ring. Since most of the known silver–aromatic interactions are asymmetric with the shorter Ag–C distance invariant at 2.47 Å, it appears that a back-donation interaction is generally of lesser importance.

In the case of naphthalene(AgClO$_4$)$_4$·4H$_2$O there is one large and new perturbing effect which has been added to the electronic environment of the system. It may be that the water of hydration has altered the electronic requirements of the silver ion such that the hydrated silver ion is no longer as good an electron acceptor and may be considered to be a weaker Lewis acid than the free silver ion. Hence, back-donation in this case becomes more important relative to the overall Ag–π interaction. It might be more logical to consider the 2.52 (1) Å distance from the silver to the midpoint of the nearest C–C bond as a more accurate measure of the

Ag–π interaction rather than the Ag–C distance of 2.61 (1) Å.

It is interesting to note that for anthracene(AgClO$_4$)$_4$·H$_2$O[13] each water of hydration is associated with two silver ions and relatively little perturbing effect upon the "normal" asymmetric Ag–C interaction is observed.

Unusual Structural and Magnetic Resonance Properties of Dicyclopentadienylhexacarbonyldichromium

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Abstract: The proton nmr spectra at various temperatures and in solvents of varying polarity have shown that the title compound, **1**, exists as a solvent- and temperature-dependent mixture of anti and gauche rotamers. The barrier to internal rotation ($\Delta G_{298}{}^{\ddagger}$) is 12.1 ± 0.7 kcal mol^{-1}, which is substantially lower than that in the molybdenum analog, **2**. Marked line broadening, which is reversible, in **1** occurs at temperatures above about $-10°$; presumably some paramagnetic state or species become populated. In order to obtain structural data bearing on these anomalies in the solution properties of **1**, its structure was determined X-ray crystallographically. It is essentially isomorphous with **2**, as expected, belonging to space group $P2_1/c$, with $Z = 2$ and $a = 10.468$ (1) Å, $b = 7.625$ (1) Å, $c = 12.227$ (2) Å, and $\beta = 127.22$ (1)°. The molecule has a crystallographic center of symmetry and has virtual symmetry of C_{2h}. Using 1269 reflections with intensities exceeding three times their estimated standard deviations the structure was refined to discrepancy indices (defined in the usual way) of $R_1 = 0.027$ and $R_2 = 0.033$. Hydrogen atoms were refined isotropically and all other atoms anisotropically. The Cr–Cr distance, 3.281 (1) Å, is far longer than would be expected for an unstrained single bond; it is actually about 0.06 Å longer than the Mo–Mo bond in **2**. There is other evidence of internal steric strain. Reasons for the long Cr–Cr bond and its bearing on other molecular properties are discussed.

Among the great variety of intramolecular rearrangements which have been shown to be the basis for stereochemical nonrigidity in organometallic[1] and metal carbonyl[2] type molecules, one that is of general importance is hindered rotation about metal–metal bonds. This process plays a key role in the rearrangements of certain binuclear metal carbonyl species.[2]

We recently reported a quantitative study of the equilibrium and kinetic aspects of internal rotation in (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$,[3] in which it was shown that the molecule exists as a mixture of *anti* and *gauche* rotamers, with the equilibrium ratio strongly dependent on solvent polarity. The barrier to internal rotation ($\sim$15 kcal/mol) was evaluated from nmr line shape variation over a temperature range.

The results of that investigation raised certain questions pertaining to the nature of the forces causing the barrier and to how the magnitude of the barrier would vary on changing the metal atoms from Mo to Cr. An nmr study of (η^5-C$_5$H$_5$)$_2$Cr$_2$(CO)$_6$ was therefore undertaken. When the nmr results were found to be different from what might naively have been expected, it was considered worthwhile to conduct an X-ray crystallographic investigation of the structure as well. The results of both phases of the study are reported and discussed here.

Experimental Section

The compound was prepared according to the procedure of King and Stone,[4] and recrystallized from toluene at $-20°$.

Nmr Spectra. Samples were prepared by placing the solid compound, under nitrogen, in nmr tubes closed with serum stoppers. Vacuum degassed solvents were then introduced with a syringe.

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(4) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 104 (1963).

Spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature accessory. Temperature measurements were made with a copper–constantin thermocouple inserted into the probe just below the sample and were recorded with a Leeds and Northup Numatron digitized readout thermometer, Model 625. The thermocouple had been previously calibrated with methanol and ethylene glycol standards and found to be very reproducible ($\pm 1°$). The temperatures are thus expected to be accurate to within $\pm 2°$.

