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Semiempirical Molecular Orbital Calculations. V. The Electronic Structure of Arenechromium Tricarbonyls and Chromium Hexacarbonyl[1a]

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Charge and configuration self-consistent Mulliken–Wolfsbefg–Helmholz calculations were performed on $XC_6H_5Cr(CO)_3$ molecules (X = H, NH_2) and on $Cr(CO)_6$. The results have been used to describe the bonding in these molecules and to discuss the main features of their electronic spectra.

Introduction

The nature of the bonding in organometallic π complexes and carbonyls of the transition metals has been qualitatively understood for some time and a number of quantitative and semiquantitative calculations have been performed.[2-20] The calculations upon sandwich complexes (ferrocene, dibenzenechromium, etc.) have considered only the π orbitals of the rings and those upon the half-sandwich complexes or arenemetal carbonyls have usually neglected the carbonyls. The importance of the σ orbitals of the ring in ring–metal bonding can be seen from the overlaps quoted in Table I. Some of the overlaps which are neglected (*i.e.*, those involving the 2s and $2p_\sigma$ orbitals of the ring) are larger than those which are included by considering the ring $2p_\pi$ orbitals alone. This is not to suggest that overlap alone determines the extent of interaction between orbitals; however, it does give some indication. The carbonyl groups must also be included in any quantitative calculations upon the arenemetal carbonyls, especially if one wishes to discuss the electronic spectra.[21-23]

The present paper reports the results of semiempirical molecular orbital calculations in which all of the valence orbitals of the molecules considered have been included.

Method of Calculation

The computational scheme used has been described briefly elsewhere.[24] For benzenechromium tricarbonyl ($C_6H_6Cr(CO)_3$) the bond lengths used were: Cr–C(ring) = 2.19 Å; Cr–C(CO) = 1.88 Å; Cr–O = 3.06 Å. For the benzene moiety the distances used were: C–C = 1.40 Å and C–H = 1.10 Å. The angles CO–Cr–CO were taken to be 90° and the carbonyl groups were assumed to be eclipsed with respect to three alternate carbon atoms in the ring. This is an idealization of the structure published recently by Bailey and Dahl,[25] who showed that the carbonyls were staggered with respect to the ring carbons; however, this should not affect the results to any significant degree, especially as there is probably free rotation of the benzene ring in solutions. The z axis coincided with the threefold axis of the molecule and the benzene ring lay in the xy plane. In the aniline complex $[NH_2C_6H_5Cr(CO)_3]$ the C(ring)–N distance was taken to be 1.426 Å and the N–H distance to be 1.036 Å. The NH_2 group was made copolanar with the ring and was attached to a carbon atom positioned directly above one of the CO groups.[26] Otherwise, the parameters were the same as in the benzene complex. Similar calculations were also performed upon free aniline and benzene for comparison using the C–C and C–H distances quoted above. In $Cr(CO)_6$ the Cr–C distance used was 1.92 Å and the Cr–O distance was 3.08 Å. A calculation was also performed on molecular CO (carbon monoxide) using an interatomic distance of 1.128 Å. The Coulomb integrals (H_{ii}) for the chromium 3d, 4s, and 4p orbitals were obtained as a function of atomic charge and orbital population by fitting suitable expressions to the data given by Ballhausen and Gray.[27] For the carbon, nitrogen, and oxygen 2s and 2p orbitals, the Coulomb integrals were taken from the tabulation by Cusachs

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TABLE I

SOME CHROMIUM–CARBON (RING) OVERLAP INTEGRALS[a]

Orbitals, chromium ring	SCF overlap[b]	Overlap-matched overlap[c]
4s–2s	0.330	0.338
4s–$2p_\sigma$	0.236	0.241
$3d_\sigma$–2s	0.125	0.112
$3d_\sigma$–$2p_\sigma$	0.130	0.148
$3d_\pi$–$2p_\pi$	0.094	0.090
$4p_\sigma$–2s	0.436	0.446
$4p_\sigma$–$2p_\sigma$	−0.003	0.007
$4p_\pi$–$2p_\pi$	0.207	0.195

