accordingly, increase from 2.753 (1) to 2.815 (7) Å in the first step and then to 2.883 (1)–2.892 (1) Å in the second. The magnitude of the increase per $^1/_6$ unit of bond order, ca. 0.065 Å, is consistent with the general pattern presented by other tri- and hexanuclear cluster structures.

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Supplementary Material Available: Tables of calculated and observed structure factors (39 pages). Ordering information is given on any current masthead page.

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Molecular and Electronic Structures of Three Pyridine- and Piperidine-Substituted Chromium Carbonyl Compounds: $Cr(CO)_5(C_5H_5N)$, $Cr(CO)_5(C_5H_{10}NH)$, and *cis*-$Cr(CO)_4(C_5H_{10}NH)[P(OMe)_3]$

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The problem of metal–ligand bonding in $Cr(CO)_5L$ compounds, and related ones, where L is an aliphatic amine or an aromatic amine, has been addressed by X-ray work on a novel crystalline solid containing equimolar amounts of $Cr(CO)_5NHC_5H_{10}$ and $Cr(CO)_5NC_5H_5$ and on *cis*-$Cr(CO)_4(HNC_5H_{10})[P(OMe)_3]$ as well as by Fenske–Hall calculations on $Cr(CO)_5NH_3$ and other data collected from the literature. The theoretical results show that in the $Cr(CO)_5L$ compounds the $b_1(d_{x^2-y^2})$ orbital lies above the $a_1(d_{z^2})$ orbital in agreement with some but contrary to other previous proposals. The structures show that the replacement of an aliphatic by an aromatic amine has no significant effect on the structure of the $Cr(CO)_5$ group and that the two substituents $C_5H_{10}NH$ and $P(OMe)_3$ exert their structural effects on the $Cr(CO)_4$ residue essentially independently. The crystals containing the $Cr(CO)_5(C_5H_{10}NH)$ and $Cr(CO)_5(C_5H_5N)$ molecules belong to space group $P2_1/n$ and have the following unit cell parameters: $a = 13.851$ (2) Å, $b = 11.026$ (1) Å, $c = 17.693$ (2) Å, $\beta = 109.93$ (2)°, $V = 2540$ (1) Å^3, and $Z = 4$. The structure was refined with use of 2209 data to $R_1 = 0.041$ and $R_2 = 0.049$. The compound *cis*-$Cr(CO)_4(C_5H_{10}NH)[P(OMe)_3]$ crystallized in space group $P2_12_12_1$ with $a = 8.088$ (1) Å, $b = 11.587$ (2) Å, $c = 18.431$ (2) Å, $V = 1727.4$ (5) Å^3, and $Z = 4$. Refinement using 1326 data converged with $R_1 = 0.043$ and $R_2 = 0.054$ for the preferred enantiomorph.

Introduction

There is a mountainous volume of literature on the subject of metal–ligand π bonding in metal carbonyls and substituted metal carbonyls. After so many attempts by so many authors, employing such a variety of physical, chemical, and theoretical methods, it may seem presumptuous to suppose that one more contribution can significantly affect our general understanding of the problem. In some respects, the situation is already well understood while in others the attainment of an unambiguous consensus seems as elusive a goal as ever. Nevertheless, we have the temerity to offer a few additional experimental results (which mostly have the virtue of being unambiguous facts) and observations (which are heuristic rather than dogmatic) to this important but tortuous problem.

With respect to molecules of the type $Cr(CO)_5L$, there are two questions we shall deal with: (1) How does the replacement of one CO ligand in $Cr(CO)_6$ affect the bonding and the pattern of molecular orbitals when the ligand L is one with little or no π-acceptor capacity? (2) Does the ligand pyridine show any significant ability to act as a π acceptor, especially when compared as directly as possible with an aliphatic amine, which is assumed to have none, or with a phosphite, which is assumed to be a fairly effective π acceptor?

To deal with the first question, we have employed both Fenske–Hall nonempirical molecular orbital calculations and the results of infrared and X-ray crystallographic studies of $Cr(CO)_5(HNC_5H_{10})$, where $C_5H_{10}NH$ is piperidine. To deal with the second question, we have made accurate structure determinations of three molecules, $Cr(CO)_5(HNC_5H_{10})$ (**1**), $Cr(CO)_5NC_5H_5$ (**2**), and $Cr(CO)_4(HNC_5H_{10})[P(OMe)_3]$ (**3**). As a matter of pure, and entirely unanticipated, good luck we obtained a crystalline substance containing **1** and **2** in a 1:1 ratio and thus obtained the structures of both molecules in one neat package. The structure of **3** gives us the desired structural comparison of the effects of a non-π-accepting ligand, $C_5H_{10}NH$, and a fairly good π-accepting ligand in the same molecule where each has its own trans-CO group along with two CO groups that are simultaneously cis to both substituents.

Table I. Infrared Spectral Data for the Amine Derivatives[a]

compd	ν_{CO}, cm^{-1}
$Cr(CO)_5(NHC_5H_{10})$	2069 ($A_1{}^2$), 1933 (E), 1917 ($A_1{}^1$)
$Cr(CO)_5(NC_5H_5)$	2071 ($A_1{}^2$), 1939 (E), 1920 ($A_1{}^1$)
cis-$Cr(CO)_4(NHC_5H_{10})[P(OCH_3)_3]$	2020 (A′), 1921 (A′), 1897 (A″), 1870 (A′)

[a] Spectra were recorded in hexane solution and are accurate to ±1 cm^{-1}.

Experimental Section

Preparation of Metal Carbonyl Amine Compounds. $Cr(CO)_5NHC_5H_{10}$ was prepared from $Cr(CO)_6$ (Strem Chemical Co.) and piperidine (Aldrich Chemical Co., 98%) by the previously published photochemical technique in the THF solvent.[2] Both reagents were used as received. Yellow crystals suitable for X-ray analysis were obtained from hexane solution at 0 °C. The IR spectrum in the ν(CO) region displayed the expected three bands (Table I).

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[2] Dennenberg, R. J.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *11*, 72.

0020-1669/81/1320-4090$01.25/0

Table II. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Procedures

formula	$Cr_2O_{10}N_2C_{20}H_{16}$	$CrPO_7NC_{12}H_{20}$
mol wt	547.86	373.3
space group	$P2_1/c$	$P2_12_12_1$
a, Å	13.851 (2)	8.088 (1)
b, Å	11.026 (1)	11.587 (2)
c, Å	17.693 (2)	18.431 (2)
β, deg	109.93 (2)	
V, Å^3	2540 (1)	1727.4 (5)
Z	4	4
d_{calcd}, g/cm^3	1.54	1.44
cryst size, mm	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.40
μ(Mo Kα), cm^{-1}	9.47	8.14
radiation	graphite-monochromated Mo Kα ($\lambda = 0.710\,73$)	
scan type	ω–2θ	ω–2θ
scan width ($\Delta\omega$), deg	$0.60 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
max counting time, s	30	30
collection range	$+h, +k, \pm l$	$+h, +k, +l$
no. of unique data	4427	1758
no. of data, $I > 3\sigma(I)$	2209	1326
p	0.05	0.05
no. of variables	307	199
R_1^{a}	0.041	0.043
R_2^{a}	0.049	0.054
esd	1.29	1.49
largest shift^b	0.02	0.04
largest peak^c	0.28	0.50

^{a} $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. ^{b} Largest parameter shift in final refinement cycle. ^{c} Largest peak in a final difference Fourier, e/Å^3.

cis-$Cr(CO)_4[P(OMe)_3]NHC_5H_{10}$ was prepared from *cis*-$Cr(CO)_4[NHC_5H_{10}]_2$ (obtained from a 4-day reflux of excess NHC_5H_{10} and $Cr(CO)_6$ in heptane) and $P(OMe)_3$ in a 1:1 molar ratio in refluxing CH_2Cl_2 for 10 min. A reduction in reaction solution volume followed by addition of MeOH afforded yellow crystals of the desired product.