Line shape analysis of the spectra was carried out using the program EXCHSYS written by G. M. Whitesides and J. K. Krieger.[5]

The exchange process (interconversion of two rotamers, *vide infra*) was treated as a one to one exchange of uncoupled sites. Due to low solubility at the lower temperatures, we could not obtain reliable thermodynamic parameters for the isomer equilibrium. For the purpose of the line shape calculations the gauche: trans rotamer ratio of 1.25/1.0, which gave the best agreement between observed and calculated spectra at $-48°$ in 1/1, v/v, acetone-d_6/toluene-d_8 solvent, was used at all temperatures. Since the calculated line shape could be very satisfactorily fitted to the observed ones in the intermediate exchange rate region, it is believed, as expected,[6] that neglect of the slight change in equilibrium with temperature had a negligible effect on the accuracy of the parameters.

Collection of X-Ray Data. A dark green crystal plate, measuring approximately $0.4 \times 0.3 \times 0.07$ mm, obtained from the sample crystallized from toluene was mounted and sealed in a glass capillary. The crystals appear to be thermally unstable at about 25°, but, at 15°, the prevailing temperature in the room housing the diffractometer, they are apparently quite stable. Decline in intensity of the standard reflections during the period of data collection was negligible. The crystal alignment and data-collection procedures have been described elsewhere.[7] ω scans of several strong reflections gave peak widths of about 0.25°. Fifteen reflections were centered and their setting angles refined by least squares to obtain unit cell dimensions and an orientation matrix for data collection.

Data were collected using the θ–2θ scan technique and a variable scan rate ranging from 2.0 to 24.0°/min depending on the intensity of the reflections. The intensities of five standard reflections were monitored every 100 reflections and showed only random fluctuation with time. Unique data were collected up to 2θ(Mo Kα) of 54.9° using a scan range from 2θ(Mo Kα_1) $-$ 0.85° to 2θ(Mo Kα_2) $+$ 0.90°. A total of 2018 reflections was collected, of which 1269 had intensities greater than 3σ after Lorentz and polarization corrections were made. The standard deviation, σ, was defined as before.[7] The parameter p used in the expression[7] for σ was given the value 0.03.

The unit cell dimensions were refined using 15 intense reflections having $2\sigma > 25°$ randomly selected as to direction. The refined parameters are $a = 10.468$ (1) Å, $b = 7.625$ (1) Å, $c = 12.227$ (2) Å, and $\beta = 127.22$ (1)°. The systematic absenses indicate space group $P2_1/c$, and assuming $Z = 2$ the reasonable density of 1.72 g cm^{-3} is calculated.

Computer programs used in data reduction and in the solution and refinement of the structure were as follows. DATARED by Frenz was used for data reduction. Absorption corrections were performed using the numerical subroutines of Coppens's DATAPP as included in AGNOST by Cahen. The Fourier program JIMDAP by Ibers is a version of Zalkin's FORDAP. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\Sigma w(|F_o| - |F_c|)^2$. Atomic distances and angles were calculated using a local modification of Baur's SADIAN program. RSCAN by Doedens was used for an analysis of structure factors and ORTEP by Johnson was used for drawing illustrations on a Gerber plotter. The function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen was used. LIST by Snyder was used for listing the data.

Solution and Refinement of the Structure. The crystal is isomorphous and the molecule was expected to be isostructural with $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$.[8] A three-dimensional Patterson map re-

vealed the chromium atom at essentially the same set of fractional coordinates as those of the molybdenum atom in crystalline $(\eta^5\text{-}C_5H_5)_2Mo(CO)_6$.[9] Accordingly, the entire set of positional parameters from the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ structure was used as input for isotropic least-squares refinement. One cycle gave the following discrepancy indices

$$R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.113$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.15$$

where w is the weighting factor given by $4F_o^2/\sigma^2(F_o^2)$.

Scattering factors were taken from the International Tables.[10] Anomalous dispersion effects were included in the scattering factor of the chromium atom.[11]

In view of the dissimilar dimensions of the crystal, the data were examined for evidence of absorption effects; preliminary results suggested that corrections would be useful. The minimum and maximum transmission factors for that portion of the data set having intensities greater than 3σ were 0.709 and 0.906, respectively. Two cycles of least-squares refinement neglecting hydrogen atoms and with all nonhydrogen atoms having anisotropic temperature factors yielded discrepancy indices of $R_1 = 0.038$ and $R_2 = 0.059$. The positions of the hydrogen atoms on the cyclopentadienyl rings were calculated and subsequently identified on a difference Fourier map. The hydrogen positions as located on the difference map were introduced and refinement converged with an additional three cycles of least squares. This included anisotropic temperature factors for all nonhydrogen atoms and isotropic factors for the hydrogen atoms. The final residuals were $R_1 = 0.027$ and $R_2 = 0.033$. In the final cycle, the parameter shifts of all nonhydrogen atoms were less than 0.35 esd and less than 0.95 esd for the hydrogen atoms. The standard deviation of an observation of unit weight is 1.26.

