for the other pairs of bands that are observed to coalesce.

C. Band Widths, Intermolecular Effects, and Other Considerations. There remains a time-dependent perturbation, the H_1 of eq 6. The effect of this perturbation on the bands can be calculated approximately using the Redfield theory.[6] The theory requires the time correlation functions of the H_1, and in simple cases it gives the widths as a mean-squared amplitude of H_1 times a correlation time τ_c. It is this time that enters into the calculation. τ_c is on the order of 1 to 100 ps and is mostly an intrawell time rather than a time for motion between wells.[6,5] In general, the theory predicts that most simple bands will broaden as the temperature increases, although, as in NMR, it is possible for bands to narrow as the temperature increases. The time τ_c can be very short (picoseconds), corresponding to very fast rates. However, these rates are for intrawell relaxation and, for this type of process, such a short time is thought to be the correct order of magnitude.

In comparing our results to the experiments, it is important to remember that a solid matrix can contribute to the static splittings. A liquid solvent and a solid matrix can each contribute to the width. The time dependence of fluctuations of the solvent will vary with temperature. The effects of the matrix on the spectrum have been illustrated in the equations of ref 6 and evaluated to some extent.

When bands coalesce to form just one band and then apparently narrow as the temperature increases, as observed[1] for the spectrum of isotopically pure **1**, it is difficult to separate the effect of a continuing diminution of the splitting from the effect of the changing width of each component.

III. Conclusions

We have presented a model to account for the observed collapse of the carbonyl stretching bands of **1** and similar compounds. The collapse is due to the increasing amplitude of torsion of the carbonyl groups as the temperature increases. The motion of each carbonyl is almost entirely in its own well and therefore the rate of reaction or change of conformation does not enter our description. There are two types of coalescing bands observed. In the first the bands are split by interaction of the carbonyl groups with the framework. In the second, there is both an isotopic and an interaction effect. The collapse of both types is accounted for. An important point is that the change of the vibrational Hamiltonian from case to case is essentially determined by symmetry arguments. The tricarbonyls may rotate from potential well to well, but our theory does not require an extremely rapid rate of motion. If extreme rates do occur, an occurrence we think unlikely, they would contribute to the observed band collapse in addition to the one-well mechanism.[5]

More information could in principle be obtained from ab initio calculations of the vibrations of **1** as a function of torsional angle.[12] We expect such calculations to show that the stretching frequencies change steeply over the range of motion of one well in a manner consistent with our interpretation of the experimental results. It is possible that the solvent or matrix effects will have to be separated from the intramolecular effects to make this comparison quantitative. The referee suggested a further possibility—that the changes in the bending bands, which will qualitatively follow those of the stretches, will, with the help of the ab initio calculations, distinguish between the mechanisms for the exchange of the carbonyls.

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An Investigation of the Homolytic Dissociation of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and Related Complexes. The Role of Ligand Substitution on the Solution Thermochemistry of Metal–Metal Bond Cleavage

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Abstract: Thermodynamic parameters for dissociation of the metal–metal bonded dimers $[\eta^5\text{-}C_5R_5Cr(CO)_2(L)]_2$ (R = H, L = CO, P(OMe)$_3$; R = Me, L = CO) have been studied by several techniques including variable-temperature FTIR spectroscopy, magnetic susceptibility, NMR spectroscopy, and solution calorimetry. Values for the Cr–Cr bond strength are in the range 11–15 kcal/mol. Results obtained via NMR techniques in this system disagree with all other results probably due to a multiplicity of populated states for the radical monomers. For the radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PR_3)\}$ (R = Ph, Et), no sign of dimer formation is found even at −80 °C, indicating that the Cr–Cr bond strength is <8 kcal/mol for these compounds. Calorimetric measurements of the heats of reaction of Hg and $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ forming $Hg[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ have been measured for R = H, Me and indicate average Hg–Cr bond strengths of 20.3 and 20.7 kcal/mol, respectively. Synthetic and spectroscopic details are described for $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ as well as its structure as determined by X-ray crystallography. The Cr–Cr distance, 3.3107 (7) Å, is longer than that reported for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$; however, the increased tendency to form radicals for this complex is due more to entropic than enthalpic factors.

Introduction

In spite of the importance of metal–metal bonded complexes in organometallic chemistry, there are relatively few reliable metal–metal bond dissociation energies available for complexes in solution. There are several techniques available for obtaining metal–metal bond strength estimates. These are illustrated by the well-studied complex manganese carbonyl:

$$Mn_2(CO)_{10} \rightarrow 2\{Mn(CO)_5\} \qquad (1)$$

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Early kinetic and thermodynamic work yielded a wide range of values of the Mn–Mn bond strength, from 19 to 41 kcal/mol,[1] while recent ion cyclotron resonance experiments yielded a gas-phase value of 41 ± 9 kcal/mol[2] and solution-phase studies via photoacoustic calorimetry a value of 38 ± 5 kcal/mol.[3] Electrochemical data have been used in a closed cycle to yield $\Delta G^\circ = 25 \pm 1$ kcal/mol for the dissociation.[4]

Direct measurement of metal–metal bond strengths in solution is probably restricted to the range 10–40 kcal/mol. If the bond strength is less than 10 kcal/mol, entropic factors will limit its formation,[5] while if the metal–metal bond is significantly stronger than about 40 kcal/mol, it can be expected that ligand dissociation will become the dominant reaction channel. For example in $Mn_2(CO)_{10}$, the Mn–Mn bond is strong enough that CO dissociation, possibly yielding a solvated intermediate, is a competitive reaction with metal–metal bond cleavage:

$$Mn_2(CO)_{10} \rightarrow CO + Mn_2(CO)_9 + S \rightleftharpoons Mn_2(CO)_9(S) \quad (2)$$

One tactic to increase the observed rate of cleavage of the metal–metal bond is to utilize ligand substitution. For example, kinetic studies[6] of reductive elimination in the manganese carbonyl system indicate that substitution of carbon monoxide by phosphine results in observation of radical pathways:

$$[Mn(CO)_4(P(p\text{-}CH_3OC_6H_4)_3)]_2 \rightleftharpoons 2\{Mn(CO)_4(P(p\text{-}CH_3OC_6H_4)_3)_2\} \quad (3)$$

That such increased dissociation is due strictly to *enthalpies* of bond dissociation—the usual measure of "bond-strength"—has not been clearly demonstrated. The influence of steric strain on $[Rh(porphyrin)]_2$ complexes has been utilized by Wayland and co-workers[7] in generating reactive radical species in solution.