Infrared Spectra. The infrared spectra were recorded in 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an infrared data station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

X-ray Crystallography. A. The crystals obtained from the recrystallization of $Cr(CO)_5(C_5H_{10}NH)$ were examined under a microscope. Since the color and morphology of all of the crystals appeared to be essentially identical, a well-formed crystal of dimensions 0.30 × 0.30 × 0.25 mm was chosen. The crystal was attached to the end of a thin glass fiber and mounted on an Enraf-Nonius CAD-4 automated diffractometer. Several intense reflections were located and centered automatically and then examined by a slow ω-scan motion. The observed narrow, symmetric peaks indicated that the chosen crystal was of good quality. A least-squares analysis of the setting angles of 25 such reflections provided unit cell parameters (Table II). The observation of systematic absences in $h,0,l$ for $l \neq 2n$ and $0,k,0$ for $k \neq 2n$ suggested the space group $P2_1/c$. Intensities were measured to $2\theta = 50°$ with use of our standard data collection procedures[3] (Table II). The data were corrected for Lorentz and polarization effects, and a total of 2209 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure.

The positions of the two independent Cr atoms were located by the direct-methods program MULTAN,[4] and these were confirmed by the results of a three-dimensional Patterson synthesis. Subsequent refinement of these positions produced values for the agreement factors of $R_1 = 0.410$ and $R_2 = 0.503$, which also indicated the suitability of these coordinates. A difference Fourier synthesis revealed the positions of all other nonhydrogen atoms. The structure was refined to convergence with use of anisotropic thermal parameters by full-matrix least squares. At this point, the two independent molecules were found to be incommensurate in ways that led us to formulate one molecule as $Cr(CO)_5(C_5H_5N)$. A best-fit least-squares plane was calculated for each type of ligand and produced results for molecule **1**, which showed the expected chair conformation for the six-membered ring, while the results for molecule **2** indicated a planar six-membered ring. A difference Fourier map did not produce positions acceptable for hydrogen atoms in either molecule. Therefore, a fixed contribution for the hydrogen atoms on the two different types of rings was included in the refinement. The least-squares refinement converged at the parameters listed in Table II.

Figure 1. Stereoview of the unit cell of the compound containing both $Cr(CO)_5(C_5H_{10}NH)$ (**1**) and $Cr(CO)_5(C_5H_5N)$ (**2**) molecules.

B. Crystals of $Cr(CO)_4[P(OCH_3)_3](C_5H_{10}NH)$ were examined by the same procedures described above. The unit cell parameters obtained from the CAD-4 routines showed, not unexpectedly, that this material was isomorphous to the molybdenum analogue.[5] Data were collected to $2\theta = 50°$ according to standard procedures and the data-collection parameters given in Table II. Of the 1758 unique reflections examined, 1326 had $I > 3\sigma(I)$ and were considered observed. The data were treated as described above.

The refinement of the structure presented no problems. The positional parameters were taken from Darensbourg and Atwood,[5] and successful refinement of the isotropic model by the full-matrix least-squares method to values of $R_1 = 0.096$ and $R_2 = 0.126$ proved that the two complexes were isostructural as well as isomorphous. Following anisotropic refinement, a difference Fourier map revealed the positions of several of the hydrogen atoms. However, only the position of the amine hydrogen was refined (with use of a fixed thermal contribution), and the remaining 10 hydrogen atom positions were calculated (with use of a C–H bond distance of 0.95 Å) around the piperidine ring. During the final stages of refinement, the reflection 0,0,2 with $|F_o| = 34.9$ and $|F_c| = 58.3$ was excluded from the calculations. At this point, least-squares analysis of an enantiomorphic model produced significantly lower discrepancy indices ($R_1 = 0.043$; $R_2 = 0.054$ vs. $R_1 = 0.046$; $R_2 = 0.058$) demonstrating that our crystal had chirality opposite to that used in the molybdenum study. The final refinement parameters are presented in Table II.

The positional and thermal parameters for the atoms in both structures are presented in Tables III and IV. Tables of observed and calculated structures are available as supplementary material.

Molecular Orbital Calculations. The method of Fenske and Hall[6] was carried out, with use of programs kindly provided by Professor M. B. Hall, on the molecules $Cr(CO)_6$, $Cr(CO)_5$, and $Cr(CO)_5(NH_3)$. Chromium hexacarbonyl was treated in the point group O_h with bond lengths from the literature, and the $Cr(CO)_5$ fragment was obtained by deleting one of the carbonyl groups (symmetry C_{4v}). For $Cr(CO)_5NH_3$, the bond lengths and angles were taken as approximately those found in $Cr(CO)_5(NHC_5H_{10})$ but idealized to give the $Cr(CO)_5$ portion C_{4v} symmetry, with 90° C–Cr–C angles. The NH_3 group had local C_{3v} symmetry, and the C_4 and C_3 axes were made collinear. The calculation on $Cr(CO)_5(NH_3)$ was done with two rotational orientations of the ammonia molecule, but the same results were obtained aside from a shuffling of the symmetry labels. In each case, the orientation was such as to create a mirror plane, which in one case contained two equatorial CO groups and in the other bisected two opposite equatorial OC–Cr–CO angles.

Results

Structures of Compounds 1 and 2. These two molecules, $Cr(CO)_5(C_5H_{10}NH)$, **1**, and $Cr(CO)_5(C_5H_5N)$, **2**, were found together in equal numbers in the monoclinic crystals, which we had expected to contain only molecules of **1**. The crystallographic asymmetric unit consists of one molecule of each kind. The packing of these molecules in the unit cell is shown in Figure 1. Molecules of **1** and **2** form alternating sheets

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(3) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(4) All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, employing the Enraf-Nonius structure determination package.

(5) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314.