A final difference Fourier map showed no peaks greater than 0.20 e/Å^3. A list of observed and calculated structure factor amplitudes is given in Table I; see paragraph at end of paper regarding supplementary material. The atomic coordinates and their estimated standard deviations are given in Table II. Thermal param-

Table II. Atomic Positional Parameters

Atom	x	y	z
Cr	0.18350 (4)	-0.00356 (5)	0.14348 (3)
O(1)	0.1511 (3)	0.3399 (3)	0.0084 (2)
O(2)	0.3389 (2)	0.2523 (3)	0.3761 (2)
O(3)	-0.0348 (3)	-0.0325 (3)	0.2250 (2)
C(1)	0.1523 (3)	0.2066 (3)	0.0514 (3)
C(2)	0.2780 (3)	0.1539 (4)	0.2872 (3)
C(3)	0.0397 (3)	-0.0206 (3)	0.1855 (2)
Cp(1)^a	0.2358 (3)	-0.2867 (4)	0.1742 (3)
Cp(2)	0.2119 (4)	-0.2394 (4)	0.0526 (3)
Cp(3)	0.3282 (4)	-0.1141 (4)	0.0850 (4)
Cp(4)	0.4253 (3)	-0.0869 (4)	0.2270 (3)
Cp(5)	0.3677 (3)	-0.1931 (4)	0.2823 (3)
H(1)	0.173 (3)	-0.358 (4)	0.183 (3)
H(2)	0.139 (3)	-0.274 (4)	-0.024 (3)
H(3)	0.341 (4)	-0.063 (5)	0.030 (3)
H(4)	0.502 (4)	-0.014 (4)	0.264 (3)
H(5)	0.404 (4)	-0.198 (4)	0.369 (3)

^{a} Cp denotes a cyclopentadienyl carbon atom.

eters and root-mean-square amplitude of vibration are given in Table III.

Results

Structure. As expected the molecule is isostructural with $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$.[8] Table IV presents some pertinent bond distances, and Table V presents some bond angles. As shown in Figure 1 the molecular

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(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1971).

Table III. Thermal Parameters and Rms Amplitudes of Vibration

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Rms amplitudes (Å) Max	Int	Min	Equiv isotropic[a] B's[b]
Cr	0.00721 (5)	0.00991 (7)	0.00572 (4)	0.00000 (5)	0.00308 (4)	−0.00029 (5)	0.188	0.171	0.156	2.30
O(1)	0.0174 (4)	0.0119 (4)	0.0108 (3)	−0.0024 (3)	0.0063 (3)	0.0012 (3)	0.282	0.224	0.189	3.99
O(2)	0.0139 (4)	0.0253 (5)	0.0100 (3)	−0.0040 (4)	0.0052 (3)	−0.0075 (3)	0.309	0.276	0.171	4.41
O(3)	−0.0150 (3)	−0.0270 (5)	0.0093 (2)	−0.0041 (3)	0.0085 (3)	−0.0024 (3)	0.264	0.218	0.184	4.09
C(1)	0.0093 (4)	0.0118 (5)	0.0063 (2)	−0.0001 (3)	0.0033 (3)	−0.0016 (3)	0.217	0.191	0.159	2.76
C(2)	0.0086 (4)	0.0170 (5)	0.0074 (3)	−0.0007 (4)	0.0039 (3)	−0.0012 (3)	0.224	0.205	0.173	3.16
C(3)	0.0100 (4)	0.0133 (5)	0.0064 (2)	−0.0013 (3)	0.0039 (3)	−0.0010 (3)	0.206	0.197	0.168	2.91
Cp(1)	0.0121 (4)	0.0110 (5)	0.0119 (4)	0.0024 (4)	0.0066 (3)	0.0028 (3)	0.256	0.231	0.188	3.42
Cp(2)	0.0111 (4)	0.0136 (5)	0.0094 (3)	0.0026 (4)	0.0047 (3)	−0.0020 (4)	0.267	0.196	0.173	3.35
Cp(3)	0.0140 (5)	0.0165 (6)	0.0142 (4)	0.0041 (4)	0.0104 (4)	0.0020 (4)	0.267	0.235	0.221	3.74
Cp(4)	0.0076 (4)	0.0158 (6)	0.0151 (4)	0.0008 (4)	0.0051 (3)	−0.0017 (4)	0.304	0.241	0.220	3.74
Cp(5)	0.0120 (5)	0.0165 (6)	0.0086 (3)	0.0048 (4)	0.0033 (3)	0.0025 (4)	0.161	0.230	0.267	3.71

[a] Isotropic thermal parameter as calculated from $B = 4[V^2 \det(B_{ij})]^{1/3}$. [b] The B values for hydrogen are as follows: H(1), 3.7 (7); H(2), 3.2 (6); H(3), 5.7 (8); H(4), 5.6 (8); H(5), 4.1 (6).

