO)_3]_2$ and the smaller ΔG value of the former is attributable to the larger entropy change as it dissociates in solution.

The isotropic shifts versus $1/T$ plot (Fig. 2) is linear within the range of temperature investigated. In both cases, a positive intercept is obtained, indicating behaviour according to the Curie-Weiss law. As was discussed in our earlier paper [10], the main contribution to the isotropic shift comes from the contact term which originates from the delocalization of the unpaired electron from chromium onto the ligand orbital(s). The larger (absolute) isotropic shift of the monomer radical and the smaller δ(Cp) value observed in the diamagnetic dimer **1** reflect the stronger π-acceptor property of the carbonyl ligand when compared to trimethyl phosphite [14]. The carbonyl ligand reduces the build-up of negative charge on the metal to a greater extent resulting in a more efficient overlap of the Cp MO's with the appropriate metal *d* orbitals. Consonant with this is the observed shorter average Cr–C(Cp) bond distance (2.195 Å) in **1** [15] compared with that in **2** (2.204 Å) [13].

Acknowledgements

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References

1 D.A. Roberts and G.L. Geoffroy, in G.Wilkinson, F.G.A. Stone and E.W. Abel (Eds.) Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, Oxford, 1982, Chap. 40, and refs. therein.
2 M.H. Chisholm (Ed.), Reactivity of Metal–Metal Bonds, ACS, Symp. Ser. No. 155, American Chemical Society, Washington, DC, 1981.
3 D.R. Bidinosti and N.S. McIntyre, Can. J. Chem., 48 (1970) 593.
4 D.R. Bidinosti and N.S. McIntyre, J. Chem. Soc., Chem. Commun., (1966) 555.
5 H.J. Svec and G.A. Junk, J. Am. Chem. Soc., 89 (1967) 2836; idem, J. Chem. Soc., (A), 1970, 2102.
6 D.R. Bidinosti and N.S. McIntyre, J. Chem. Soc., Chem. Commun., (1967) 1.
7 A.R. Cutler and M. Rosenblum, J. Organomet. Chem., 120 (1976) 87.
8 J.L. Hughey, IV, C.P. Anderson, and T.J. Meyer, J. Organomet. Chem., 125 (1977) C49.
9 E.L. Muetterties, B.A. Sosinsky and K.I. Zamaraev, J. Am. Chem. Soc., 97 (1975) 5299.
10 L.Y. Goh, S.K. Khoo and Y.Y. Lim, J. Organomet. Chem., 399 (1990) 115.
11 S.J. McLain, J. Am. Chem. Soc., 110 (1988) 643.
12 R. Birdwhistell, P. Hackett and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
13 L.Y. Goh, M.J. D'Aniello, Jr., S. Slater, E.L. Muetterties, I. Travanaiepour, M.I. Chang, M.F. Fredrich and V.W. Day, Inorg. Chem., 18 (1979) 192.
14 J.E. Huheey, Inorganic Chemistry, 2nd ed., Harper & Row, London, 1978, p. 406.
15 R.D. Adams, D.E. Colins, and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.