(6) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr(CO)_5(C_5H_{10}NH)$ and $Cr(CO)_5(C_5H_5N)$[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cr(1)	0.59613 (5)	0.59769 (7)	0.31280 (4)	4.18 (3)	3.60 (3)	3.62 (3)	0.22 (3)	1.26 (2)	0.24 (3)
Cr(2)	0.13635 (6)	0.63193 (8)	0.29760 (4)	5.12 (3)	4.84 (4)	4.50 (3)	0.25 (3)	2.38 (2)	−0.65 (3)
O(1)	0.4289 (3)	0.7153 (3)	0.1730 (2)	7.9 (2)	5.3 (2)	5.6 (2)	1.3 (2)	−0.2 (2)	0.5 (2)
O(2)	0.7595 (3)	0.7209 (4)	0.2611 (2)	7.7 (2)	9.1 (3)	6.5 (2)	−1.9 (2)	4.0 (1)	−0.1 (2)
O(3)	0.6079 (3)	0.4034 (3)	0.1988 (2)	6.6 (2)	5.4 (2)	6.1 (1)	0.3 (2)	2.4 (1)	−1.4 (2)
O(4)	0.7572 (3)	0.4478 (4)	0.4356 (2)	8.5 (2)	7.9 (2)	7.2 (2)	3.6 (2)	0.4 (2)	2.0 (2)
O(5)	0.4330 (3)	0.4428 (4)	0.3450 (2)	8.0 (2)	5.5 (2)	11.3 (2)	−1.5 (2)	5.1 (1)	0.4 (2)
O(6)	0.1374 (3)	0.8715 (4)	0.2138 (2)	9.7 (2)	6.1 (2)	9.8 (2)	0.6 (2)	4.2 (2)	2.1 (2)
O(7)	−0.0748 (3)	0.5811 (4)	0.1773 (2)	6.8 (2)	9.5 (3)	6.3 (2)	−0.8 (2)	0.7 (2)	−0.8 (2)
O(8)	0.3553 (3)	0.6770 (5)	0.4082 (3)	5.2 (2)	10.4 (3)	10.0 (2)	−0.5 (2)	2.0 (2)	−1.3 (2)
O(9)	0.1426 (3)	0.3747 (4)	0.3602 (3)	10.9 (2)	5.4 (2)	9.1 (2)	0.9 (2)	3.7 (2)	1.4 (2)
O(10)	0.2206 (3)	0.5260 (4)	0.1783 (2)	10.9 (2)	11.1 (3)	6.5 (2)	4.7 (2)	5.1 (1)	0.2 (2)
N(1)	0.5902 (2)	0.7391 (3)	0.3992 (2)	3.6 (1)	3.7 (2)	2.9 (1)	0.1 (1)	0.9 (1)	0.3 (1)
N(2)	0.0718 (3)	0.7099 (5)	0.3841 (2)	9.2 (2)	8.2 (3)	9.2 (2)	−4.3 (2)	6.9 (1)	−5.6 (2)
C(1)	0.4908 (4)	0.6757 (4)	0.2275 (3)	5.9 (2)	3.3 (2)	4.1 (2)	0.0 (2)	1.4 (2)	0.2 (2)
C(2)	0.6979 (4)	0.6789 (5)	0.2826 (3)	5.8 (2)	4.9 (3)	3.8 (2)	−0.6 (2)	1.5 (2)	−0.4 (2)
C(3)	0.6017 (3)	0.4801 (5)	0.2419 (3)	4.7 (2)	4.7 (3)	4.5 (2)	0.1 (2)	1.7 (1)	0.1 (2)
C(4)	0.6982 (4)	0.5080 (5)	0.3922 (3)	5.6 (2)	5.3 (3)	4.7 (2)	1.0 (2)	1.6 (2)	0.7 (2)
C(5)	0.4931 (4)	0.5049 (5)	0.3355 (3)	6.1 (2)	3.7 (2)	5.4 (2)	0.5 (2)	2.2 (2)	−0.1 (2)
C(6)	0.1356 (4)	0.7848 (5)	0.2472 (3)	5.7 (2)	5.4 (3)	6.2 (2)	0.5 (2)	2.9 (2)	−0.1 (2)
C(7)	0.0025 (4)	0.6021 (5)	0.2241 (3)	6.4 (2)	5.0 (3)	4.8 (2)	0.2 (2)	2.4 (2)	−0.6 (2)
C(8)	0.2726 (4)	0.6605 (5)	0.3683 (3)	6.1 (2)	6.6 (3)	6.0 (2)	0.3 (2)	3.2 (2)	−0.5 (2)
C(9)	0.1403 (4)	0.4725 (5)	0.3402 (3)	6.5 (2)	5.9 (3)	4.9 (2)	0.2 (2)	2.1 (2)	−0.8 (2)
C(10)	0.1895 (4)	0.5685 (5)	0.2250 (3)	6.9 (2)	6.9 (3)	5.2 (2)	2.3 (2)	2.9 (2)	0.5 (2)
C(11)	0.6456 (4)	0.8524 (5)	0.3958 (3)	5.0 (2)	4.3 (2)	4.7 (2)	−0.7 (2)	1.7 (2)	−0.0 (2)
C(12)	0.6318 (4)	0.9525 (5)	0.4502 (3)	6.2 (2)	4.5 (3)	6.0 (2)	−1.2 (2)	2.4 (2)	−1.5 (2)
C(13)	0.6614 (4)	0.9087 (6)	0.5359 (3)	6.6 (3)	7.2 (3)	4.8 (2)	−0.1 (3)	1.3 (2)	−1.8 (2)
C(14)	0.6023 (5)	0.7961 (5)	0.5390 (3)	10.2 (3)	6.2 (3)	3.8 (2)	−0.9 (3)	2.8 (2)	−0.0 (2)
C(15)	0.6190 (4)	0.6992 (5)	0.4840 (3)	7.8 (3)	5.0 (3)	3.7 (2)	−0.1 (2)	1.7 (2)	0.4 (2)
C(16)	0.0012 (4)	0.6411 (5)	0.4072 (3)	7.6 (2)	5.3 (3)	8.8 (2)	−2.2 (2)	5.6 (2)	−2.8 (2)
C(17)	−0.0425 (4)	0.6935 (7)	0.4662 (3)	8.2 (2)	10.7 (4)	9.2 (3)	−3.4 (3)	6.4 (2)	−3.9 (3)
C(18)	0.0025 (5)	0.7973 (7)	0.5084 (4)	18.5 (3)	7.9 (4)	13.8 (3)	−2.9 (3)	13.6 (2)	−4.1 (3)
C(19)	0.0747 (5)	0.8646 (6)	0.4860 (3)	11.4 (3)	7.5 (3)	9.7 (3)	−2.4 (3)	6.2 (2)	−5.3 (2)
C(20)	0.1173 (4)	0.8094 (5)	0.4280 (3)	9.8 (3)	5.5 (3)	9.4 (2)	−2.7 (2)	6.9 (2)	−3.3 (2)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
H1	0.5187 (0)	0.7563 (0)	0.3802 (0)	5.0000 (0)	H14B	0.6246 (0)	0.7663 (0)	0.5925 (0)	5.0000 (0)
H11A	0.6214 (0)	0.8813 (0)	0.3420 (0)	5.0000 (0)	H15A	0.5787 (0)	0.6304 (0)	0.4862 (0)	5.0000 (0)
H11B	0.7167 (0)	0.8343 (0)	0.4112 (0)	5.0000 (0)	H15B	0.6896 (0)	0.6775 (0)	0.5028 (0)	5.0000 (0)
H12A	0.5619 (0)	0.9772 (0)	0.4321 (0)	5.0000 (0)	H16	−0.0183 (0)	0.5624 (0)	0.3856 (0)	5.0000 (0)
H12B	0.6740 (0)	1.0195 (0)	0.4481 (0)	5.0000 (0)	H17	−0.1000 (0)	0.6569 (0)	0.4748 (0)	5.0000 (0)
H13A	0.6463 (0)	0.9699 (0)	0.5679 (0)	5.0000 (0)	H18	−0.0158 (0)	0.8230 (0)	0.5529 (0)	5.0000 (0)
H13B	0.7329 (0)	0.8914 (0)	0.5560 (0)	5.0000 (0)	H19	0.0954 (0)	0.9432 (0)	0.5075 (0)	5.0000 (0)
H14A	0.5312 (0)	0.8152 (0)	0.5225 (0)	5.0000 (0)	H20	0.1769 (0)	0.8433 (0)	0.4212 (0)	5.0000 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$ where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

