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EXTENDED CNDO/2 STUDIES OF THE ISOELECTRONIC SERIES $AM(CO)_3$ ($AM = \eta^6$-C_6H_6Cr, η^5-C_5H_5Mn, η^4-C_4H_4Fe, η^3-C_3H_5Co, η^2-C_2H_4Ni) AND OF $(\eta^6$-$C_6H_6)_2Cr$

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Summary

The electronic structure of isoelectronic $AM(CO)_3$ ($AM = \eta^6$-C_6H_6Cr, η^5-C_5H_5Mn, η^4-C_4H_4Fe, η^3-C_3H_5Co, η^2-C_2H_4Ni) and of $(\eta^6$-$C_6H_6)_2Cr$ is investigated within an extended CNDO/2 formalism using both experimental and standard geometries. The computed trends for bond strengths and stretching frequencies (as measured by Wiberg indices or bicentric energy terms) and for reactivity (charge distributions) correlate with the experimental ones. For chromium complexes, the extended CNDO/2 results seem more reasonable, for example the charge and the orbital populations on chromium, than are the ab initio single ζ results. A general agreement is observed between CNDO/2 and SCCC electronic structures.

Introduction

Recently the CNDO/2 formalism was extended to study the electronic structure of transition metal complexes [1—3]. This semiempirical formalism has been applied to a large set of $Ni(PX_3)_4$ complexes [4], which had been experimentally investigated by many authors, to test the validity of the extended CNDO/2 method to reproduce the trend in physicochemical data within the series. In this work the merits of the Chatt and Wilkinson pattern, which is classically used to describe the electronic content of metal—ligand bonds, has been discussed. It should be noticed that, up to now, the work has been performed (due to a lack of experimental geometries within the $Ni(PX_3)_4$ series) using a standard geometrical model identical to the one which was widely and profitably used by Gordon and Pople [5] and ourselves [6] in non-metallic chemistry. This assumption may be considered as a dubious one and it is desirable to prove its validity by the study of another series of chemical interest in which calculations could be done both on experimental and standard geometries.

This extended CNDO/2 formalism also provided an answer to the problem of an "umbrella or parachute" structure of trismethylenemethane tricarbonyliron, $(CH_2)_3CFe(CO)_3$ [7], which had arisen from controversial experimental approaches where a failure in the relationship between interatomic distance and bond strength in iron—carbon bonds was observed. Consequently, we considered the electronic structures of the isoelectronic series $AM(CO)_3$ (AM = η^6-C_6H_6Cr, η^5-C_5H_5Mn, η^4-C_4H_4Fe, η^3-C_3H_5Co, η^2-C_2H_4Ni) and of $(\eta^6\text{-}C_6H_6)_2Cr$ for which (except for the Ni derivative) experimental geometries are known [8—14]. For η^6-$C_6H_6Cr(CO)_3$ the recently calculated electron diffraction geometry was considered [8]. Thus it is possible to compare the results obtained from these experimental geometries with the results obtained from standard geometries. In this work standard geometries were used for $AM(CO)_3$: r(M—C(H)) = 2.1, r(C—H) = 1.08, r(C—C) = 1.40, r(M—C(O)) = 1.85, r(C—O) = 1.15 and ∠ OC—M—CO = 90°. In the case of the nickel complex extrapolated "experimental" geometry was used: r(Ni—C(H)) = 1.95, r(C—H) = 1.08, r(C—C) = 1.34, r(Ni—C(O)) = 1.79, r(C—O) = 1.14 Å and ∠ OC—Ni—CO = 103°.

Previous calculations using various methods have been reported for some of these molecules. Guest et al. [15] have reported the results of ab initio single ζ calculations and the photoelectron spectra of dibenzenechromium and benzenetricarbonylchromium. Self-consistent semiempirical calculations on the latter molecule have been reported by Brown and Rawlinson [16] and by Carroll and McGlynn [17]. Molecular orbital calculations and the photoelectron spectrum of η^5-$C_5H_5Mn(CO)_3$ have been investigated recently [18]. Using a CNDO approach Clarke has considered the bonding in some π-allylmetal compounds including η^3-$C_3H_5Co(CO)_3$ [19]. In a comparative study of the whole $AM(CO)_3$ series by Brown, Fitzpatrick and Mathews, using a self-consistent charge and configuration method, correlations between both the carbonyl stretching frequencies and the reactivities and the calculations were observed [20]. Recently a comparative bonding study of conical fragments and especially of $M(CO)_3$ was developed by Hoffmann and coworkers [21].