Table IV. Interatomic Distances (Å)

Cr–Cr	3.281 (1)	C(3)–O(3)	1.142 (3)
Cr–C(1)	1.870 (3)	Cp(1)–Cp(2)	1.398 (4)
Cr–C(2)	1.866 (3)	Cp(2)–Cp(3)	1.403 (4)
Cr–C(3)	1.846 (3)	Cp(3)–Cp(4)	1.398 (4)
Cr–Cp(1)[a]	2.203 (3)	Cp(4)–Cp(5)	1.404 (4)
Cr–Cp(2)	2.227 (3)	Cp(5)–Cp(1)	1.398 (4)
Cr–Cp(3)	2.197 (3)	Cp(1)–H(1)	0.91 (3)
Cr–Cp(4)	2.174 (3)	Cp(2)–H(2)	0.81 (3)
Cr–Cp(5)	2.174 (3)	Cp(3)–H(3)	0.85 (3)
C(1)–O(1)	1.141 (3)	Cp(4)–H(4)	0.84 (3)
C(2)–O(2)	1.146 (3)	Cp(5)–H(5)	0.88 (3)

[a] Cp denotes cyclopentadienyl carbon atom.

Table V. Interatomic Angles (deg)

Cr–C(1)–O(1)	172.0 (2)	C(1)–Cr–C(2)	79.2 (1)
Cr–C(2)–O(2)	178.7 (2)	C(1)–Cr–C(3)	110.4 (1)
Cr–C(3)–O(3)	172.9 (2)	C(2)–Cr–C(3)	80.8 (1)
Cp(5)–Cp(1)–Cp(2)[a]	108.2 (3)	Cp(1)–Cr–Cp(2)	36.8 (1)
Cp(1)–Cp(2)–Cp(3)	108.0 (3)	Cp(2)–Cr–Cp(3)	37.0 (1)
Cp(2)–Cp(3)–Cp(4)	107.9 (3)	Cp(3)–Cr–Cp(4)	37.3 (1)
Cp(3)–Cp(4)–Cp(5)	108.1 (3)	Cp(4)–Cr–Cp(5)	37.7 (1)
Cp(4)–Cp(5)–Cp(1)	107.8 (3)	Cp(5)–Cr–Cp(1)	37.3 (1)

[a] Cp denotes a cyclopentadienyl carbon atom.

geometry can best be described by attributing a pseudo-square-pyramidal configuration to each half with a *pentahapto*cyclopentadienyl ring occupying the apical position and three carbonyl ligands and the metal-metal bond completing the square base. The molecule is crystallographically centrosymmetric which implies an anti rotational configuration between the two halves.

The packing of the molecules in the crystal is normal. The shortest intermolecular contact which does not involve hydrogen atoms is between oxygen atoms at a distance of 3.10 Å.

The carbon atoms of the cyclopentadienyl ring define a perfect plane pentagon within the significance of the results. As Table VI shows, no carbon atom lies more than 0.006 (3) Å from the mean plane, and the range of C–C distances is from 1.398 (4) to 1.404 (4) Å. The hydrogen atoms were readily located, and refinement proceeded smoothly. The resulting C–H distances have an average value of 0.86 ± 0.03 Å, which is below the range, 0.94–0.98 Å, generally considered to be optimum crystallographically[12] and previously found in some well-behaved structures, e.g., $(\eta^5\text{-}C_5H_5)Cu(PPh_3)$.[13]

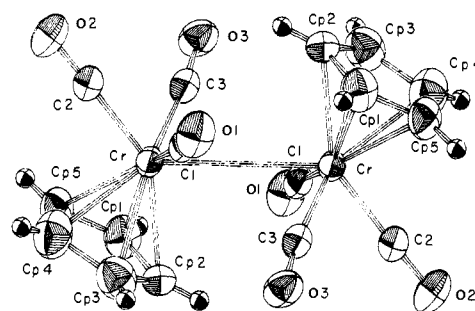(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Figure 1. An ORTEP diagram of the $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ molecule. The thermal ellipsoids include 50% probability of electron density. The hydrogen atoms were artificially assigned an isotropic temperature factor of 1.0 Å².