The best-studied system on metal–metal bond strengths as a function of ligand substitution appears to be the work of Muetterties and co-workers[8a] on the series of complexes $[\eta^3\text{-}C_3H_5Fe(CO)_2(L)]_2$. Using ESR spectroscopy, thermodynamic parameters for Fe–Fe bond dissociation were studied in several different solvents. Representative data in pentane solution (where disproportionation to ionic complexes is unlikely[8b]) are shown in eq 4. Surprisingly, entropies of dissociation appear to be responsible for the greater degree of dissociation of the phosphine-substituted complexes.

$$[\eta^3\text{-}C_3H_5Fe(CO)_2(L)]_2 \underset{\text{pentane}}{\rightleftharpoons} 2\{(\eta^3\text{-}C_3H_5Fe(CO)_2(L)\} \quad (4)$$

L	ΔH, kcal/mol	ΔS, cal/(mol deg)
CO	13.5	37
PMe_2Ph	13.5	46
$P(OMe)_3$	14	46.5

There has been considerable recent interest in stable 17 e^- organometallic radicals,[9] in particular the persistent chromium-centered radicals $\{\eta^5\text{-}C_5R_5Cr(CO)_2(L)\}$ (R = H, Me; L = CO, tertiary phosphines).[10] These complexes can exist as either dimers or radical monomers in the solid state, depending on the specific ligand set.[10,11] They fragment in solution to yield monomer–dimer mixtures. These complexes present a good opportunity to investigate the role of ligand substitution on metal–metal bond strengths on a quantitative basis.

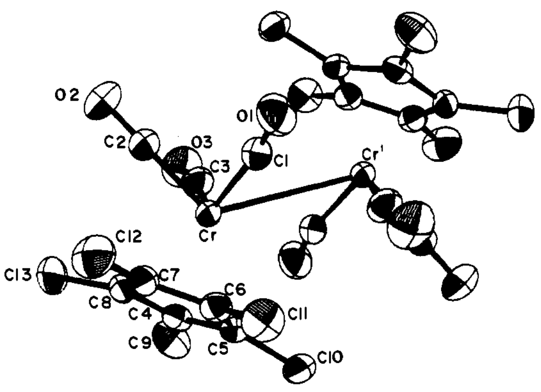

Figure 1. X-ray crystal structure of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. Structural parameters are given in Tables I and II.

McLain[12] has reported equilibrium data for the parent complex shown in eq 5. While our work was in progress, Goh and co-workers[13] also reported data obtained via NMR studies for this and several related complexes. Their data are in apparent disagreement with McLain's results. In view of the difficulties in making these measurements we had separately investigated dimerization of $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ by FTIR spectroscopy, solution calorimetry, magnetic susceptibility, and also NMR techniques similar to those used by Goh and co-workers. We now present a comprehensive account of the synthesis of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and the thermochemistry of monomer–dimer equilibria in the chromium system. Spectroscopic and magnetic properties and the X-ray crystal structure of one polymorph of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ are also presented as well as estimates of the heteronuclear metal–metal bond strength in the complexes $Hg[Cr(CO)_3(C_5R_5)]_2$.

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5H_5Cr(CO)_3\} \quad (5)$$

	ΔH, kcal/mol	ΔS, cal/(mol deg)
toluene	15.8±0.4	37.1±1.4
THF	14.8±0.4	34.3±1.3

Experimental Section

Syntheses were carried out utilizing normal Schlenk techniques and dried, deaerated solvents. Infrared spectra were run on a Bruker IFS-85

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or a Perkin-Elmer 1850 FTIR spectrometer and NMR spectra on a Bruker AM-400 NMR spectrometer; the crystal structure was determined on an Enraf-Nonius CAD-4 diffractometer. Calorimetric measurements were made using a Setaram C-80 Calvet calorimeter or a Guild Isoperibol calorimeter housed in a Vacuum/Atmosphere glovebox and described in detail elsewhere.[14]

Synthesis of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. A solution of 10 g (0.045 mol) of $Cr(CO)_6$ in 400 mL of acetonitrile was refluxed for 48 h. The resulting bright yellow solution of $Cr(CO)_3(MeCN)_3$ was filtered, the solvent was removed under reduced pressure, and the dry, yellow residue was suspended in 200 mL of ethanol. To this was added 8.0 mL (0.051 mol) of pentamethylcyclopentadiene, and the mixture was stirred at room temperature and in the dark for 36 h, turning a dark green/black color. The solvent was then removed under reduced pressure, the dried residue was dissolved in 150 mL of hexanes, and the solution of $\eta^5\text{-}C_5Me_5Cr(CO)_3H$ was filtered and treated with 14.0 mL (0.14 mol) of isoprene. On stirring for several hours at room temperature in the dark, followed by cooling overnight at 243 K, copious amounts of black crystals of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ precipitated and were filtered and recrystallized from 1:4 toluene–hexanes to give 8.5 g of product (yield 70%). The compound may also be purified by sublimination at 50 °C.

Crystal Structure of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. A black crystal, 0.20 × 0.26 × 0.26 mm, was mounted inside a glass capillary and used for the collection of intensity data on an Enraf-Nonius CAD-4 diffractometer. The unit cell parameters were obtained by a least-squares analysis of 25 centered reflections in the range $13.90 < 2\theta < 26.82$. The data were collected by the θ–2θ scan technique, with variable scanning rate, using monochromated Mo Kα radiation. A total of 3684 unique reflections were measured in the range $1.0 < 2\theta < 50$, of which 1989 were considered observed, i.e. $I > 3\sigma I$. Three standard reflections were measured every 7200 s of radiation time and showed no significant variation during the course of data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods using the program MULTAN80.[15] Difference Fourier map calculations revealed the positions of all the hydrogen atoms. These were assigned temperature factors equal in magnitude to the equivalent isotropic values of their parent atoms and were included in the calculations, but not refined. Full-matrix least-squares refinement minimizing the function $\sum w||F_o| - |F_c||^2$, where $w = 1/\sigma^2(|F_o|)$, resulted in $R = 0.039$ and $R_w = 0.053$. The esd of an observation of unit weight was 1.846, the maximum shift to error ratio was 0.00, and the final difference Fourier synthesis was essentially featureless. The scattering factors used were those of Cromer and Waber.[16] The anomalous dispersion coefficients were taken from Cromer.[16] All calculations were performed on a PDP 11/23 computer using the structure determination package of Enraf Nonius, SDP.[17] The program ORTEP[18] was used for the preparation of Figure 1. The title compound crystallizes in space group $P2_1/n$ with $a = 15.263$ (5) Å, $b = 8.970$ (6) Å, $c = 9.320$ (2) Å, $\beta = 98.87$ (2)°, $V = 1269.26$ Å^3; $Z = 4$, $D_{calc} = 1.419$ Mg m^{-3}, $\mu = 8.715$ cm^{-1}.

Equilibrium Constant Measurements Utilizing IR Spectroscopy. Equilibrium measurements were made in a specially configured cell purchased from Harrick Scientific, Ossining, NY. A high-pressure jacketed cell with 5 mm thick Ge windows was attached via T fittings to a 40 mL stainless steel reaction vessel such that rotation of the cell could be used to fill it with fresh sample from the reservoir. Teflon spacers, 0.1 to 0.75 mm in thickness, were used to separate the windows and chosen to give good absorbance values for the stock solutions of the dimers which were in the range 1–5 mM. The top of the 40-mL vessel was fitted with a T fitting which included a feed through precision thermistor thermometer (Omega Engineering) and high-pressure valve. The reaction vessel was wrapped with 1/4 copper tubing and the entire apparatus was wrapped with glass wool. Thermostated N_2 gas, obtained by controlled heating of boil-off of liquid N_2, was passed through the jacketed cell and then the copper tubing around the vessel. The entire apparatus was housed in a styrofoam insulated container located in the sample beam of the Perkin-Elmer 1850 FTIR spectrometer. Precision thermistors from Omega Engineering were calibrated with ice–water and dry ice–acetone. Resistances were in agreement with the tolerances listed. In addition to the thermistor in direct contact with the solution, two other matched thermistors were used—one positioned on the outside of the cell and one in the middle of the styrofoam box. Temperatures were measured at all three points and at equilibrations did not differ by more than 1–2 deg even at −80 °C. The temperature of the thermistor in direct contact with the solution was used for temperature in the cell. The infrared beam to the windows was blocked except during measurements. The constant outflow of N_2 gas prevented condensation of water on the cell.