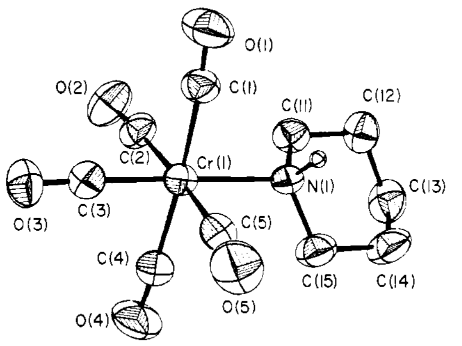

Figure 2. The $Cr(CO)_5(C_5H_{10}NH)$ molecule.

parallel to the *bc* planes. The centers of inversion at 0,0,0 and 0,$^1/_2$,$^1/_2$ relate pairs of $Cr(CO)_5(C_5H_5N)$ molecules, and centers of inversion at 0,$^1/_2$,$^1/_2$ and $^1/_2$,$^1/_2$,$^1/_2$ relate pairs of $Cr(CO)_5(C_5H_{10}NH)$ molecules. There are no intermolecular contacts that are less than the sum of van der Waals radii.

The structures of the individual molecules of **1** and **2** are shown in Figures 2 and 3, respectively, where the atom numbering schemes are also defined. The bond lengths and angles for these two compounds are presented in Tables V and VI.

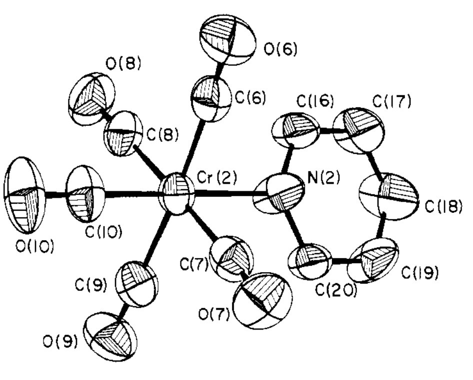

Figure 3. The $Cr(CO)_5(C_5H_5N)$ molecule. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density.

The $Cr(CO)_5N$ portions of the two molecular structures are extremely similar, and thus it was only upon examining the structures of the heterocyclic rings in the final stages of refinement that we were forced to recognize that both the expected piperidine (**1**) and the unexpected pyridine (**2**) complexes were present.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr(CO)_4[P(OCH_3)_3](C_5H_{10}NH)$[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cr	−0.0295 (1)	−0.47773 (8)	−0.15689 (5)	3.00 (3)	2.84 (3)	2.52 (3)	0.05 (4)	−0.10 (4)	−0.09 (3)
P	0.0608 (2)	−0.4938 (1)	−0.03805 (8)	3.99 (7)	4.24 (7)	2.38 (6)	0.13 (7)	0.17 (6)	0.05 (6)
O(1)	−0.1457 (6)	−0.4467 (4)	−0.3107 (2)	5.4 (2)	6.4 (3)	3.5 (2)	0.7 (2)	−1.5 (2)	0.3 (2)
O(2)	−0.3691 (6)	−0.4112 (5)	−0.1104 (3)	3.3 (2)	8.1 (3)	6.4 (3)	1.1 (2)	0.9 (2)	−2.3 (2)
O(3)	0.0586 (7)	−0.2245 (3)	−0.1560 (3)	8.4 (3)	2.8 (2)	7.0 (3)	−0.6 (2)	−0.7 (3)	0.3 (2)
O(4)	−0.1630 (7)	−0.7231 (4)	−0.1582 (3)	5.6 (2)	3.9 (2)	7.4 (3)	−1.5 (2)	−0.1 (3)	−0.2 (2)
O(5)	0.2521 (6)	−0.4948 (5)	−0.0318 (2)	4.5 (2)	9.9 (3)	2.8 (2)	−0.6 (3)	−0.8 (2)	−0.1 (2)
O(6)	0.0276 (10)	−0.3982 (6)	0.0194 (3)	16.2 (5)	17.5 (4)	4.4 (2)	11.3 (4)	−4.0 (3)	−5.7 (2)
O(7)	0.0256 (9)	−0.6080 (5)	0.0057 (3)	9.6 (4)	13.0 (4)	7.1 (3)	−5.2 (3)	−3.5 (3)	6.5 (2)
N	0.2195 (6)	−0.5300 (4)	−0.1906 (2)	3.3 (2)	2.7 (2)	2.2 (2)	−0.1 (2)	−0.1 (2)	0.1 (2)
C(1)	−0.0974 (8)	−0.4605 (5)	−0.2541 (3)	3.6 (3)	4.2 (3)	3.0 (2)	0.4 (3)	0.2 (2)	0.1 (2)
C(2)	−0.2385 (9)	−0.4356 (6)	−0.1274 (3)	4.5 (3)	4.4 (3)	3.1 (2)	0.1 (3)	−0.2 (3)	−0.7 (2)
C(3)	0.0320 (8)	−0.3210 (5)	−0.1564 (3)	4.3 (3)	3.8 (2)	3.2 (2)	0.7 (3)	−0.4 (3)	0.3 (2)
C(4)	−0.1059 (8)	−0.6317 (5)	−0.1576 (4)	3.0 (2)	4.4 (3)	3.6 (3)	0.6 (2)	0.1 (3)	−0.3 (3)
C(5)	0.3436 (10)	−0.5047 (9)	0.0363 (4)	6.2 (4)	11.7 (6)	4.0 (3)	−1.1 (6)	−2.5 (3)	−0.4 (4)
C(6)	−0.0788 (14)	−0.3078 (7)	0.0229 (5)	10.5 (6)	7.2 (4)	7.6 (4)	3.9 (5)	−2.6 (5)	−3.9 (3)
C(7)	−0.1227 (20)	−0.6537 (9)	0.0213 (5)	26 (1)	13.0 (6)	5.0 (4)	−12.5 (6)	2.2 (6)	1.5 (4)
C(8)	0.2732 (8)	−0.4895 (6)	−0.2641 (3)	3.7 (3)	4.6 (3)	2.6 (2)	0.4 (3)	−0.0 (2)	1.2 (2)
C(9)	0.4496 (8)	−0.5169 (6)	−0.2815 (3)	4.0 (3)	6.1 (3)	3.6 (3)	−0.5 (4)	0.8 (3)	0.8 (3)
C(10)	0.4814 (10)	−0.6448 (7)	−0.2750 (4)	3.8 (3)	7.5 (4)	6.0 (4)	0.7 (4)	1.8 (3)	−1.6 (3)
C(11)	0.4371 (9)	−0.6852 (6)	−0.2012 (4)	4.6 (4)	4.1 (3)	7.9 (4)	1.9 (3)	1.1 (4)	0.2 (3)
C(12)	0.2523 (8)	−0.6567 (5)	−0.1852 (3)	3.4 (3)	3.4 (3)	4.3 (3)	0.4 (3)	0.6 (3)	0.6 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(1)	0.2847 (0)	−0.4917 (0)	−0.1558 (0)	3.9000 (0)	H(7)	0.4164 (0)	−0.6849 (0)	−0.3097 (0)	5.0000 (0)
H(2)	0.2601 (0)	−0.4078 (0)	−0.2658 (0)	5.0000 (0)	H(8)	0.5053 (0)	−0.6474 (0)	−0.1665 (0)	5.0000 (0)
H(3)	0.2049 (0)	−0.5241 (0)	−0.2997 (0)	5.0000 (0)	H(9)	0.4537 (0)	−0.7662 (0)	−0.1981 (0)	5.0000 (0)
H(4)	0.5198 (0)	−0.4772 (0)	−0.2486 (0)	5.0000 (0)	H(10)	0.2257 (0)	−0.6818 (0)	−0.1375 (0)	5.0000 (0)
H(5)	0.4732 (0)	−0.4932 (0)	−0.3297 (0)	5.0000 (0)	H(11)	0.1845 (0)	−0.6964 (0)	−0.2192 (0)	5.0000 (0)
H(6)	0.5952 (0)	−0.6599 (0)	−0.2837 (0)	5.0000 (0)					