[a] At 4.2 au. [b] The chromium orbitals are taken from J. W. Richardson, *et al.*, *J. Chem. Phys.*, **36**, 1057 (1962); **38**, 796 (1963). They are identified as follows: 3d: Cr^+ ($3d^5$); 4s: Cr^0 ($3d^44s^2$); 4p: Cr^0 ($3d^54p^1$). The carbon orbitals are taken from E. Clementi, Tables of Atomic Functions, supplement to paper in *IBM J. Res. Develop.*, **9**, 2 (1965); the double ζ functions used are those for the C^0 ($2s^22p^2$), ^3P term. [c] See Table IV and L. C. Cusachs, D. G. Carroll, B. L. Trus, and S. P. McGlynn, *Intern. J. Quantum. Chem.* (Slater Issue), in press.

and Reynolds,[28] modified as described in ref 24. The equation used for the hydrogen 1s orbital was taken from ref 24. For a given atom, orbitals with the same n and l quantum numbers were given the same value of H_{ii}; in other words, the populations of the three carbon 2p orbitals were averaged in calculating H_{ii}. This was done to keep the calculation rotationally invariant[29] even though there are strong arguments for using a smaller H_{ii} for the carbon $2p_\pi$ orbitals of the ring than that used for the $2p_\sigma$'s.[30]

The resonance integrals (H_{ij}) were obtained using Cusachs' expression[31]

$$H_{ij} = 0.5(2 - |S_{ij}|)(H_{ii} + H_{jj})S_{ij}$$

applied as described in ref 32.

Wave Functions.—In order to keep the computational time to a minimum, it was considered best to use only one Slater-type function for each orbital. On the other hand, it is known that this type of function, with Slater's original orbital exponents, can lead to serious errors as compared with the more accurate functions which are available.[33] As a result, it has become almost a necessity to use SCF functions,[34–36] especially for transition metal d orbitals. However, even here there are opportunities, if not for error, then at least for large uncertanties.

TABLE II

$2p_\sigma$–$2p_\sigma$ AND $2p_\pi$–$2p_\pi$ OVERLAP INTEGRALS FOR DIFFERENT ATOMIC STATES OF CARBON[a]

	^3P		^1S		^1D	
R, au	σ	π	σ	π	σ	π
2.6	0.235	0.330	0.175	0.378	0.212	0.349
4.6	0.196	0.078	0.216	0.113	0.206	0.091

[a] Multi-ζ wave functions for the different states of the configuration $2s^22p^2$ are taken from ref 36, Table 01–03.

As an illustration, the carbon–carbon $2p_\sigma$–$2p_\sigma$ and $2p_\pi$–$2p_\pi$ overlaps calculated using Clementi's many-term SCF functions for the ^3P, ^1S, and ^1D states of the configuration $2s^22p^2$ are given in Table II. The differences are considerable and would probably be greater if the states arising from the configuration $2s2p^3$ (which is actually the more likely for carbon in benzene) were included. The same is true in the case of the overlaps between various chromium 3d and carbon 2p orbitals quoted in Table III. In the case of the chromium 4s orbital, the SCF wave function usually used is taken from Cr(I) with configuration $3d^44s^2$, whereas in transition metal complexes it is more likely to be Cr(II), and the 4s-orbital population is usually quite small.[37]

TABLE III

SOME CHROMIUM 3d–CARBON 2p OVERLAP INTEGRALS AT 4.2 AU FOR VARIOUS WAVE FUNCTIONS

Chromium	Carbon	σ	π
Cr^+ ($3d^5$)[a]	C^0, ^3P[a]	0.111	0.090
Cr^0 ($3d^44s^2$)[a]	C^0, ^1S[a]	0.089	0.080
Cr^0 ($3d^6$)[b]	C^0, ^3P[a]	0.148	0.128
Cr^0 ($3d^6$)[b]	C^0, ^1S[a]	0.139	0.136
Cr^+ ($3d^5$)[b]	C^0, ^3P[a]	0.127	0.093
Cr^+ ($3d^5$)[b]	C^0, ^1S[a]	0.120	0.100

[a] See ref 36. [b] See ref 35.