To load the cell, the entire assembly was taken into the glovebox and filled with the solution to be studied. The cell was then loaded into the spectrometer. The use of the Ge windows was important since some of the radicals were observed to react slowly with CaF_2. In addition, the thick metal windows serve to stabilize the temperature and speed up equilibration.

Since the spectra of the solvents change with temperature, it was necessary to collect solvent spectra for computer subtraction at each temperature. Experiments with a blank cell showed that the path length (determined by interference pattern) changed by less than 5% over an 80-deg range. All equilibria studied were fully reversible as determined by temperature cycling. The solutions of the radicals were stable for days with no sign of decomposition under these conditions.

Enthalpy of Solution and Dissociation of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in THF. Samples of the green-black crystalline complex $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ (0.1–0.2 g) were sealed in glass ampules. The Guild calorimeter was loaded with 500 mL of THF (distilled under argon from Na^+benzophenone$^-$ into flame-dried glassware) and allowed to equilibrate at 25 °C. Electrical calibrations with a precision resistor were made before and after breaking the ampule. The enthalpy of solution, +18.7 ± 0.9 kcal/mole, was the average of eight separate measurements. This value was found to be in agreement with the value measured indirectly and described later. Infrared spectra run at the end of the calorimetric runs showed that, at these dilutions, there were no detectable peaks due to the dimer.

Enthalpy of Reaction of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and Hg. The enthalpy of reaction was measured between the solid complex $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and liquid Hg/THF at 40 °C in the Calvet calorimeter. The Calvet cell was taken into the glovebox and loaded with 0.05 g of the dimeric complex in the sample chamber. The sample holder was closed and sealed with 1.5 mL of redistilled Hg. After adding 3.5 mL of freshly distilled THF, the cell was closed and taken out of the glovebox and loaded in the calorimeter. After equilibration—about 2 h—the reaction was initiated by inverting the calorimeter. Continuous rotation of the calorimeter was done throughout the reaction to ensure good mixing. Blank experiments were made to correct for any heat of mixing and rotation. The heat of reaction, −7.1 ± 0.2 kcal/mol, is the average of six experiments. Conversion to $Hg[Cr(CO)_3C_5Me_5]_2$ was found to be complete by examination of the FTIR spectrum.

In a second type of experiment, a dilute THF solution of the $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ radical was reacted with Hg/THF. The heat of reaction per mole of $Hg[Cr(CO)_3C_5Me_5]_2$ produced was −26.6 ± 1.0 kcal/mol, based on five measurements.

Results

Synthesis of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. The dimer can be prepared in high yield as shown in eq 6–8. As described in the experimental

$$Cr(CO)_6 + 3MeCN \rightarrow Cr(CO)_3(MeCN)_3 + 3CO \quad (6)$$

$$Cr(CO)_3(MeCN)_3 + C_5Me_5H \rightarrow \eta^5\text{-}C_5Me_5Cr(CO)_3H + 3MeCN \quad (7)$$

$$2\{\eta^5\text{-}C_5Me_5Cr(CO)_3H\} + \text{isoprene} \rightarrow [\eta^5\text{-}C_5Me_5Cr(CO)_3]_2 + \text{methylbutene} \quad (8)$$

section, the green-black crystalline dimer can be prepared in overall yields of up to 70% (based on $Cr(CO)_6$). The reaction of the hydride with isoprene, eq 8, is of the type reported previously for reactions of conjugated dienes with the hydrides $\eta^5\text{-}C_5H_5M(CO)_3H$ (M = Cr, Mo, W), and presumably involves a radical pair mechanism.[19]

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Table I. Positional Parameters of the Non-Hydrogen Atoms of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$

atom	x	y	z	B, Å²
Cr	0.39641 (4)	0.50342 (8)	0.03808 (7)	2.322 (9)
O(1)	0.3916 (3)	0.4775 (5)	−0.2826 (4)	4.79 (9)
O(2)	0.2796 (3)	0.2449 (4)	−0.0379 (4)	4.86 (9)
O(3)	0.4694 (3)	0.2609 (4)	0.2341 (5)	5.5 (1)
C(1)	0.4045 (3)	0.4870 (5)	−0.1593 (5)	3.36 (8)
C(2)	0.3248 (3)	0.3450 (5)	−0.0089 (5)	3.01 (9)
C(3)	0.4498 (3)	0.3556 (5)	0.1562 (6)	3.5 (1)
C(4)	0.1185 (3)	0.1407 (5)	0.2664 (4)	2.66 (8)
C(5)	0.0903 (3)	0.2377 (5)	0.3726 (4)	2.40 (7)
C(6)	0.1548 (3)	0.2348 (5)	0.4954 (5)	2.63 (8)
C(7)	0.2225 (3)	0.1373 (5)	0.4641 (5)	2.83 (8)
C(8)	0.2014 (3)	0.0782 (5)	0.3232 (5)	2.84 (8)
C(9)	0.0784 (4)	0.1246 (6)	0.1124 (5)	4.2 (1)
C(10)	0.0134 (3)	0.3416 (5)	0.3518 (6)	3.6 (1)
C(11)	0.1570 (4)	0.3370 (6)	0.6232 (5)	4.2 (1)
C(12)	0.3092 (3)	0.1156 (7)	0.5579 (7)	4.8 (1)
C(13)	0.2585 (3)	−0.0199 (6)	0.2397 (6)	4.7 (1)

Table II. Bond Distances (Å) and Angles (deg) for $[C_5Me_5Cr(CO)_3]_2$

Distances

Cr–Cr′	3.311 (1)	Cr–C(7)	2.177 (2)	C(5)–C(6)	1.410 (3)
Cr–C(1)	1.866 (3)	Cr–C(8)	2.182 (2)	C(5)–C(10)	1.496 (3)
Cr–C(2)	1.816 (3)	C(1)–O(1)	1.137 (3)	C(6)–C(7)	1.418 (3)
Cr–C(3)	1.862 (3)	C(2)–O(2)	1.157 (3)	C(6)–C(11)	1.500 (3)
Cr–C(4)	2.236 (2)	C(3)–O(3)	1.145 (3)	C(7)–C(8)	1.410 (3)
Cr–C(5)	2.260 (2)	C(4)–C(5)	1.428 (3)	C(7)–C(12)	1.508 (3)
Cr–C(6)	2.226 (2)	C(4)–C(8)	1.429 (3)	C(8)–C(13)	1.485 (4)
		C(4)–C(9)	1.479 (3)		