Results

A. The $AM(CO)_3$ series

1. Wiberg indices. The bond indices as defined by Wiberg [22] are collected in Tables 1 and 2 for $AM(CO)_3$ using the standard and experimental geometries. In these tables average values are reported as the symmetry of the carbonyls is removed in most of the calculations.

In both the standard and experimental cases the M—C(O) Wiberg indices decrease from Cr to Co, while for the nickel complex there is a slight increase relative to cobalt. This decrease corresponds to the weakening of the M—C(O) bonds across the series, and agrees with the increased reactivity of the cobalt complex (S_N1) relative to the unreactive chromium and manganese complexes [23,24]. The slight increase in Wiberg indices for the Ni complex, using the ge-

TABLE 1

WIBERG INDICES. STANDARD GEOMETRY

	Cr	Mn	Fe	Co	Ni
M—C(O)	0.774	0.734	0.578	0.504	0.538
C—O	2.237	2.322	2.399	2.448	2.371
M—C(H)	0.294	0.217	0.430	0.205	0.506
C—H	0.938	0.933	0.912	0.928	0.931

ometry considered, shows that this complex is not appreciably different from the other complexes. It may be noticed that, from our previous work [20], the SCCC M—C(O) overlap populations were shown to decrease across the series. Tables 1 and 2 indicate the validity of using a standard geometrical model to predict changes, in the metal—carbon Wiberg indices, since they show that the trend across the series and the size of the variations from Cr to Ni complexes are the same. However the M—C(O) Wiberg indices computed with experimental geometries are greater than the standard ones in all cases. Corresponding to the decrease in M—C(O) there is an increase in the C—O Wiberg indices across the experimental and standard series from Cr to Co; this correlates with the increase in both A_1 and E carbonyl stretching frequencies. The Ni complex is again somewhat anomalous. The M—C(H) Wiberg indices show a general increase across the series and the standard and experimental values vary in the same way with manganese and cobalt being exceptions to the general increase. Previously the M—C(A) overlap populations increased across the series with the position of nickel and cobalt being anomalous [20].

The Wiberg indices of the M—C bonds in η^3-$C_3H_5Co(CO)_3$ are 0.282 for the terminal carbons of the allyl group and 0.228 for the central carbon (using the experimental geometry). This result shows that the bonding to the central carbon is weaker than that to the terminal carbons even though the bond to the former is shorter (1.98 vs. 2.10 Å) (Fig. 1). Thus, as in $(CH_2)_3CFe(CO)_3$ [7], bond length is not correlated with bond strength. Similarly the bond to the carbonyl in the σ_v plane is weakest as the M—C(O) index of this carbonyl is 0.403 while that of the other carbonyls is 0.606, while the Co—C(O) bond lengths are the same for all carbonyls.

2. *Bicentric energy components.* Another measure of the strength of the chemical bonds is the bicentric energy components (Tables 3 and 4) as given by Pople's partitioning of the total energy. The absolute values of the bicentric

TABLE 2

WIBERG INDICES. EXPERIMENTAL GEOMETRY

	Cr	Mn	Fe	Co	Ni
M—C(O)	0.807	0.797	0.602	0.538	0.563
C—O	2.231	2.286	2.394	2.396	2.365
M—C(H)	0.248	0.192	0.427	0.265	0.494
C—H	0.939	0.945	0.919	0.920	0.922

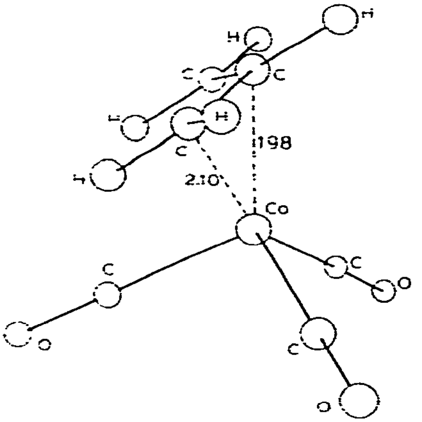

Fig. 1. Experimental geometry of η^3-$C_3H_5Co(CO)_3$.