It is possible to find a single Slater-type function which will reproduce the overlap of a given many-term SCF function over the range of chemically significant interatomic distances; the uncertainty thereby engendered will be of the same order as that surely intrinsic to choice of any atomic SCF function as a representation of the orbital in a molecular environment.[38] The orbital exponents so found and used here are given in Table IV. The hydrogen 1s-orbital exponent used was 1.0 rather than the value 1.2 which appears to be better suited to hydrogen in a molecule. This was done to keep the treatment uniform, inasmuch as the wave functions used for the other atoms were all for the free-atom case. Some chromium–carbon overlaps obtained using the overlap-matched wave functions are compared with the SCF values in Table I; the agreement is reasonable. It must be stressed, however, that these approximate overlap-matched wave functions are useful only for the calculation of overlaps; however, as the energy terms required in the calculation are obtained from valence state ionization potentials (VSIP's) and not from the wave functions, this represents no difficulty.

Procedure.—Intial charge and configuration were chosen for each atom and the corresponding H_{ii}'s and H_{ij}'s were calculated. The resulting secular equation $|H_{ij} - S_{ij}E| = 0$ was solved for eigenvalues and eigenvectors and a Mulliken population analysis[39] was per-

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TABLE IV

OVERLAP-MATCHED ORBITAL EXPONENTS USED IN THIS WORK[a]

Atom	Proper orbital	Overlap-matched orbital	Overlap-matched orbital exponent[b]
Carbon	2s	1s	1.02
Carbon	2p	2p	1.42
Hydrogen	1s	1s	1.0
Oxygen	2s	1s	1.42
Oxygen	2p	1p	1.23
Nitrogen	2s	1s	1.22
Nitrogen	2p	2p	1.69
Chromium	3d	3d	2.17
Chromium	4s	4s	1.31
Chromium	4p	4p	0.77

[a] See ref 38 for a full discussion of the overlap-matched wave functions. [b] The overlap-matched orbitals were Slater type and of the form: $\varphi(n, l, m, Z) = r^{n-1} \exp(-Zr) Y_l^m(\theta, \phi)$, where Z is the orbital exponent.

formed in which the overlap populations were divided equally among the two basis functions involved; from this, a new set of charges and configurations was calculated. When the difference between the input and output charges was less than 0.01 charge unit, the calculation was said to be self-consistent.

A set of three programs was coded for the IBM 7040. The first program calculated the full overlap matrix, including all ligand–ligand overlaps, from the atomic coordinates and orbital descriptions; this matrix, together with an initial guess at the orbital populations and atomic charges, served as input for the second program which solved the secular equation, performed a Mulliken population analysis, and checked for charge self-consistency. The third program[40] took the final wave functions and calculated transition moments for the transitions of interest, as well as the transfer of charge involved in these transitions.

At this point, even though it is admitted that various forms of the Mulliken–Wolfsberg–Helmholz method have found wide application in recent years, it must be stressed that the MWH method is, as yet, without any real theoretical justification. Indeed, several authors[41,42] have warned against the dangers of using the results of semiempirical calculations as anything more than very crude indicators. This is particularly true when dealing with excited-state properties; therefore, the following discussion, especially that part of it concerned with assignments of electronic transitions, must be viewed in this light.

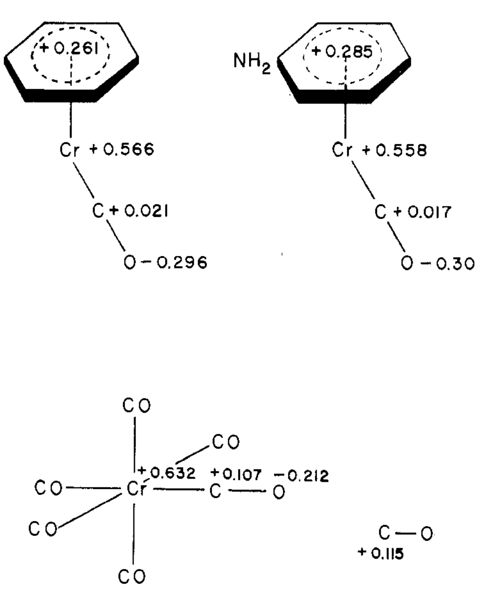

Figure 1.—Self-consistent charge distributions.