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$ where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

Table V. Bond Distances (Å) and Bond Angles (Deg) for $Cr(CO)_5(C_5H_{10}NH)$

A. Distances

Cr(1)-N(1)	2.204 (3)	O(1)-C(1)	1.136 (5)
C(1)	1.909 (5)	O(2)-C(2)	1.144 (5)
C(2)	1.894 (5)	O(3)-C(3)	1.162 (5)
C(3)	1.824 (5)	O(4)-C(4)	1.128 (5)
C(4)	1.896 (6)	O(5)-C(5)	1.134 (5)
C(5)	1.906 (6)	C(11)-C(12)	1.519 (6)
N(1)-C(11)	1.478 (5)	C(12)-C(13)	1.508 (7)
C(15)	1.483 (5)	C(13)-C(14)	1.498 (8)
		C(14)-C(15)	1.514 (7)

B. Angles

N(1)-Cr(1)-C(1)	91.7 (2)	Cr(1)-C(1)-O(1)	174.8 (4)
C(2)	93.9 (2)	Cr(1)-C(2)-O(2)	175.1 (5)
C(3)	179.6 (2)	Cr(1)-C(3)-O(3)	177.7 (4)
C(4)	92.9 (2)	Cr(1)-C(4)-O(4)	175.0 (5)
C(5)	91.5 (2)	Cr(1)-C(5)-O(5)	174.5 (5)
C(1)-Cr(1)-C(2)	90.3 (2)	Cr(1)-N(1)-C(11)	115.3 (3)
C(3)	88.7 (2)	Cr(1)-N(1)-C(15)	115.6 (3)
C(4)	175.1 (2)	C(11)-N(1)-C(15)	109.1 (4)
C(5)	89.0 (2)	N(1)-C(11)-C(12)	114.2 (4)
C(2)-Cr(1)-C(3)	86.1 (2)	C(11)-C(12)-C(13)	110.7 (4)
C(4)	91.0 (2)	C(12)-C(13)-C(14)	109.7 (4)
C(5)	174.6 (2)	C(13)-C(14)-C(15)	110.9 (5)
C(3)-Cr(1)-C(4)	86.7 (2)	N(1)-C(15)-C(14)	113.2 (4)
C(5)	88.5 (2)		
C(4)-Cr(1)-C(5)	89.3 (2)		

Table VI. Bond Distances (Å) and Bond Angles (Deg) for $Cr(CO)_5(C_5H_5N)$

A. Distances

Cr(2)-N(2)	2.194 (4)	O(6)-C(7)	1.129 (6)
Cr(2)-C(6)	1.905 (6)	O(7)-C(7)	1.132 (6)
Cr(2)-C(7)	1.895 (6)	O(8)-C(8)	1.137 (6)
Cr(2)-C(8)	1.902 (6)	O(9)-C(9)	1.132 (6)
Cr(2)-C(9)	1.906 (7)	O(10)-C(10)	1.153 (5)
Cr(2)-C(10)	1.824 (6)	C(16)-C(17)	1.491 (7)
N(2)-C(16)	1.403 (6)	C(17)-C(18)	1.391 (9)
N(2)-C(20)	1.369 (6)	C(18)-C(19)	1.407 (9)
		C(19)-C(20)	1.478 (7)

B. Angles

N(2)-Cr(2)-C(6)	92.3 (2)	Cr(2)-C(6)-O(6)	175.3 (5)
C(7)	90.6 (2)	Cr(2)-C(7)-O(7)	176.0 (5)
C(8)	91.5 (2)	Cr(2)-C(8)-O(8)	177.4 (5)
C(9)	92.8 (2)	Cr(2)-C(9)-O(9)	174.9 (5)
C(10)	179.4 (2)	Cr(2)-C(10)-O(10)	177.9 (6)
C(6)-Cr(2)-C(7)	89.1 (2)	Cr(2)-N(2)-C(16)	118.8 (3)
C(6)-Cr(2)-C(8)	90.4 (2)	Cr(2)-N(2)-C(20)	119.4 (3)
C(6)-Cr(2)-C(9)	174.8 (2)	C(16)-N(2)-C(29)	120.0 (4)
C(6)-Cr(2)-C(10)	87.1 (2)	N(2)-C(16)-C(17)	119.0 (5)
C(7)-Cr(2)-C(8)	177.9 (2)	C(16)-C(17)-C(18)	118.6 (5)
C(7)-Cr(2)-C(9)	90.1 (2)	C(17)-C(18)-C(19)	121.0 (5)
C(7)-Cr(2)-C(10)	89.1 (2)	C(18)-C(19)-C(20)	117.9 (5)
C(8)-Cr(2)-C(9)	90.3 (3)	N(2)-C(20)-C(19)	120.6 (5)
C(8)-Cr(2)-C(10)	88.8 (2)		
C(9)-Cr(2)-C(10)	87.8 (2)		

The four equatorial CO groups in **1**, with an average Cr–C distance of 1.901 (5) Å, are bent slightly away from the piperidine ligand, giving an average N–Cr–C angle of 92.5 (2)°. The axial carbonyl group (trans to the piperidine) has a Cr–C distance of 1.824 (5) Å. The Cr–N(1) distance is 2.204 (3) Å; this is not significantly longer than the same distances in $Cr(CO)_3(dien)_3$,[7] which average 2.185 (6) Å. A best-fit least-square plane through the piperidine ligand (containing N(1) and C(15)) is perpendicular to the plane defined by the equatorial carbonyl groups and forms a dihedral angle of 37.1° with the plane defined by N(1), C(2), C(3), and C(5). The C–N and C–C distances for the atoms in the ring average 1.481 (5) and 1.510 (8) Å, respectively. The average angle within the ring is 111.3 (4)°, and the mean deviation of the six atoms from their mean plane is 0.24 Å.