Angles

Cr–C(1)–O(1)	166.8 (2)	C(6)–C(5)–C(10)	125.9 (2)
Cr–C(2)–O(2)	179.6 (2)	C(5)–C(6)–C(7)	108.1 (2)
Cr–C(3)–O(3)	169.0 (3)	C(5)–C(6)–C(11)	125.7 (2)
C(1)–Cr–C(2)	78.5 (1)	C(7)–C(6)–C(11)	125.5 (2)
C(1)–Cr–C(3)	117.7 (1)	C(6)–C(7)–C(8)	108.3 (2)
C(2)–Cr–C(3)	78.5 (1)	C(6)–C(7)–C(12)	124.4 (2)
C(5)–C(4)–C(8)	107.1 (2)	C(8)–C(7)–C(12)	126.9 (3)
C(5)–C(4)–C(9)	127.3 (2)	C(4)–C(8)–C(7)	108.2 (2)
C(8)–C(4)–C(9)	125.0 (2)	C(4)–C(8)–C(13)	125.3 (3)
C(4)–C(5)–C(6)	108.3 (2)	C(7)–C(8)–C(13)	126.1 (3)
C(4)–C(5)–C(10)	125.1 (2)		

As reported previously,[10f] solutions of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in hydrocarbon solvents are red-brown and highly air sensitive, in contrast to the air stable, very deep green-black crystals of the complex. Cooling a solution results in reversible color changes consistent with dissociation of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ to $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$, which is investigated quantitatively as described later.

Structure of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. An ORTEP view of the molecular structure of the $P2_1/n$ polymorph of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ is shown in Figure 1; the atomic coordinates are listed in Table I and the bond distances and angles in Table II. The two identical halves of the molecule are related by a center of symmetry and are joined by an exceptionally long Cr–Cr bond of length 3.3107 (7) Å, very similar to the 3.310 (1)-Å value found for a $P2_1/c$ polymorph.[14a] Both distances are considerably longer than the Cr–Cr bond length of the highly strained chromium compound $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, for which a Cr–Cr distance of 3.281 (1) Å has been reported,[11b] the Mo–Mo bond lengths of the $P2_1/c$ and $P2_1/n$ isomorphs of $[\eta^5\text{-}C_5Me_5Mo(CO)_3]_2$ (3.278 (14), 3.281 (1) Å, respectively[20a,b]), and a $P2_1/n$ isomorph of $[\eta^5\text{-}C_5Me_5W(CO)_3]_2$, for which a W–W bond length of 3.288 (1) Å has been reported.[20c] The carbonyl groups cis to the Cr–Cr bond are also distinctly nonlinear (Cr–C(1)–O(1) = 166.8 (2)°, Cr–C(3)–O(3) = 169.0 (3)°), being bent away from the other metal atom more, in fact, than the corresponding carbonyl groups of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ (172.0 (2), 172.9 (2)°) or the isomorphs of the molybdenum and tungsten analogues (168.2–170.6°); the C(1)–Cr′ distance is 3.134 (3) Å. Thus our original notion of greater steric crowding for $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ seems valid.

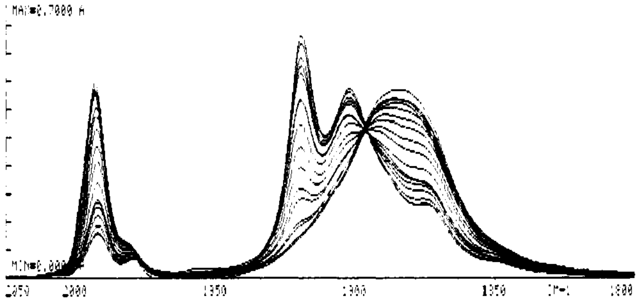

Figure 2. Infrared spectra at different temperatures, +35 to −35 °C, of the complex $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in THF. Peaks at 1919, 1902, and 1876 cm^{-1} are due to $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and peaks at 1994 and 1885 cm^{-1} are due to $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$.

Table III. Equilibrium Constants as a Function of Temperature for the Reaction

$$[C_5Me_5Cr(CO)_3]_2 \xrightarrow{THF} 2\{C_5Me_5Cr(CO)_3\}$$

T, °C	k_{eq}, M × 10⁻³	T, °C	K_{eq}, M × 10⁻³
0	24.6	−25	1.89
−10	7.08	−30	1.15
−15	4.67	−40	0.33
−20	3.12	−50	0.093

Investigation of Monomer–Dimer Equilibria. In addition to the color changes mentioned above, the monomer–dimer equilibrium shown in eq 9 was investigated quantitatively using several techniques: FTIR spectroscopy, solution calorimetry, magnetic susceptibility, and NMR measurements. These results are described, as are FTIR measurements of the monomer–dimer equilibria for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2$. Attempts to detect dimers from the radical monomers $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PPh_3)\}$ and $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PEt_3)\}$ were unsuccessful to −80 °C, allowing estimation of an upper-limit for bond strengths in these complexes as discussed later.

$$[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5Me_5Cr(CO)_3\} \qquad (9)$$

Variable-Temperature FTIR Spectra of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, and $[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2$. Changes in the FTIR spectra of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in THF solution as a function of temperature are shown in Figure 2. Lowering the temperature results in a smooth increase in peaks due to the metal–metal bonded dimer and a concomitant decrease in peaks due to the radical. Equilibria appeared to be established rapidly at all temperatures. Peak positions in THF are shown in Figure 2; bands due to the dimer and monomer in toluene occur at 1920 (s), 1900 (s, br), 1875 (m) cm^{-1} and 1994 (s), 1890 (s, br) cm^{-1}, respectively. The presence of only three ν(CO) bands in the spectrum of the dimer provides evidence that the complex exists in both solvents, as in the solid state, only in the trans (C_{2h}) rotamer. The solutions are very air-sensitive, are thermally labile with respect to slow decarbonylation to the dimeric $[\eta^5\text{-}C_5Me_5Cr(CO)_2]_2$[10f] above about 320 K, and undergo photochemical decarbonylation to the same species at all temperatures. However, the results obtained were entirely reproducible and reversible if the system was maintained under nitrogen or argon, protected from light, and not heated above about 320 K for periods of time longer than required to reach thermal equilibrium.

Equilibrium data, collected in Table III, were calculated [after making corrections for solvent expansion[21]] in several ways from these spectra. The most direct was monitoring the decrease in the monomer peak at 1994 cm^{-1}. In addition, equilibrium con-

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(20) (a) Leoni, P.; Marchetti, M.; Pasquali, M.; Zanello, P. *J. Chem. Soc.* **1988**, 635. (b) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C. *Acta Crystallogr.* **1988**, *C44*, 568. (c) Rheingold, A. L.; Harper, J. R. *Acta Crystallogr.* **1991**, *184*, C47.

(21) *International Critical Tables of Numerical Data*; McGraw-Hill: New York, 1928; Vol. 3, p 29.

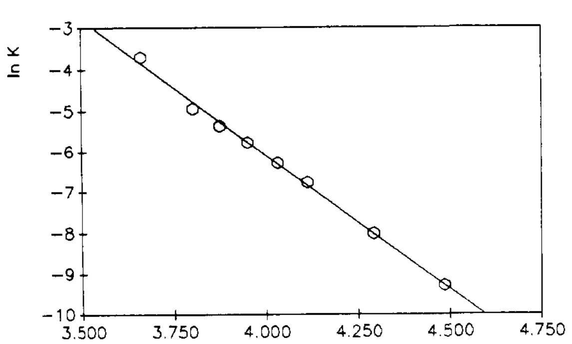

Figure 3. Plot of ln K_{eq} versus $1/T$ for the equilibrium $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ (THF) $\rightleftharpoons 2\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$.