Table VI. Weighted Least-Squares Plane through the Cyclopentadienyl Carbon Atoms

Equation of plane[a]
Cp(1)–Cp(2)–Cp(3)–Cp(4)–Cp(5) $6.95x - 5.61y - 3.61z = 2.62$
Displacement of atoms from this plane (Å)

Cp(1)	−0.003	H(1)	−0.066
Cp(2)	0.005	H(2)	−0.034
Cp(3)	−0.006	H(3)	−0.005
Cp(4)	0.004	H(4)	−0.003
Cp(5)	−0.001	H(5)	−0.036
Cr	−1.843		

[a] Equations have the form $Ax + By + Cz = D$ where x, y, and z are fractional coordinates.

The five distances from cyclopentadienyl carbon atoms to the chromium atom range from 2.174 (3) to 2.227 (6) Å, with a mean value of 2.20 Å. This is quite similar to the corresponding distances found in other compounds such as $(\eta^5\text{-}C_5H_5)Cr(NO)_2NCO$[14] (2.20 Å), $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(SPh)_2$[15] (2.21 Å), and *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NMe_2)_2$[16] (range 2.21–2.32 Å).

The Cr–CO distances, which have an average value of 1.86 Å, lie as expected between the extremes of 1.92 Å for $Cr(CO)_6$[17] where Cr–C π bonding, per bond, is minimal and 1.82 Å for $Cr(dien)(CO)_3$[18] and $(CCH_3)_6$-

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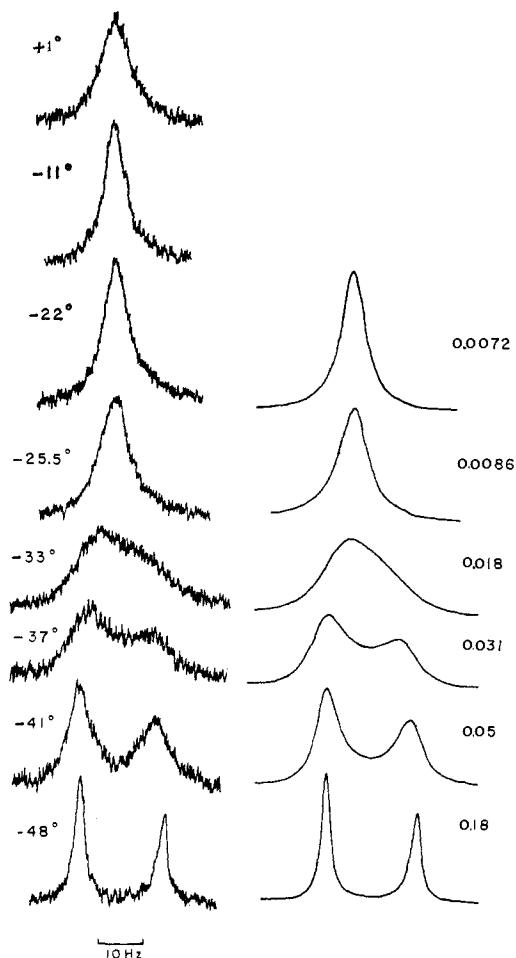(18) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

Figure 2. Pmr spectra at various temperatures of [(η^5-C$_5$H$_5$)Cr-(CO)$_3$]$_2$ in 1/1 (v/v) acetone-d_6-toluene-d_8 solvent. The mean residence times for the calculated spectra are given in seconds.

Figure 3. An Arrhenius plot of the apparent exchange rates of the gauche and anti forms of [(η^5-C$_5$H$_5$)Cr(CO)$_3$]$_2$ as a function of temperature.

Cr(CO)$_3$[19] where there is considerable Cr-C π bonding and are very similar to those in the arene tricarbonyl complexes C$_6$H$_6$Cr(CO)$_3$[20] (1.84 Å) and (C$_6$H$_5$COOMe)-Cr(CO)$_3$[21] (1.85 Å).

The nonlinearity of the Cr-C-O groups is quite marked for those cis to the Cr-Cr bond, which have angles of 172.0 (2) and 172.9 (2)°, while it is only slight, 178.7 (2)°, for the one which is trans to the Cr-Cr bond. The direction in which the former ones bend is such that the bending could, at least in part, be attributed to nonbonded repulsions.