Results and Discussion

The MO wave functions obtained are not presented here for reasons of space.[43] The final charge distributions are shown in Figure 1. In preliminary calculations, the chromium 4s and 4p orbitals had negative populations at charge self-consistency[44] (4s = −0.118, 4p = −0.554 in $C_6H_6Cr(CO)_3$). This was taken to mean that, within the limits of the treatment given here, the 4s and 4p orbitals were not important in the ground state;[45] therefore, these orbitals were omitted in the final calculations.[46] It is possible that by a judicious choice of orbital exponents and/or coulomb integrals for the 4s and 4p orbitals, or by calculating the charges in a different manner,[47] small positive populations would have been obtained. However, this probably would not have affected the results obtained in any significant manner.

There is, as one would expect,[48] a net charge transfer from the ring to the metal in the arenemetal tricarbonyl complexes, more in the case of the aniline complex than the benzene complex: 0.285e and 0.261e, respectively. Despite this, the chromium is positively charged because of the electron-withdrawing effect of the carbonyl groups. The traditional view of metal–carbonyl bonding calls for donation of charge by the σ orbitals of the carbonyl and a back donation from the metal to the carbonyl π orbitals.[49–51] In the cases considered here it appears that the π back donation is by far the larger (0.64 e per CO group as opposed to 0.534 e for the forward σ donation to the metal[52]). The charge-

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(40) L. C. Cusachs and B. L. Trus, *J. Chem. Phys.*, in press.

(41) (a) R. F. Fenske, *Inorg. Chem.*, **4**, 33 (1965); (b) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(42) (a) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 1004 (1964); (b) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 369 (1967).

(43) The MO coefficients, orbital energies, and orbital populations for the molecules considered have been deposited as Document No. 10012 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(44) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

(45) C. K. Jørgensen, S. M. Homer, W. E. Hatfield, and S. Y. Tyree, Jr., *Intern. J. Quantum Chem.*, **1**, 191 (1967).

(46) However, the 4s and 4p orbitals were found to play an important role in bonding in $Ni(CO)_4$: W. C. Nieuwpoort, Ph.D. Dissertation, University of Amsterdam, Amsterdam, 1965.

(47) For example, one could use orthogonal or Löwdin orbitals (P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950)) in carrying out the Mulliken population analysis, or the overlap populations might be divided in the ratio of the one-center populations, instead of being equally divided between the two orbitals involved.

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

(49) L. E. Orgel, "An Introduction to Transition Metal Chemistry," Methuen, London, 1960, p 135.

(50) G. Doggett, *Trans. Faraday Soc.*, **61**, 392 (1965).

(51) W. C. Nieuwpoort, Ph.D. Dissertation, University of Amsterdam, Amsterdam, 1965.

(52) See, however, ref 51 where, in a nonempirical calculation on $Ni(CO)_4$, the π back donation was found to be less than the σ donation to the metal.

self-consistent Mulliken–Wolfsberg–Helmholz method has been criticized recently[45] in that it apparently underestimates the ionic character of the bonding in transition metal complexes. However, the dipole moments calculated from the Mulliken point charges obtained in this work are larger than the experimental values—see Table V. This method of calculation is, of course, an approximation to the correct dipole moment, but Newton, *et al.*,[30] have shown that it does in many cases give a value close to the correct one (correct, that is, so far as the input wave functions are concerned). It is impossible to say whether or not the above criticism is correct,[53] for the absolute values of the atomic charges in a molecule are not quantities which can be directly measured. What is more important in semiempirical calculations is how variations in measurable quantities are predicted. The results in Table V predict the dipole moment of the aniline complex to be greater than that of the benzene complex, in agreement with experiment; furthermore, the ratio of the calculated to the experimental values is the same (1.874) in both the aniline and benzene complexes.