Table IV. Equilibrium Constants as a Function of Temperature for the Reaction

$$[C_5H_5Cr(CO)_2(P(OMe)_3)]_2 \xrightarrow{THF} 2\{C_5H_5Cr(CO)_2(P(OMe)_3)\}$$

T, °C	K_{eq}, M × 10^{-3}	T, °C	K_{eq}, M × 10^{-3}
-38	137	-61	9.1
-43	94.4	-66	4.6
-49	43.3	-75	1.5
-55	19.6		

stants were also determined based on peak areas and computer simulation of the spectra. The exact positions and shapes of the peaks were somewhat temperature and solvent dependent, but equilibrium data from all three methods were in reasonable agreement. Stock solutions at three different absolute concentrations were studied and the data in Table I are our best spectroscopic estimate.

A plot of ln K_{eq} versus $1/T$ is shown in Figure 3. From this analysis, we calculated $\Delta H = 13.1 \pm 0.3$ kcal/mol and $\Delta S = 40.4 \pm 1.3$ cal/(mol deg). In view of possible uncertainties in variation of the extinction coefficient with temperature, and as discussed later, these error limits should probably be increased beyond the statistical limits. Similar data were obtained in toluene solution from which we derived $\Delta H = 14.7 \pm 0.4$ kcal/mol and $\Delta S = 45.0 \pm 1.4$ cal/(mol deg). The observed slightly higher enthalpy of dissociation in toluene is in agreement with previous observations[13] for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, as shown in eq 5.

In view of possible problems with extinction coefficients, we decided to collect data for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ using FTIR spectroscopy to compare with the published work of McLain,[12] who used UV-vis spectroscopy. In the temperature range 10–65 °C we obtained $\Delta H = 14.7 \pm 0.3$ kcal/mol and $\Delta S = 35.1 \pm 0.9$ cal/(mol deg). These data are in reasonable agreement with McLain's values of 15.8 ± 0.4 kcal/mol and 37.1 ± 1.4 cal/(mol deg), considering the different techniques used. As mentioned earlier, actual errors may be somewhat higher than statistical limits.

Yellow solutions of $[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2$ in THF turn emerald green on cooling to −78 °C, in keeping with literature reports:[11e]

$$[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)\} \quad (10)$$

Variable-temperature FTIR data for this complex are shown in Figure 4, and equilibrium data calculated from these spectra are collected in Table IV. From these data we calculate $\Delta H = 11.7 \pm 0.3$ kcal/mol and $\Delta S = 42.0 \pm 3.0$ cal/(mol deg).

Enthalpy of Solution and Dissociation of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. The heat of solution of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in THF includes both the heat of solution and heat of dissociation, as shown in eq 11.

$$\underset{\text{(solid)}}{[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2} \xrightarrow{\text{i.}} \underset{\text{(THF solution)}}{[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2} \xrightarrow{\text{ii.}} \underset{\text{(THF solution)}}{2\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}} \quad (11)$$

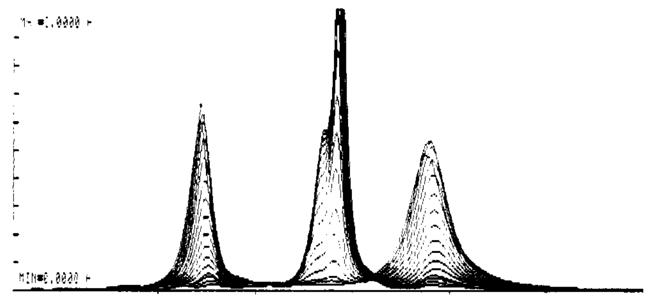

Figure 4. Infrared spectra in THF at different temperatures for the equilibrium $[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)\}$. Peaks at 1868 and 1858 cm^{-1} are due to $[\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)]_2$ and those at 1925 and 1809 cm^{-1} are due to $\{\eta^5\text{-}C_5H_5Cr(CO)_2(P(OMe)_3)\}$.

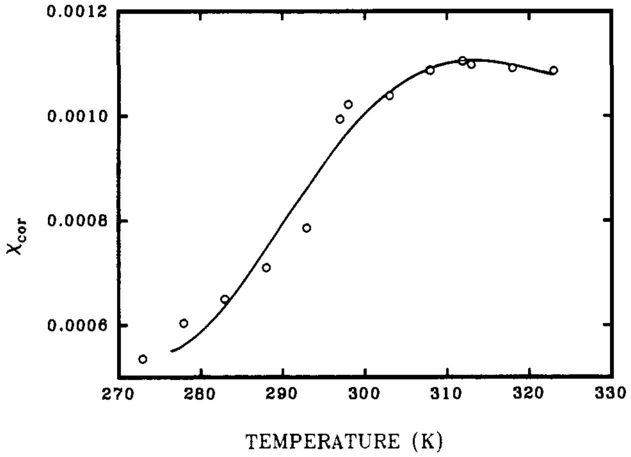

Figure 5. Plot showing variation of corrected magnetic susceptability with temperature for the complex $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in toluene solution.

The observed enthalpy of solution, +18.7 ± 0.9 kcal/mol, is the sum of both processes. An indirect measure of the enthalpy of solution from heats of reaction with mercury (discussed later) yielded a value of +19.5 ± 1.2 kcal/mol.

The enthalpy of solution (with no dissociation) can be estimated from model complexes. The enthalpies of solution (but not including dissociation) of $[\eta^5\text{-}C_5Me_5Mo(CO)_3]_2$ and $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ in THF are 7.1 ± 0.3 and 4.6 ± 0.5 kcal/mol, respectively.[22] The average of these two values, 5.9 ± 1.3 kcal/mol, is a reasonable estimate for the enthalpy of solution of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$. Subtracting this from the net heat of dissolution yielded a calorimetric measure of the enthalpy of dissociation of 12.8 ± 2.2 kcal/mol, a value in good agreement with the FTIR value of 13.1 ± 0.3 kcal/mol.

Variable-Temperature Magnetic Properties. Magnetic susceptibilities of solutions of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ (0.018 M) in toluene-d_8 were measured over the temperature range 273–323 K utilizing the Evans method[23] and were corrected for diamagnetic contributions.[24] The variations in the corrected solution susceptibilities, χ_{cor}, with temperature are illustrated in Figure 5.

Assuming (a) a temperature-independent magnetic moment of 1.772 μ_B (calculated utilizing the g values given below for $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$) for the monomer in solution, (b) applicability of the spin-only relationship between magnetic moment and magnetic susceptibility, and (c) Curie law behavior,[23] reasonable values of the magnetic susceptibility of the monomer, χ_{mon}, were

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[22] Kiss, G., Hoff, C. D. Unpublished results.