The most arresting feature of this structure is the very long chromium-to-chromium distance, 3.281 (1) Å. It has been estimated from structural data for Cr(dien)-(CO)$_3$[18] that the single bond covalent radius of chromium in that compound is 1.48 Å. In a strictly comparable way, a covalent radius of 1.62 Å was estimated for the molybdenum atom in Mo(dien)(CO)$_3$.[22] From these numbers it may be estimated that in the (η^5-C$_5$H$_5$)$_2$-M$_2$(CO)$_6$ compounds we might expect the Cr-Cr distance to be much shorter than the Mo-Mo distance, the expected decrease being roughly 2(1.62 − 1.43) = 0.38 Å. Instead, d(Cr-Cr) is about 0.06 Å *greater* than d(Mo-Mo).

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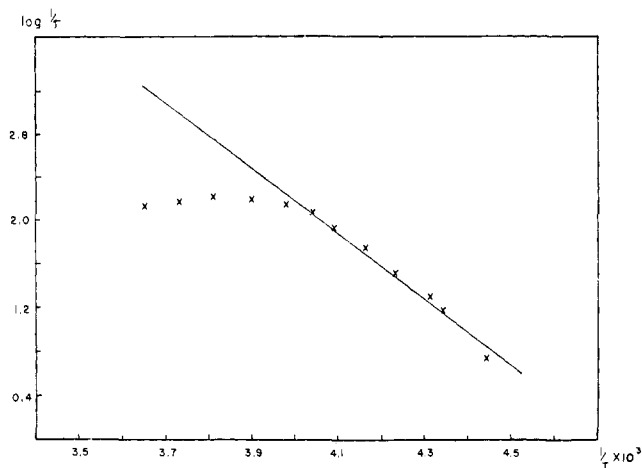(22) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

Nmr Spectra. The proton nmr spectrum of (η^5-C$_5$H$_5$)$_2$Cr$_2$(CO)$_6$ in toluene-d_8 solvent at 25° consists of one very broad resonance ($\nu_{1/2} \approx$ 18 Hz) at τ 4.16. At higher temperatures, the line becomes *broader*. At −61° the resonance has narrowed to a width at half-height of about 1.5 Hz and has shifted to τ 5.90.

In a mixed solvent, acetone-d_6 and toluene-d_8, in 1/1 volume ratio, at −61° the spectrum consists of two narrow lines ($\nu_{1/2} \approx$ 1.5 Hz) at τ 5.36 and 5.55. The relative intensity of the line at τ 5.36 increases with increasing proportion of acetone in the mixed solvent, as in the case of (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$.[3]

As shown in Figure 2, when the temperature is raised the two resonances broaden and then coalesce. The single signal continues to sharpen until the temperature reaches about −11°, where $\nu_{1/2}$ is about 5.5 Hz, and thereafter becomes broader as the temperature is raised.

A line shape analysis shows that the rates satisfy the Arrhenius equation up to about −22°, above which there is progressively greater deviation. This is shown in Figure 3. The linear portion of the plot yielded the thermodynamic activation parameters log A = 14.2 ± 0.6 and E_a = 13.7 ± 0.5 kcal/mol. According to the Eyring equation $\Delta H^\ddagger$ = 13.24 ± 0.5 kcal/mol; $\Delta S^\ddagger$ = +4.7 ± 2.0; $\Delta G^\ddagger_{298}$ = 12.1 ± 0.7. The rearrangement rates in the intermediate exchange region were unaffected by fourfold changes in concentration.

Discussion

The remarkable length of the Cr-Cr bond is the first point that deserves comment. As already noted, it is longer by several tenths of an ångström than would naively have been expected by simple reference to the Mo-Mo bond length in (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$. It is, in fact, 0.06 Å longer than the Mo-Mo bond itself. It is instructive to compare this situation with that which prevails in Mn$_2$(CO)$_{10}$[23] and Tc$_2$(CO)$_{10}$.[24] The Mn-Mn distance, 2.923 (3) Å, is about 0.11 Å shorter than the Tc-Tc distance, 3.036 (6) Å. The explanation for the unexpected result for the chromium compound is to be found, we think, in the presence of substantial nonbonded repulsions.

(23) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).
(24) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

The $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ molecules are exceptionally sterically crowded, particularly with regard to the interaction between the two halves. It is well to stress that this interaction results from the proximity of three ligands on each metal atom, *viz.*, the two CO groups which are cis to the M–M bond and the cyclopentadienyl group, with the corresponding set of three ligands on the other metal atom. The other two CO groups point well away from the region of contact and make no direct contribution to it, although they contribute indirectly because their presence imposes a buttressing effect on each set of three ligands that do make the direct contacts.