In the pyridine compound, **2**, the Cr(2)–N(2) distance, 2.194 (4) Å, is identical within experimental error with that of

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

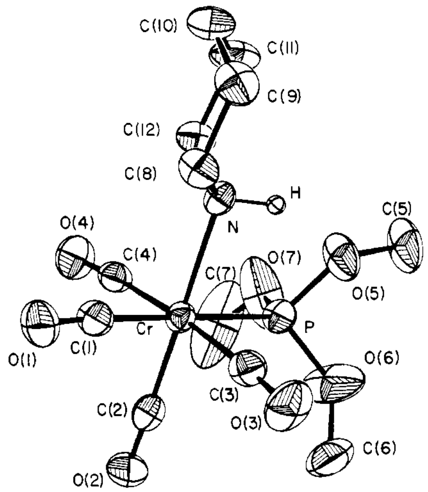

Figure 4. The *cis*-$Cr(CO)_4(C_5H_{10}NH)[P(OMe)_3]$ molecule. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density.

Cr(1)–N(1), 2.204 (3) Å; the difference and its esd are 0.010 (5) Å. The six ring atoms, however, are coplanar within experimental error, the largest deviation of any one atom from the mean plane being 0.04 Å. The average distances and angles within the ring are as follows: C–N, 1.386 (6) Å; C–C, 1.44 (1) Å; angles, 119.5 (5)°. These are very similar to those recently found[8] in $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$, where the average values were 1.37 (1) Å, 1.40 (1) Å, and 120.0 (9)°, respectively. The mean plane of the pyridine ring is perpendicular to the plane defined by the four equatorial carbonyl carbon atoms and bisects the C(6)–Cr(2)–C(8) angle.

Structure of Compound 3. The molecular structure and atom numbering scheme are shown in Figure 4. Table VII lists the bond lengths and angles. Just as the crystals are isomorphous to those of the homologous molybdenum compound, so are the two $M(CO)_4(C_5H_{10}NH)[P(OMe)_3]$ molecules very similar in structure. All of the previous discussion[5] concerning ligand labilization and intramolecular hydrogen bonding are therefore applicable to the chromium compound. In this case the H(1)···O(5) distance, 2.302 (4) Å, is even shorter, although the P–Cr–N angle is not quite so acute; these differences arise from the fact that the Cr–N and Cr–P distances are each about 0.14 Å shorter than their analogues in the molybdenum compound. It may also be noted that the amplitude of thermal vibration for O(5) is approximately half as great as for O(6) and O(7), which is indicative of restraint due to the hydrogen bond.

Infrared Spectra. The infrared spectra of the three compounds in the CO-stretching region are listed in Table I, and two of the spectra are displayed in Figure 5. In accord with the great structural similarity between **1** and **2**, their IR spectra are nearly identical. This near identity is emphasized in Figure 5 in a way that is pertinent to the unanticipated isolation of the crystalline substance containing equimolar amounts of **1** and **2** from a solution of what was assumed to be pure **1**. From Figure 5 it is obvious that if a sample of **1** were contaminated by a small percentage of **2** this would not be evident in the infrared spectrum. The spectrum shown for **1** in Figure 5 was recorded on a sample from the same batch used to obtain the crystals containing **1** and **2**. It is possible that the very weak shoulder on the high-frequency side of the 1933-cm^{-1} band of **1** is caused by a very small amount of **2**. We estimate that no more than 10% of **2** could be present in our bulk sample of **1**.

Table VII. Bond Distances (Å) and Bond Angles (Deg) for $Cr(CO)_4[P(OCH_3)_3](C_5H_{10}NH)$

	A. Distances		
Cr–P	2.316 (2)	O(5)–C(5)	1.462 (7)
Cr–N	2.193 (4)	O(6)–C(6)	1.358 (10)
Cr–C(1)	1.885 (6)	O(7)–C(7)	1.342 (15)
Cr–C(2)	1.842 (7)	N–C(8)	1.498 (6)
Cr–C(3)	1.884 (6)	N–C(12)	1.495 (7)
Cr–C(4)	1.888 (6)	C(8)–C(9)	1.497 (8)
P–O(5)	1.551 (5)	C(9)–C(10)	1.509 (9)
P–O(6)	1.556 (5)	C(10)–C(11)	1.483 (10)
P–O(7)	1.575 (5)	C(11)–C(12)	1.559 (9)
O(1)–C(1)	1.126 (6)	N–H(1)	0.941 (4)
O(2)–C(2)	1.138 (7)	O(5)–H(1)	2.302 (4)
O(3)–C(3)	1.138 (6)		
O(4)–C(4)	1.156 (7)		
	B. Angles		
P–Cr–N	87.5 (1)	P–O(5)–C(5)	124.7 (4)
P–Cr–C(1)	178.0 (2)	P–O(6)–C(6)	133.7 (6)
P–Cr–C(2)	91.8 (2)	P–O(7)–C(7)	127.1 (8)
P–Cr–C(3)	89.4 (2)	Cr–N–C(8)	115.8 (3)
P–Cr–C(4)	91.9 (2)	Cr–N–C(12)	114.6 (3)
N–Cr–C(1)	91.6 (2)	C(8)–N–C(12)	108.4 (4)
N–Cr–C(2)	179.0 (2)	Cr–C(1)–O(1)	176.0 (5)
N–Cr–C(3)	91.4 (2)	Cr–C(2)–O(2)	178.4 (6)
N–Cr–C(4)	92.1 (2)	Cr–C(3)–O(3)	175.5 (6)
C(1)–Cr–C(2)	89.2 (3)	Cr–C(4)–O(4)	175.5 (5)
C(1)–Cr–C(3)	88.8 (2)	N–C(8)–C(9)	113.9 (5)
C(1)–Cr–C(4)	89.9 (3)	C(8)–C(9)–C(10)	110.7 (5)
C(2)–Cr–C(3)	89.2 (3)	C(9)–C(10)–C(11)	109.9 (5)
C(2)–Cr–C(4)	87.3 (3)	C(10)–C(11)–C(12)	109.8 (6)
C(3)–Cr–C(4)	176.2 (3)	N–C(12)–C(11)	111.4 (5)
Cr–P–O(5)	112.7 (2)	Cr–N–H(1)	101.1 (3)
O(6)	122.1 (3)	C(8)–N–H(1)	107.7 (4)
O(7)	119.6 (3)	C(12)–N–H(1)	108.6 (4)
O(5)–P–O(6)	97.2 (4)	C(5)–O(5)–H(1)	142.8 (4)
O(5)–P–O(7)	97.8 (3)	O(5)–H(1)–N	127.1 (3)
O(6)–P–O(7)	102.6 (4)		