[23] For useful discussions of the procedures involved, see: (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Evans, D. F.; Fazakerly, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931. (c) Crawford, T. H.; Swanson, J. *J. Chem. Ed.* **1971**, *48*, 382. (d) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

[24] Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968.

calculated for each temperature. Equation 12 was then used to calculate the concentration of the monomer [M] at each temperature.

$$[\mathrm{M}] = [\text{total chromium}](\chi_{\mathrm{cor}})/(\chi_{\mathrm{mon}}) \qquad (12)$$

Equilibrium constants based on these data were calculated, and values of $\Delta H = 14.0 \pm 1.0$ kcal/mol and $\Delta S = 42.8 + 2.9$ cal/(mol deg) derived from these data. These are in excellent agreement with data obtained by FTIR spectroscopy in toluene—14.7 ± 0.4 kcal/mol and 45.0 ± 1.4 cal/(mol deg), a reasonable finding since Curie law behavior may well be expected of a magnetically dilute sample such as that under consideration here.

Utilizing ^{1}H NMR Spectroscopy. Since the chemical shifts of both $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ and $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ can be determined, at high and low temperatures, respectively, one may also anticipate being able to utilize chemical shift data to determine the relative amounts of the two species in solution, and hence the equilibrium constants for dissociation. The $\eta^5\text{-}C_5Me_5$ methyl resonances of the solutions utilized in the magnetic susceptibility experiment discussed above were recorded; as has been noted previously, a single resonance is observed at all temperatures, consistent with rapid monomer–dimer exchange. Indeed, the resonance is broadened at all temperatures above 198 K, below which the dimer is essentially the only species in solution.

In the absence of chemical exchange with the dimer, the isotropic shift, δ_{iso}, of the methyl groups of the radical monomer would be related to the observed chemical shift, δ_{obs}, as follows:[25]

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{obs}} - \delta_{\mathrm{diamagnetic}} \qquad (13)$$

Here $\delta_{\mathrm{diamagnetic}}$ may be approximated satisfactorily by the chemical shift of the dimer, $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ ($\delta_{\mathrm{dimer}} = 1.54$). However, δ_{iso} in principle contains both contact (δ_{con}) and dipolar or pseudocontact (δ_{dip}) contributions,[25] i.e.

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{con}} + \delta_{\mathrm{dip}} \qquad (14)$$

As mentioned above, the radical $[\eta^5\text{-}C_5Me_5Cr(CO)_3]$ exists in a $^2A''$ ground state, with principal values of the g tensor 1.9973, 2.0192, and 2.1215. Thus, in spite of claims to the contrary,[13] the radical is not magnetically isotropic and a dipolar contribution to the isotropic shifts is to be expected and may be estimated utilizing published magnetic and structural information.[26] The dipolar contribution δ_{dip} is found to be relatively insignificant, varying between 1.8 ppm at 320 K and 2.2 ppm at 273 K.

From eqs 13 and 14, the contact shift of the monomer would then be given by

$$\delta_{\mathrm{con}} = \delta_{\mathrm{obs}} - \delta_{\mathrm{dip}} - 1.54 \qquad (15)$$

Utilizing the observed chemical shifts, contact shifts for the solution at various temperatures were thus determined and, as anticipated, a plot of the contact shifts vs T^{-1} (Figure 6) results in distinctly non-Curie law behavior except above about 320 K, where essentially only monomer contributes to the observed chemical shifts. Since, however, monomer–dimer exchange results in a significant dimer contribution to the observed, averaged methyl chemical shifts, δ_{av}, the following relationship would be expected to pertain:

$$\delta_{\mathrm{av}} = P_{\mathrm{dimer}}\delta_{\mathrm{dimer}} + P_{\mathrm{monomer}}\delta_{\mathrm{monomer}} \qquad (16)$$

Here P_{dimer} and P_{monomer} are the respective mole fractions of dimer and monomer, and $\delta_{\mathrm{monomer}}$ is the contact shift calculated for the monomer at each temperature assuming that it is proportional to T^{-1}. The degree of dissociation, α, at any temperature can be calculated from

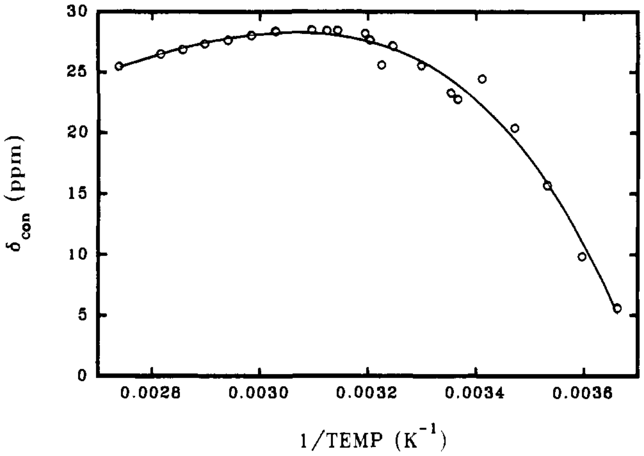

Figure 6. Contact shift versus $1/T$ for the complex $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in toluene-d_8.

$$\alpha = P_{\mathrm{monomer}}/(2 - P_{\mathrm{monomer}}) \qquad (17)$$

$$P_{\mathrm{monomer}} = (\delta_{\mathrm{av}} - \delta_{\mathrm{dimer}})/(\delta_{\mathrm{monomer}} - \delta_{\mathrm{dimer}}) \qquad (18)$$

The equilibrium constant K may then be calculated by use of eq 19

$$K = 4\alpha^2[\mathrm{dimer}]_0/(1 - \alpha) \qquad (19)$$

where $[\mathrm{dimer}]_0$ = the initial dimer concentration assuming no dissociation. Values of ΔH and ΔS of 18.8 ± 1.4 kcal/mol and 56.6 ± 4.8 cal/(mol deg) are obtained. These are similar to the values obtained elsewhere from similar data[13] and are also significantly higher than the thermodynamic parameters obtained here utilizing IR data. The reason for the discrepancies may well lie in the fact that the $^2A'$ first excited state of the radical is probably significantly thermally populated at the temperatures utilized in this study.[10e] Thus the observed chemical shifts would reflect not only the weighted averages of the chemical shifts of the monomer, in its $^2A''$ ground state, and the dimer but also the presumably varying contribution of the chemical shift of the $^2A'$ excited state. While this argument appears plausible to the authors, other factors could be involved as well.

Enthalpy of Reaction of Hg with $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (R = Me, H). The following heats of reaction (kcal/mole) were measured by Calvet calorimetry:

$$[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2(\text{solid}) + Hg(\text{liq}) \xrightarrow[40\ ^\circ C]{THF} Hg[Cr(CO)_3C_5Me_5]_2(\text{soln}) \qquad (20)$$

$$\Delta H = -7.1 \pm 0.2 \text{ kcal/mol}$$

$$[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2(\text{soln}) + Hg(\text{liq}) \xrightarrow[40\ ^\circ C]{THF} Hg[Cr(CO)_3C_5Me_5]_2(\text{soln}) \qquad (21)$$

$$\Delta H = -26.6 \pm 1.0 \text{ kcal/mol}$$

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2(\text{solid}) + Hg(\text{liq}) \xrightarrow[40\ ^\circ C]{THF} Hg[Cr(CO)_3C_5H_5]_2(\text{soln}) \qquad (22)$$

$$\Delta H = -6.4 \pm 0.1 \text{ kcal/mol}$$

These data can be used to calculate average Hg–Cr bond strengths for the two complexes. The difference between eqs 20 and 21, 19.5 + 1.2 kcal/mol, provides an independent check on the heat of dissolution measured as described above.