Table V

Calculated and Experimental Dipole Moments (μ) for the Aniline and Benzene Complexes in Debye Units

Compound	μ_{calcd}	$\mu_{\text{exptl}}{}^{a}$	$\mu_{\text{calcd}}/\mu_{\text{exptl}}$
$NH_2C_6H_5Cr(CO)_3$	10.12	5.40	1.87
$C_6H_6Cr(CO)_3$	9.52	5.08, 4.92	1.87

[a] See E. O. Fischer and S. Schreiner, *Chem. Ber.*, **92,** 938 (1959); E. W. Randell and L. E. Sutton, *Proc. Chem. Soc.*, 93 (1959); W. Strohmeier and H. Hellman, *Ber. Bunsenges. Physik. Chem.*, **68,** 481 (1964).

Strohmeier and Hellmann[54] have discussed the partial dipole moments in metal carbonyl derivatives. They took a value of 0.8 D for the M–CO partial dipole moment in $Cr(CO)_6$, the carbonyl group being considered positively charged. This then was used to calculate the M–ring partial dipole moment (5.80 D) in $C_6H_6Cr(CO)_3$ using the experimental total μ and assuming the ring to be positive. There is little justification for the assumption made by Strohmeier and Hellmann that the same M–CO partial μ will apply in both $Cr(CO)_6$ and $C_6H_6Cr(CO)_3$. In the calculations reported here, the Cr–CO partial μ obtained in $Cr(CO)_6$ is 2.15 D, the carbonyl group being negative, or, using the reduction factor of 1.874 mentioned before, 1.15 D; this is indeed close to the value used by Strohmeier and Hellmann but it is in the opposite direction. In $C_6H_6Cr(CO)_3$ the Cr–CO partial μ is found to be 4.17 D (reduced, 2.22 D) and the ring–Cr partial μ is found to be 2.12 D (reduced, 1.13 D), the values in parentheses being $\mu_{\text{calcd}}/1.874$.

A final observation with regard to the dipole moments of half-sandwich complexes concerns the variation of the dipole moments with ring substituents. This variation (*i.e.*, μ being greater for electron-donating substituents and smaller for electron-withdrawing ones) has been suggested as a "proof" for net charge transfer to the metal from the ring. This, however, is an invalid suggestion because the same variation would occur even if the ring were negatively charged provided the carbonyl groups were more so.

Infrared Spectra.—A qualitative picture of the bonding in transition metal π complexes involves a donation of charge from the arene to the metal and then in turn from the metal to the carbonyl groups, increasing the strength of the M–CO bond as compared with $M(CO)_6$ and decreasing the C–O bond strength as compared with CO and $M(CO)_6$. An electron-donating substituent on the ring, such as an amino group, should increase the charge transfer to the metal and further increase the M–CO bond order while at the same time reducing the C–O bond order as compared with the unsubstituted complex. These predictions have been confirmed using the variations in the C–O and M–CO infrared stretching frequencies as a function of ring substituent.[7,55,56] In Table VI we compare the C–O force constants with the calculated C–O overlap populations. The Cr–CO overlap populations are also given. The decreasing C–O force constant on going from CO to $NH_2C_6H_5Cr$-

Table VI

Force Constants [k (mdynes/Å)] for the C–O Bond Compared to the C–O and Cr–CO Overlap Populations

Molecule	k_{C-O}	C–O overlap population	Cr–CO overalp population
CO	18.53[a]	1.385	. . .
$Cr(CO)_6$	16.49[b]	1.317	0.415
$C_6H_6Cr(CO)_3$	11.95[c]	1.216	0.537
$NH_2C_6H_5Cr(CO)_3$	11.76[c]	1.212	0.540

[a] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 193. [b] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2,** 553 (1963). [c] See ref 55.

Table VII

The Spectroscopically Important MO's and Energies (eV) for $Cr(CO)_6$, $C_6H_6Cr(CO)_3$, and $NH_2C_6H_5Cr(CO)_3$

$Cr(CO)_6$		$C_6H_6Cr(CO)_3$		$NH_2C_6H_5Cr(CO)_3$	
. . .		. . .		6a′	−6.07
$2e_g$	3.67	8e	−5.40	5a″	−6.11
$2t_{1g}$	−5.92	$3a_1$	−6.11	4a″	−6.30
$2t_{2g}$	−6.46	$2a_2$	−6.14	5a′	−6.33
$2t_{1u}$	−6.74	7e	−6.33	4a′	−6.56
t_{2u}	−7.54	6e	−6.72	3a″	−6.69
$1t_{2g}$	−12.01	$2a_1$	−10.66	3a′	−10.60
$1t_{1u}$	−12.79	5e	−10.78	2a′	−10.64
$1e_g$	−13.77	4e	−11.67	2a″	−10.72
a_{1g}	−14.58	3e	−12.46	1a′	−11.02
$1t_{1g}$	−14.94	$1a_1$	−12.76	1a″	−11.75
. . .		2e	−12.87	. . .	
. . .		$1a_2$	−13.71	. . .	
		1e	−13.98	. . .	
		. . .			
		. . .			