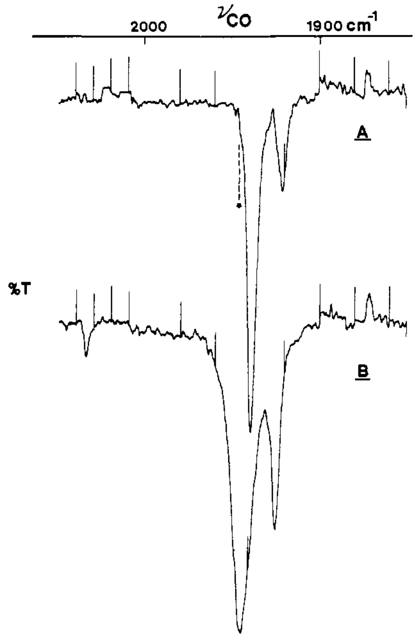

Figure 5. Infrared spectra in the CO-stretching region for $Cr(CO)_5(C_5H_{10}NH)$, A, and $Cr(CO)_5(C_5H_5N)$, B. The A_1 mode of the piperidine compound is too weak to be seen at the concentration used. The asterisk and dotted line show where the strongest band (1939 cm^{-1}) in the $Cr(CO)_5(C_5H_5N)$ spectrum would appear in the spectrum of the piperidine compound. Note that the wavenumber scale changes at 2000 cm^{-1}, as indicated by the 20-cm^{-1} markers.

The Fenske–Hall Calculation. Ours is not the first calculation to be made on $Cr(CO)_6$ by a method of the same basic type. Our results are in general agreement with those of

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(8) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 1287.

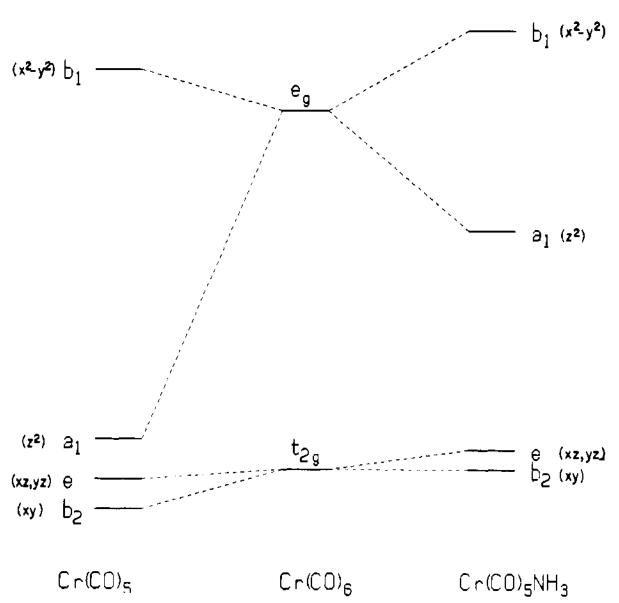

Figure 6. Energies of the metal d orbitals (crudely speaking) for $Cr(CO)_6$ and the two species with C_{4v} symmetry, $Cr(CO)_5$ and $Cr(CO)_5(NH_3)$, derived therefrom, according to a Fenske–Hall calculation.

Caulton and Fenske,[9] who pointed out and discussed the fact that while the method is fairly accurate for ground states (i.e., filled MO's) it is less accurate for electronically excited states when these are formed simply by promotion of an electron from a filled orbital to a calculated virtual orbital. In general, the energy spread of the virtual orbitals is calculated to be too great, although there is no reason to doubt that the correct ordering is given. The calculations reported here were undertaken with this in mind, and we are concerned only with the qualitative features of the results, which are shown schematically in Figure 6.

Discussion

The origin of the $Cr(CO)_5(C_5H_5N)$ that turned up in the crystals containing both $Cr(CO)_5(C_5H_{10}NH)$ and $Cr(CO)_5(C_5H_5N)$ is not known with certainty, but there are two possibilities. The piperidine, which was used as received, could have been contaminated with a small amount of pyridine. Alternatively, the chromium hexacarbonyl, also used as received, was prepared by a process involving pyridine, possibly that shown in the equation below, whereby pyridine itself or $Cr(CO)_5(C_5H_5N)$ could have been carried into the preparation of the $Cr(CO)_5(C_5H_{10}NH)$:

$$Cr(C_5H_7O_2)_3 + Mg + CO \xrightarrow[I_2]{C_5H_5N} \xrightarrow{H_3O^+} Cr(CO)_6 \text{ and other products}$$

It is not clear why the crystals containing equimolar amounts of the different molecules **1** and **2** were obtained, since attempts to selectively precipitate this crystalline substance from a solution of an equimolar mixture of **1** and **2** were unsuccessful.

Structural Comparisons. We have been afforded the opportunity to compare the structures of **1** and **2** using data in which the possibility of systematic error between two different crystal structure determinations has been entirely eliminated.

The most chemically interesting features of these two structures are those that directly pertain to the electronic nature of the piperidine and pyridine ligands. First, since the two molecules have essentially identical structures and nearly identical IR spectra, we must conclude that the pyridine and piperidine are electronically equivalent in these systems. We can discuss the observed geometries as averages of all of the dimensions for both molecules. The important distances then are the following: Cr–C(eq), 1.902 (6) Å; C–O(eq), 1.134 (6) Å; Cr–C(ax), 1.824 (6) Å; C–O(ax), 1.158 (6) Å. The equatorial Cr–C distances are comparable to the average Cr–C distance[10] of 1.913 (2) Å in $Cr(CO)_6$, and the large difference between the equatorial and axial bond lengths (0.078 Å) is indicative of the good donor properties of the amine ligands. In fact, the magnitude of this difference is as great as the analogous shift observed for $Cr(CO)_5(SPMe_3)$[11] and $[Cr(CO)_5(O_2CCF_3)]^-$[12] where the two ligands were considered to act solely as σ-electron donors with no π component present in the Cr–L bond. In agreement with this are the results reported for $Cr(CO)_5L$ where L is a π acid. In cases such as L = $[C(SC_6H_5)CH_3]$, $[C(C_6H_5)OCH_3]$, or $P(OC_6H_5)_3$ the difference between the Cr–C(eq) and Cr–C(ax) distances are much smaller (0.011–0.036 Å).[11] On the basis of these simple structural parameters, then, we conclude that the piperidine and pyridine ligands bind to the $Cr(CO)_5$ fragments as good σ donors, with virtually no π-acceptor interaction in either case.