The end to end interaction is thus of a three-against-three type, formally similar to that in a 1,2-disubstituted ethane, as shown in Figure 4. The energy as a function of rotation about the M–M bond has three minima (staggered configurations) and three maxima (eclipsed configurations). Inspection of a model shows that the repulsive forces in the eclipsed configurations must be very severe; most likely if the molecule is to pass by rotation from one staggered configuration to another through the intervening eclipsed form, a good deal of angle bending will occur in order for the opposing ligands to slip by each other.

The three staggered configurations (see Figure 4) include the anti or centrosymmetric one which is found in the crystal as well as two enantiomorphous gauche ones.

The end against end repulsion would become more severe with decreasing M–M separation even if all other structure parameters were to remain constant. Thus, while the Cr–Cr bond would very probably have its greatest intrinsic strength at a shorter M–M distance than that appropriate to the Mo–Mo bond, a shorter distance would entail significantly greater repulsive forces which would nullify the potential advantage. In fact, the repulsions at any given M–M distance will be even more severe for the chromium compound because the various chromium to ligand distances are all shorter than the corresponding Mo to ligand distances by 0.10–0.15 Å. The effect of this on CO$\cdots$CO repulsions may be essentially nil, but the CO$\cdots$C$_5$H$_5$ repulsions will surely become more severe as inspection of a model clearly shows.

Now, all of the above interplay of factors leads to the following effect. Since the nonbonded repulsions at an M–M distance equal to that in the molybdenum compound are probably as strong or even stronger in the chromium compound, whereas, the Cr–Cr bond, *at that distance*, is surely weaker than the Mo–Mo bond at the same distance, the Cr–Cr bond gets stretched even further.

The second striking observation is the behavior of the proton nmr spectrum at higher temperatures. In both a nonpolar solvent where there is no detectable amount of the gauche rotamer and a polar solvent where an ample quantity of the gauche rotamer can be observed by nmr at low temperature the line width increases at higher temperatures, *i.e.*, from around −20° upwards. This broadening is reversible and cannot, therefore, be attributed to paramagnetic decomposition products. Nor does it seem likely that it is caused by exchange with another isomeric form which might be increasing its equilibrium concentration as the temperature rises.
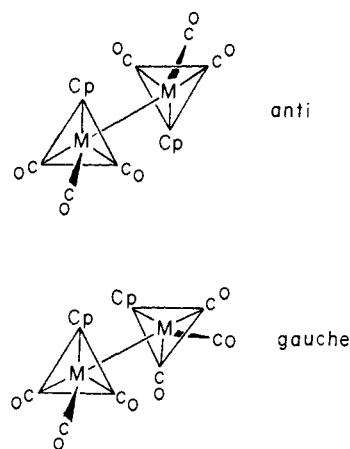

Figure 4. Diagrammatic representations of the rotational conformations of the $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ molecules, showing the anti and one of the two gauche rotamers.

Admittedly, a small concentration of another isomer could at first cause noticeable broadening, but at slightly higher temperatures resharpening as a new exchange-averaged peak would occur, contrary to what is observed.

It seems most reasonable to believe that increasing temperatures generate small concentrations of some paramagnetic species in equilibrium with the normal, diamagnetic isomers or isomers. The paramagnetic species could result from dissociation into stable radicals, $(\eta^5\text{-}C_5H_5)Cr(CO)_3$, or it could perhaps be a low-lying triplet state of the dinuclear molecule. It is, however, difficult to conceive of a satisfactory model of such a triplet molecule unless it is thought of as essentially a solvent-caged pair of radicals. Thus, details aside, a temperature-dependent equilibrium of the type

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 = 2(\eta^5\text{-}C_5H_5)Cr(CO)_3$$
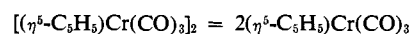
seems to be indicated. In view of the extraordinary length of the Cr–Cr bond, this does not seem unlikely.

There are other observations in the literature which contribute to the plausibility of this proposal. The compound $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ has been shown to exist as a mixture of the diamagnetic dimer and radical monomers.[25] The position of the equilibrium varies reversibly with temperature. Similarly, temperature-dependent equilibria between diamagnetic dinuclear species, $[Mn(CO)_4(PR_3)]_2$, and paramagnetic radicals, $Mn(CO)_4PR_3$, have been reported,[26] in which the position of the equilibrium is very sensitive to the identity of the groups, R. Finally, there is the report[27] of an intense epr signal in crystalline $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ obtained by sublimation, although the claim that this signal is intense enough to imply the presence of approximately 50% of the substance as radicals is a little surprising.