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(53) G. Berthier, P. Millie, and A. Veillard, *J. Chim. Phys.*, **62,** 8 (1965). have argued that the metal charges in transition metal complexes should be less than +1.0.

(54) W. Strohmeier and H. Hellmann, *Ber. Bunsenges. Physik. Chem.*, **68,** 481 (1964).

(55) D. A. Brown and D. G. Carroll, *J. Chem. Soc.*, 2822 (1965).

(56) D. A. Brown and J. R. Raju, *ibid., Sect. A*, 1617 (1966).

TABLE VIII

CALCULATED AND OBSERVED TRANSITION ENERGIES

Assignment	Polarization[a]	Calcd one-electron energy cm^{-1}	$\|D\|$, Å^2	Obsd band maxima, cm^{-1}	Direction of charge transfer
		$Cr(CO)_6$ Molecule (O_h)			
$A_{1g} \rightarrow T_{1u}\ (1t_{2g} \rightarrow t_{2u})$		36,060	1.37	35,780	Cr → CO
$A_{1g} \rightarrow T_{1u}\ (1t_{2g} \rightarrow 2t_{1u})$		42,550	0.92	44,480	Cr → CO
$A_{1g} \rightarrow T_{1u}\ (1t_{1u} \rightarrow 2t_{2g})$		51,100	0.40	51,280	CO → Cr
$A_{1g} \rightarrow T_{1u}\ (1t_{1u} \rightarrow 2t_{1g})$		55,430	0.39	See ref 48	Confined to carbonyls alone
		$C_6H_6Cr(CO)_3$ Molecule (C_{3v})			
$A_1 \rightarrow E\ (5e \rightarrow 6e)$	*xy*	32,750	0.38	26,620	Cr → ring
$A_1 \rightarrow A_1\ (5e \rightarrow 6e)$	*z*	32,750	1.50	31,220	
$A_1 \rightarrow E\ (2a_1 \rightarrow 7e)$	*xy*	34,850	1.24	38,480	Cr → CO
$A_1 \rightarrow E\ (5e \rightarrow 7e)$	*xy*	36,060	0.17	Hidden	Cr and ring → CO
$A_1 \rightarrow A_1\ (5e \rightarrow 7e)$	*z*	36,060	0.08		
$A_1 \rightarrow A_1\ (2a_1 \rightarrow 3a_1)$	*z*	36,700	0.40	45,410	Cr → CO
$A_1 \rightarrow E\ (5e \rightarrow 2a\ )$	*xy*	37,430	0.50		Cr and ring → CO
		$NH_2C_6H_5Cr(CO)_3$ Molecule (C_s)			
$A' \rightarrow A''\ (2a' \rightarrow 3a'')$	*x*	31,860	0.16	~26,000 and ~31,000	Cr → ring and CO
$A' \rightarrow A'\ (2a'' \rightarrow 3a'')$	*yz**	32,510	0.86		
$A' \rightarrow A'\ (2a' \rightarrow 4a')$	*yz**	32,910	0.69		
$A' \rightarrow A''\ (2a'' \rightarrow 4a')$	*x*	33,560	0.14		
$A' \rightarrow A'\ (3a' \rightarrow 4a')$	*y*z*	34,440	0.61	~38,500	Cr → CO
$A' \rightarrow A''\ (3a' \rightarrow 4a'')$	*x*	34,600	0.63		
$A' \rightarrow A'\ (2a' \rightarrow 5a')$	*yz*	34,845	0.14	Hidden	Ring and Cr → CO
$A' \rightarrow A''\ (2a' \rightarrow 4a'')$	*x*	35,000	0.01		
$A' \rightarrow A''\ (2a'' \rightarrow 5a')$	*x*	35,460	0.03		
$A' \rightarrow A'\ (2a'' \rightarrow 4a'')$	*yz**	35,640	0.11		
$A' \rightarrow A'\ (1a' \rightarrow 4a')$	*yz**	35,970	0.30	~40,500	N → CO
$A' \rightarrow A'\ (3a' \rightarrow 6a')$	*yz**	36,540	0.40	~45,500	Cr → CO
$A' \rightarrow A''\ (2a' \rightarrow 5a'')$	*x*	36,540	0.37		Cr and ring → CO
$A' \rightarrow A'\ (2a'' \rightarrow 5a'')$	*y*z*	37,184	0.50		