As further structural evidence in this context, we can consider the complex *cis*-$Cr(CO)_4[P(OCH_3)_3](NHC_5H_{10})$. The molecular structure of this compound provides, within one molecule, a comparison of the effects of a non-π-acceptor ligand and a relatively good π-acceptor ligand. The two mutually trans CO groups have Cr–C distances of 1.886 (6) Å, which is the same as the Cr–C distance trans to the $P(OMe)_3$ ligand, 1.885 (6) Å. The remaining CO group, trans to the piperidine, has an associated Cr–C bond length that is considerably shorter at 1.842 (7) Å. This is exactly as we would have expected for a non-π-acceptor ligand. The existence of a smaller variation among the Cr–C bond lengths found here is also predictable. The $Cr(CO)_4[P(OCH_3)_3]$ moiety, in contrast to the $Cr(CO)_5$ fragment, should show more back-bonding to all of its four CO ligands since the $P(OMe)_3$ ligand is more basic in a σ sense and less acidic in a π sense than CO.

Electronic Structure of $Cr(CO)_5$(amine) Compounds. The point of particular interest here goes back to a proposal[13] made in 1973 that upon (a) removal of one CO group from $Cr(CO)_6$ followed by (b) introduction of an amine ligand, the t_{2g} and e_g subsets of the metal d orbitals in $Cr(CO)_6$ would split further, in the patterns shown in Figure 7a. The arguments regarding $Cr(CO)_5$ are straightforward and not in question. Removal of a σ-donating and π-accepting ligand from one position (taken to be on the +*z* axis) has to cause the splittings shown, with the $a_1(d_{z^2})$ orbital becoming more stable than the $b_1(d_{x^2-y^2})$ orbital and with the $e(d_{xz},d_{yz})$ orbitals becoming less stable than the $b_2(d_{xy})$ orbital. The next step in the argument was that on introducing a new ligand, such as an amine, which is an even better σ donor than CO, but not a π acceptor, the $a_1(d_{z^2})$ orbital should be raised to an even higher energy than it had with CO in the +*z* position, while the e > b_2 pattern should remain essentially the same.

It has been shown conclusively, however, by MCD data,[14] and other indications have appeared,[15,16] for several $M(CO)_5$(amine) species, that the splitting pattern is as shown in Figure 7b. This raises the questions of what was wrong with

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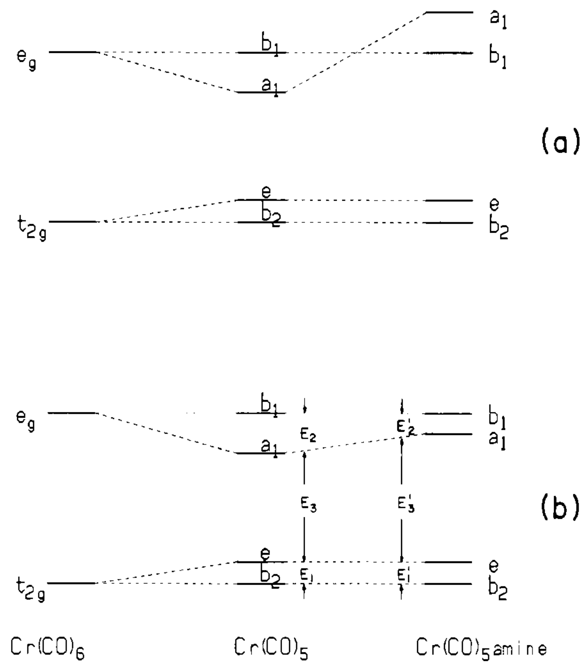

Figure 7. Some orbital splitting patterns for the d orbitals of Cr(CO)$_6$ on changing to Cr(CO)$_5$ and Cr(CO)$_5$(amine).

the previous reasoning and whether the experimental result is predictable by a semiquantitative calculation, for example, a calculation of the Fenske–Hall type.

The answer to the first question is really rather simple, in retrospect. The level pattern for Cr(CO)$_5$ in Figure 7a is correct (and is therefore repeated in Figure 7b). It is also true that the introduction of a σ donor, NR$_3$, into the vacant position of Cr(CO)$_5$ must raise the energy of the a_1 orbital. The crucial point, however, that even though NR$_3$ is *potentially* a better σ donor than CO, *other things being equal*, other things are not at all equal. The Cr–C distances, 1.82–1.91 Å, are so much shorter than the Cr–N distances, ca. 2.20 Å, that *in these molecules, CO functions as a stronger σ donor than the amine ligands.* Thus, the introduction of NR$_3$ into Cr(CO)$_5$ raises the energy of the a_1 orbital so that it is *less far below* the b_1 orbital, but it does not push it *above* the b_1 orbital, because NR$_3$ is too far from the metal atom to exert that strong a σ effect. Schematically, then, the behavior of the Cr(CO)$_6$–Cr(CO)$_5$–Cr(CO)$_5$NR$_3$ series is represented by Figure 7b. This type of pattern is predicted, though not with quantitative correctness, by the Fenske–Hall calculation, as shown in Figure 6.

From the experimental data[13,14] we may say that the actual splitting energies in Figure 7b have approximately the following values: $E_0 \approx 32\,000$ cm^{-1}; $E_1 \approx E_1' \approx 5000$ cm^{-1}; $E_2 \approx 11\,000$ cm^{-1}; $E_2' \approx 4000$ cm^{-1}; $E_3 \approx 16\,000$ cm^{-1}; $E_3' \approx 23\,000$ cm^{-1}. These give an internally consistent pattern, with $E_1 + E_2 + E_3 \approx E_0$ and $E_1' + E_2' + E_3' \approx E_0$.

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Supplementary Material Available: Tables of observed and calculated structure factors for both crystals (16 pages). Ordering information is given on any current masthead page.

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Hydrocarbon-Bridged Vanadocenes[1]

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Bent vanadocene units have been linked by hydrocarbon bridges. It is shown that the stability of the new compounds depends on the substitution of the Cp rings. Apart from analytical and mass spectroscopic data, characterization is based on NMR spectroscopy. The molecular structure of (C$_5$H$_4$CH$_3$)$_2$VC$_6$H$_4$V(C$_5$H$_4$CH$_3$)$_2$ has been determined by X-ray analysis. Covering a range of up to 190 ppm for ^{1}H and 760 ppm for ^{13}C, NMR spectroscopy has proved to be a sensitive probe for magnetic properties. It is shown that the four electrons per molecule remain essentially unpaired. The stereochemistry derived from NMR data agrees well with X-ray results.

Introduction

Metal–metal interactions may occur directly via overlapping metal orbitals in simple dimers[2] or in cluster molcules.[3] Most evidence for this comes from structural work, and diamagnetic organometallic compounds have been of prominent interest.[3] A different type of interaction is found when bridging groups prevent direct overlap and metals "know about each other" via transmitting orbitals of the bridge. This may be derived from the magnetism of transition-metal complexes,[4] most of which do not contain metal–carbon bonds.

However, organometallics bridged by acetylenes should also exhibit metal–metal interactions as pointed out by Kim et al.,[5] although they were not able to prove it. Tsutsui et al.[6] synthesized two bridged tris(cyclopentadienyl)uranium derivatives and carried out solid-state magnetic measurements. They found a remarkably reduced susceptibility for the bridged molecules. Whether this is due to an intermolecular or an

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