Finally, some comment is required on the observed barrier to interconversion of anti and gauche rotamers. As indicated in Figure 3, this process exhibits normal temperature dependencies, *i.e.*, follows the Arrhenius equation, below about −20°, and an Arrhenius ac-

(25) H. D. Murdoch and E. A. C. Lucken, *Helv. Chim. Acta*, **47**, 1517 (1964).

(26) W. Hieber and W. Freyer, *Chem. Ber.*, **92**, 1765 (1959); **93**, 462 (1960).

(27) H. J. Keller, *Z. Naturforsch. B*, **23**, 133 (1968).

tivation energy E_a of 13.7 ± 0.5 kcal mol^{-1} is obtained. For the molybdenum analog an E_a of 15.3 ± 1.0 kcal mol^{-1} was obtained. Though it might be argued that these two results are scarcely, if at all, different in a statistical sense, direct comparison of the spectra of the two systems at various temperatures shows clearly that the chromium compound has a significantly lower activation energy than the molybdenum compound since the coalescence temperature of the former is −30 ± 5° while that of the latter is +20 ± 5°.

It should first be said that the interconversion of gauche and anti rotamers which has been observed need not necessarily be attributed to the process of hindered internal rotation. In view of the remarkable length and concomitant weakness of the Cr–Cr bond, and the fact that at higher temperatures mononuclear radicals apparently exist in equilibrium with the dinuclear molecule, the possibility that the rotamers interconvert by a dissociation–recombination process cannot be dismissed automatically as in the case of rotation about normal C–C bonds. We will, however, continue this discussion on the assumption that nondissociative rotations occur, since there is no positive evidence to the contrary, but bearing in mind that this assumption could be false.

It is recognized that, in general, the origins of rotational barriers are complex, with both attractive and repulsive forces playing a role. In the present case it is possible that in the staggered conformations there is some stabilizing effect due to interaction between the cis CO groups on one metal atom and the other metal atom, arising by incipient donation of $d\pi$ electrons from the latter to π^* orbitals of the former.[28] However, we think it likely that whatever the reality of such a contribution, the rotational barriers in the $[(\eta^5\text{-}C_5H_5)\text{-}M(CO)_3]_2$ molecules are primarily repulsive dominated. On this basis, the lower barrier in the chromium compound, compared to the molybdenum one, is then readily understood on the basis of the longer M–M distance in the chromium case.

Supplementary Material Available. Table I, structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-749.

(28) A significant interaction of this type has been proposed for $Mn_2(CO)_{10}$ on the basis of semiempirical MO calculations.[29] The overall magnitude of the effect in the manganese compound is considerably enhanced over what it *might* be in the chromium compound by (a) the much shorter Mn–Mn distance and (b) the fact that there are eight Mn···C pairs but only four Cr···C pairs.
(29) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

The Interaction of an Aliphatic Carbon–Hydrogen Bond with a Metal Atom. The Structure of (Diethyldi-1-pyrazolylborato)-(*trihapto*-2-phenylallyl)(dicarbonyl)molybdenum

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Abstract: An interaction between an aliphatic carbon–hydrogen bond and a metal atom which is far stronger than any previously observed in a molecular structure determination is reported. The compound in which this occurs is (diethyldi-1-pyrazolylborato)(*trihapto*-2-phenylallyl)(dicarbonyl)molybdenum. The α carbon atom of one ethyl group is directed toward the molybdenum atom (C to Mo, 3.06 Å); the rotational orientation about the B–C bond is such as to direct one of the α hydrogen atoms toward the molybdenum. The H···Mo distance appears to be not more than 2.27 (8) Å and possibly as short as about 2.15 Å. A three-center, two-electron bond encompassing the C···H···Mo atoms is postulated to account for this strong interaction and to provide the molybdenum atom with an effective closed-shell configuration. The compound crystallizes in the space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a = 10.085$ (2), $b = 10.219$ (2), and $c = 20.654$ (4) Å. The anisotropic refinement of 2397 independent reflections with intensities three times greater than their esd's converged at $R_1 = 0.044$ and $R_2 = 0.053$.

There have been enormous strides made in recent years in both the practical development and the mechanistic elucidation of catalytic processes used to transform and synthesize industrial organic chemicals on a large scale. Processes such as hydrogenation, hydroformylation, hydrosilation, and olefin oxidation have been intensively studied with the result that the broad basic principles, if not all of the fine details, of their mechanisms are now appreciated. In the development of such knowledge a prominent role has been played by the structural characterization of compounds which are presumed to be similar to but less labile than the actual intermediates in the catalytic system itself. Thus, there are stable compounds of platinum, iridium,