[a] The asterisked components make the larger contribution to oscillator strength and polarization.

$(CO)_3$ is matched, very nearly linearly, by a decreasing C–O overlap population and, at the same time, by an increasing M–CO overlap population.[55]

The carbon–carbon overlap population in the benzene complex is calculated to be 1.11 as compared with a value of 1.19 in free benzene. This agrees with the observation by Humphrey[57] that complexing causes a shift to longer wavelengths in the carbon–carbon stretching frequency. Complexing has little effect upon the vibrational frequencies of the amino N–H bonds,[58] and the N–H overlap populations in both the complexed and free aniline are, indeed, the same (0.735).

Electronic Spectra.—The electronic spectra of arene-metal tricarbonyls and metal hexacarbonyls have been reported and discussed by several workers.[13,21–23] The spectrum of $Cr(CO)_6$ shows intense bands at 35,780 and 44,480 cm^{-1} and a shoulder at 51,280 cm^{-1}; the $C_6H_6Cr(CO)_3$ complex shows intense bands at 45,410, 38,480, and 31,220 cm^{-1} and a shoulder at 26,620 cm^{-1}. Beach and Gray[13] considered the two intense bands in $Cr(CO)_6$ (35,780 and 44,480 cm^{-1}) to be due to charge-transfer bands $^1A_{1g} \rightarrow {}^1T_{1u}$ from the chromium to the carbonyls and the shoulder at 51,280 cm^{-1} to be a forbidden $t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ transition. Ercoli and Mangini[21] suggested that the 31,220-cm^{-1} band in $C_6H_6Cr(CO)_3$ was a charge-transfer band from the chromium to the benzene ring, and Yamada, *et al.*,[22] considered both the 31,220- and 38,480-cm^{-1} bands to be of this type. Cais and Lindquist[23] suggested that the intense band observed at around 39,000 cm^{-1} in all carbonyl and half-sandwich complexes was due to transitions involving the metal–carbon bond.

The spectroscopically important MO energies are listed for the aniline and benzene complexes and for $Cr(CO)_6$ in Table VII, a dashed line being drawn above the highest filled orbital in each case. The predicted transitions are listed in Table VIII together with the values of $|D|^2$ where

$$|D|^2 = \left|\int \Psi_1^* \vec{r}\, \Psi_2 d\tau\right|$$

In $Cr(CO)_6$ the first two intense bands are calculated to be strongly allowed transitions involving charge transfer from the chromium to the carbonyl groups. The shoulder at 51,280 cm^{-1} is then assigned as an allowed charge-transfer band with the charge transfer

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(57) R. E. Humphrey, *Spectrochim. Acta*, **17**, 93 (1961).

(58) H. Sloan, Ph.D. Dissertation, National University of Ireland, Dublin, 1962.

from the carbonyls to the chromium.[59] There is a fourth allowed transition predicted at higher energies which does not involve the chromium orbitals at all, although if the chromium 4p orbitals had been included, they would have been involved in the $1t_{1u}$ MO to some extent.

A feature of the spectrum which the present treatment does not properly represent is the d–d transition $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$. The calculated t_{2g}–e_g splitting is far too large. This is caused, in part, by the large charge dependence of the chromium 3d Coulomb integrals and also by the fact that the e_g chromium 3d orbitals were given the same Coulomb integrals as the t_{2g} orbitals, causing them to interact too strongly with the carbonyl groups. A smaller (less negative) H_{ii} would have been preferable for the e_g 3d orbitals, but, in order to preserve the rotational invariance of the results, all of the 3d orbitals had to be assigned identical H_{ii} values.