In order to estimate the Hg–Cr average bond strength in solution, the enthalpy of solution of Hg in THF would be needed. The authors have not been able to find this value and it probably is not known. The enthalpy of atomization of Hg is +14.7

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(25) (a) Horrocks, W. DeW. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic Press: New York, 1973; p 127. (b) Rettig, M. F. *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic Press: New York, 1973; p 217.

(26) For this reason, the EPR signal at $g = 2.004$ reported in ref 14 cannot be attributed to the species $\{(\eta^5\text{-}C_5Me_5)Cr(CO)_3\}$.

Table V. Thermodynamic Parameters for the Monomer–Dimer Equilibria

$$[\eta^5\text{-}C_5R_5Cr(CO)_2(L)]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5R_5Cr(CO)_2(L)\}$$

compound	solvent	method[a]	ΔH[b]	ΔS[c]	ref
[η^5-$C_5H_5Cr(CO)_3$]$_2$	THF	UV–vis	14.8	34.3	12
[η^5-$C_5H_5Cr(CO)_3$]$_2$	Tol	UV–vis	15.8	37.1	12
[η^5-$C_5H_5Cr(CO)_3$]$_2$	Tol	FTIR	14.7	35.1	this work
[η^5-$C_5H_5Cr(CO)_3$]$_2$	Tol	NMR	21.3	50.7	13
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	THF	FTIR	13.1	40.4	this work
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	THF	Cal	12.8		this work
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	Tol	FTIR	14.7	45.0	this work
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	Tol	Mag	14.2	42.0	this work
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	Tol	NMR	18.8	56.6	this work
[η^5-$C_5Me_5Cr(CO)_3$]$_2$	Tol	NMR	18.3	54.7	13
[CpCr(CO)$_2$(P(OMe)$_3$]$_2$	Tol	FTIR	11.7	42.0	this work
[CpCr(CO)$_2$(P(OMe)$_3$]$_2$	Tol	NMR	18.8	69.0	13

[a] Technique used in measurement, Cal = calorimetry, mag = magnetic susceptibility. [b] Enthalpy of dissociation in kcal/mol. [c] Entropy of dissociation in cal/(mol deg).

kcal/mol.[27] The average bond dissociation energy in THF solution would be one-half the enthalpy of reaction 23:

$$Hg[Cr(CO)_3C_5R_5]_2(soln) \rightarrow Hg(soln) + 2\{^{\bullet}Cr(CO)_3C_5R_5\}(soln) \quad (23)$$

Assuming that the enthalpy of solution of Hg(g) in THF is small, the average Hg–Cr(CO)$_3$C$_5$Me$_5$ bond strength would be $^1/_2$[14.7 + 26.6] = 20.7 kcal/mol.

Using the enthalpy of solution of +4.6 kcal/mol and the enthalpy of dissociation in THF from McLain[12] of +14.8 kcal/mole we calculate the enthalpy of reaction 24 to be −25.8 ± 1.4 kcal/mol.

$$2\{^{\bullet}Cr(CO)_3C_5H_5\}(soln) + Hg(liq) \xrightarrow[40\ ^{\circ}C]{THF} Hg[C_5H_5Cr(CO)_3]_2(soln) \quad (24)$$

This value leads to an estimate of the average Hg–Cr bond strength in this complex of 20.3 kcal/mol, quite close to the value obtained for the pentamethyl analogue.

Discussion

The goal of this work was to assess the role of ligand substitution on the metal–metal bond strength. In addition we report synthetic details for preparation of [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$ as well as structural determination of one of its polymorphs. Since our preliminary report[10f] on the chemistry of [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$, thermochemical data on the Cr–H bond strengths have been reported,[28] many of the spectroscopic properties reported earlier have been confirmed, and the X-ray crystal structure of a second polymorph of the dimeric complex [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$ has been determined.[13]

Thermodynamic parameters for the monomer–dimer equilibria for some of these complexes have been reported by Goh and co-workers[13] based on NMR techniques. There results are in apparent disagreement with the earlier work of McLain[12] on [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$ and also with our current data on [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$ and [η^5-C$_5$H$_5$Cr(CO)$_2$(P(OMe)$_3$)]$_2$.

Since any understanding of trends in this area requires accurate data, we have investigated [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$ via FTIR spectroscopy, solution calorimetry, magnetic susceptibility, and also NMR spectroscopy. The various results are summarized in Table V. The data obtained by us via NMR spectroscopy, and also by Goh and co-workers,[13] are in disagreement with all other data. The earlier values of McLain on [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$, obtained via UV–vis spectroscopy,[12] are in basic agreement with our FTIR data. It seems likely that, in this system, possibly due to an accessible excited state for the radical monomer, the NMR method may not be reliable, or at least need modification, for reliable determination of thermodynamic data.

The most striking observation in this work is that the increased dissociation of [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$ compared to [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$ is due as much or more to entropic than enthalpic factors. In THF solution, the enthalpies of dissociation differ by 1.7 kcal/mol and the entropies by 6.1 cal/(mol deg). In toluene solution, our data indicate that the enthalpies of dissociation are identical, but that the entropies differ by 9.9 cal/(mol deg), accounting entirely for the free energy difference (on the order of 3 kcal/mol at room temperature).

These results bear strong resemblance to the earlier work of Muetterties and co-workers[8a] on [η^3-C$_3$H$_5$Fe(CO)$_2$(L)]$_2$ described in eq 4. Interestingly, the complex {η^3-C$_3$H$_5$Fe(CO)$_2$(PPh$_3$)} showed no signs of dimer formation in the iron complexes—as is the case for η^5-C$_5$H$_5$Cr(CO)$_2$(PPh$_3$).[10a] The similarity in the two systems may stem from the fact that the parent complexes are both first row metal tricarbonyls with their ligand sets differing only in hapticity of the organic ligand: η^3-allyl for iron versus η^5-cyclopentadienyl for chromium. The chromium complexes appear to show more effect on enthalpy of dissociation, as might be expected for steric reasons.

The more favorable entropies of dissociation of the pentamethylcyclopentadienyl complex are probably due to restricted rotation in the dimers. It would be expected that an increased entropy of dissociation would be observed for the higher molecular weight complexes. Gas-phase estimates, calculated using the Sackur-Tetrode equation and based on translational entropy alone, yield ΔS = 39.4 and 40.6 cal/(mol deg) for [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$ and [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$, respectively. It seems most likely that restricted rotation in the substituted complexes accounts for most of the entropic factors. For example, [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$ exists in solution as a mixture of rotamers,[29] but the infrared spectrum of [η^5-C$_5$Me$_5$Mo(CO)$_3$]$_2$ indicates that this complex is restricted to the trans C_{2h} isomer.[30] Formation of dimers from the substituted radicals may force restriction to a much more ordered system but need not have a significantly reduced "bond strength".

In addition to the importance of entropic factors, there is an influence of carbonyl substitution on enthalpies of dimerization. Metal–metal bond dissociation enthalpies in toluene solution (kcal/mol) parallel increases in Cr–Cr bond lengths: [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$, 15.8 (ref 13) or 14.7 (this work) ± 3.231 Å; [η^5-C$_5$Me$_5$Cr(CO)$_3$]$_2$, 14.7 ± 3.3107 Å; [η^5-C$_5$H$_5$Cr(CO)$_2$(P(OMe)$_3$)]$_2$, 11.3 ± 3.343 Å. Infrared spectra of {η^5-C$_5$H$_5$Cr(CO)$_2$(PPh$_3$)} and {η^5-C$_5$H$_5$Cr(CO)$_2$(PEt$_3$)} show no sign of dimer formation down to −80 °C. An upper limit of 8 kcal/mol can be placed on the Cr–Cr bond strength for these complexes.

In attempting to analyze the relationship of bond length to bond strength in this system it must be kept in mind that the parent complex [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$ already exhibits severe crowding. As mentioned above, d(Cr–Cr) is actually 0.06 Å *longer* than d(Mo–Mo) in [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$. It has been estimated that the Cr–Cr distance should be 0.38 Å *shorter* than the Mo–Mo distance.[11b] Thus the potential energy curve may already be displaced 0.44 Å toward dissociation based on the ideal internuclear distance. Further substitutions result in additional lengthening of the Cr–Cr bond but possibly in an area of the potential energy curve which is nearer dissociation and where the rate of change, dU/dx, may be smaller. In addition, all the substituents studied result in a buildup of electron density on chromium. It is not clear what effect this would have on bond strength and effective atomic radius. A key question remains—how much is the Cr–Cr bond in the parent complex reduced already by interligand repulsion? Again it is of use to compare this system to analogous iron complexes. The Fe–Fe bond strength in the dicarbonyl dimer shown in eq 25 has been estimated as 26 kcal/mol based on kinetic studies[31] and on the order of 32 kcal/mol

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(29) Adams, R. D.; Cotton, F. A. *Inorg. Chim. Acta* **1973**, *7*, 153.

(30) The infrared spectrum of [C$_5$Me$_5$Mo(CO)$_3$]$_2$ in THF shows bands at 1933 (s), 1900 (m), and 1878 (sh), whereas [C$_5$H$_5$Mo(CO)$_3$]$_2$ shows bands at 2011 (w), 1956 (s), 1912 (s), and 1885 (sh). The absence of a band around 2000 cm^{-1} is in keeping with restriction to the trans C_{2h} isomer; see ref 11b.

(31) Cutler, A. R.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *120*, 87.

based on electrochemical data.[4] This is considerably stronger

$$[\eta^5\text{-}C_5H_4RFe(CO)_2]_2 \rightarrow 2\{Fe(CO)_2(C_5H_4R)\} \quad (25)$$

than the values in the range of 13–15 kcal/mol for both $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$. The only other first-row metal carbonyl complex for which reliable bond strength data appear to be available is $Mn_2(CO)_{10}$, as discussed in the introduction. This bond, in the range of 35–40 kcal/mol, is also considerably stronger. The observed value for the Cr–Cr bond strength is thus roughly half the approximately 30 kcal/mol bond strength in these other first-row complexes. That is in spite of the fact that the Cr–H bond strength of 61 kcal/mol shows no apparent weakening with regard to other first-row transition-metal hydrides which typically have M–H bond strengths on the order of 60 kcal/mol.[32] Thus it seems clear that phosphine substitution is not perturbing a "normal" metal–metal bond, but one that is already elongated toward dissociation. For that reason, extrapolation of the enthalpic results to other systems is not warranted. It is worth noting that the corresponding phosphine-substituted molybdenum radicals can be generated in solution but do not yield detectable concentrations of radicals in solution at moderate temperatures.[33] Apparent formation of $\eta^5\text{-}C_5Ph_5Mo(CO)_3$ radicals has been recently reported by Tyler,[34] however, which may include both steric and electronic properties of the $\eta^5\text{-}C_5Ph_5$ ligand.

In addition to steric factors influencing the enthalpies of dimerization, it can be expected that electronic effects will also play a role. We have recently reported the Cr–H bond strengths in these complexes[28] (addition of $^\bullet H$ to a metal radical should not involve the significant interligand repulsions seen combining to metal radicals):

$$L_nCr\text{-}H \rightarrow L_nCr^\bullet + H^\bullet \quad (26)$$

ΔH, kcal/mol: 59.8 $\{C_5H_5Cr(CO)_2(PPh)_3\}$; 59.9 $\{C_5H_5Cr(CO)_2(PEt_3)\}$; 61.5 $\{C_5H_5Cr(CO)_3\}$; 62.3 $\{C_5Me_5Cr(CO)_3\}$; 62.7 $\{C_5H_5Cr(CO)_2(P(OMe)_3)\}$

It is interesting to note that the two weakest Cr–H bonds are for the PPh_3 and PEt_3 complexes. Neither of these complexes form Cr–Cr dimers either. However, the strongest Cr–H bond is for the $P(OMe)_3$ complex, which forms a relatively weak Cr–Cr bond—presumably due to steric factors. It is also worth noting that the Hg–Cr bond is apparently slightly stronger for $\{Cr(CO)_3C_5Me_5\}$ (20.7 kcal/mol) than for $\{Cr(CO)_3C_5H_5\}$ (20.3 kcal/mol), in keeping with the bond strengths to hydrogen atoms.

Conclusion

This work provides detailed investigation of metal–metal bond strengths by several techniques in the series of complexes $[\eta^5\text{-}C_5R_5Cr(CO)_2(L)]_2$. For these complexes, NMR experiments do not appear to generate valid thermodynamic data due to a multiplicity of states in the radicals formed. The Cr–Cr bond length in $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ is reported and is 0.04 Å longer than in $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$. In spite of the longer metal–metal bond in the methyl-substituted complex, the Cr–Cr bond strengths, as reflected in the ΔH values of Table V, are not significantly different. While this finding is at first sight surprising, we are in fact unaware of any correlations of bond lengths and bond strengths for metal complexes that are sufficiently accurate that a precedent could be established. Instead, our results indicate that metal–metal bond elongation of considerably more than 0.03 Å is necessary to be reflected in a thermochemical measurement. In fact, the parent complex may be already displaced by 0.45 Å from the ideal internuclear distance and hence weakened by 10–15 kcal/mol. The considerably greater degree of dissociation observed for $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ than for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ is a result of relative entropy changes, and must reflect release of steric strain on dissociation. We commented above on crystallographic evidence for apparently greater distortions of carbonyl groups in $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and it is likely that a significant and decisive gain in rotational freedom of the $\eta^5\text{-}C_5Me_5$ group is gained on dissociation. It is more difficult to analyze the role of ligand substitution on enthalpies of reaction since these include both steric and electronic factors which cannot be fully separated. Additional work in progress on these and related systems is planned and may help resolve these questions.

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Registry No. $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, 70605-18-4; $Cr(CO)_3(MeCN)_3$, 16800-46-7; C_5Me_5H, 4045-44-7; $\eta^5\text{-}C_5Me_5Cr(CO)_3H$, 98773-88-7; Hg, 7439-97-6; $Hg[Cr(CO)_3C_5Me_5]_2$, 51862-21-6; $\eta^5\text{-}C_5Me_5Cr(CO)_3$, 116184-85-1; $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, 12194-12-6; $[CpCr(CO)_2(P(OMe_3))]_2$, 68122-38-3.

Supplementary Material Available: Table of general temperature factor expressions (2 pages). Ordering information is given on any current masthead page.

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