For our purposes the spectrum of $C_6H_6Cr(CO)_3$ can be divided into three regions.

(i) In the region below 34,500 cm^{-1} there is a peak at 31,220 cm^{-1} and a shoulder at 26,620 cm^{-1}. The two transitions calculated to occur at 32,750 cm^{-1} are assigned to this region. They both involve charge transfer from the chromium to the ring and, to a lesser extent, to the carbonyl groups. The transition polarized along the z direction is predicted to be much stronger than that polarized in the xy plane.[21]

(ii) The next transition (38,480 cm^{-1}) is clearly seen in the spectrum of the benzene complex, although it is not so well resolved in the other arene complexes. It is predicted to be a charge-transfer band from the chromium to the carbonyls.

(iii) In the region above 41,500 cm^{-1} there is a peak at 45,410 cm^{-1}. This transition involves charge-transfer transitions from the ring and the chromium to the carbonyls.

The spectrum of the aniline complex is very similar to that of the benzene complex except for a somewhat greater intensity at the peak in region (iii) and a considerably greater intensity at about 40,500 cm^{-1}. The calculations on the aniline complex allow the molecule only C_s symmetry. However, with free rotation of the ring it should have effective C_{3v} symmetry so that the broadening of the bands due to the splitting of the doubly degenerate transitions would not be as great as Table VIII suggests. All of the bands predicted to occur in the aniline complex can be correlated with those in the benzene complex and suggest the same assignments as given there, except for the one band calculated to occur at 35,970 cm^{-1}. This band involves charge transfer from the nitrogen of the amino group to the carbonyls and may account for the increased intensity at the longer wavelength portion of region (iii) seen in the experimental spectrum. It is also seen that the three transitions which make up the intense portion of region (iii) are predicted to be more intense in the aniline complex than in the benzene complex; this agrees with experiment.

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(59) It should be pointed out, however, that the inclusion of electron repulsion might well alter this picture. In the first two transitions involving electron transfer from orbitals localized on the chromium to orbitals delocalized over the carbonyls energy would be released, thereby lowering the calculated transition energies. This would increase the likelihood that the assignments given here for these bands are correct. However, for the third transition the opposite effect would hold and the change in electron repulsion on going from a delocalized orbital to one localized on the chromium would increase the calculated transition energy, possibly moving it completely out of the range of interest. The fourth predicted band would not be affected in this manner since both of the MO's involved are delocalized on the carbonyls; thus, it might well be better to associate the shoulder at 51,280 cm^{-1} with this transition. None of the assignments given for the half-sandwich complexes involves transitions from a delocalized to a strongly localized MO and they should not suffer from the above restrictions.

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Pentacarbonyls of Ruthenium and Osmium. III. Triphenylphosphine-Substituted Carbonyls of Ruthenium and Osmium and Their Reactions with Molecular Hydrogen

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The preparation and characterization of $Ru(CO)_4P(C_6H_5)_3$ and $Os(CO)_4P(C_6H_5)_3$ have been accomplished and a new route to the already known disubstituted $Ru(CO)_3(P(C_6H_5)_3)_2$ and $Os(CO)_3(P(C_6H_5)_3)_2$ has been found. Reaction with molecular hydrogen on some of these triphenylphosphine-substituted carbonyls has led to $OsH_2(CO)_3P(C_6H_5)_3$, $RuH_2(CO)_2(P(C_6H_5)_3)_2$, and $OsH_2(CO)_2(P(C_6H_5)_3)_2$. For the latter two compounds, the nuclear magnetic resonance and infrared spectra indicate an octahedral structure with both hydrogens in a *cis* position and the triphenylphosphine substituents in *trans* positions.

In a previous paper of this series[1] we reported the synthesis of dihydridotetracarbonylosmium, $OsH_2(CO)_4$, by the reaction of pentacarbonylosmium with molecular hydrogen at elevated temperature and pressure. We did not succeed in preparing the unstable

(1) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).