M—C(O) energies decrease from Cr to Co, then Ni increases for both the standard and experimental geometries. This parallels the trend in Wiberg indices. The absolute value of the corresponding C—O energies increases across the series from Cr to Co with the exception of the cobalt complex using experimental geometry. This trend also essentially agrees with the trend in Wiberg indices and indicates again that in these complexes a strong C—O bond corresponds to a weak M—C(O) bond. For both the experimental and the standard geometries the M—C(H) bicentric energies show a general increase in M—C(H) bonding across the series. However in the earlier members of the series there are more M—C(H) bonds. Both the Wiberg indices and the bicentric energies indicate that the nickel compound is not exceptionally unstable. Rest, using matrix isolation techniques, detected η^2-$C_2H_4Ni(CO)_3$ and noted CO vibrations at 2023(s) and 2092(m) cm^{-1} [25]. These values are greater than the values for other complexes and indicate a stronger C—O bond in the nickel complex than in the cobalt one in agreement with the SCCC calculations but not with the CNDO/2 calculations, possibly due to the SCCC calculations using a larger C—C bond than the CNDO/2 calculations.

3. Atomic charges. The atomic charges are presented in Tables 5 and 6. In general, the differences between the calculations using the experimental and standard geometries are slight. The metal charges, with the exception of the nickel complex, are between 0.44 and 0.63, while the SCCC charges were be-

TABLE 3

BICENTRIC ENERGIES. STANDARD GEOMETRY (a.u.)

	Cr	Mn	Fe	Co	Ni
M—C(O)	−0.363	−0.354	−0.309	−0.292	−0.322
C—O	−1.821	−1.864	−1.897	−1.911	−1.864
M—C(H)	−0.118	−0.129	−0.229	−0.211	−0.307
C—H	−0.734	−0.734	−0.722	−0.731	−0.732

TABLE 4

BICENTRIC ENERGIES. EXPERIMENTAL GEOMETRY (a.u.)

	Cr	Mn	Fe	Co	Ni
M—C(O)	−0.382	−0.379	−0.311	−0.289	−0.316
C—O	−1.819	−1.848	−1.890	−1.883	−1.890
M—C(H)	−0.131	−0.230	−0.200	−0.201	−0.273
C—H	−0.736	−0.727	−0.730	−0.725	−0.724

tween 0.085 and 0.182. Thus the CNDO/2 charges are much larger than the SCCC ones. Guest calculated a charge of +2.08 on chromium in η^6-$C_6H_6Cr(CO)_3$, while that of Carroll and McGlynn is 0.566. Thus the CNDO/2 charge on chromium is more reasonable than the ab initio value. The SCCC calculations indicate a general drift of charge from the hydrocarbon moiety to the carbonyls with the metal having a small positive charge while the CNDO/2 calculations indicate that the metal has a charge of approximately +0.5 while both the carbonyls and the A moieties are negatively charged in general. In the chromium complex the carbonyls are more negatively charged than the benzene ring, and in the nickel complex both A and $(CO)_3$ have approximately equal negative charges. In the other molecules the A moiety has the more negative charge. However the trend in the CNDO/2 A charges (both experimental and standard) agrees with the SCCC charges (with the exception of nickel) in showing a more negative charge from the Cr to the Fe complex and with C_4H_4 being more negative than C_3H_5. Experimentally from the ^{13}C NMR spectra of $(\eta^3$-$C_3H_5MX)_2$ the allyl group is a net electron donor [26]. The SCCC charge distribution for C_6H_6-$Cr(CO)_3$ is approximately $(C_6H_6)^{0.57}$ $Cr^{0.18}$ $(CO)_3^{-0.75}$ while the ab initio result [15] is $C_6H_6^{-0.84}$ $Cr^{2.08}$ $(CO)_3^{-1.24}$ while the CNDO/2 result (with the experimental geometry) is intermediate being approximately $C_6H_6^{-0.08}$ $Cr^{0.49}$ $(CO)_3^{-0.41}$, which has an essentially neutral benzene and the chromium and the carbonyls with charges of approximately +0.5 and −0.5 respectively. The very negative A charge in the iron complex is in agreement with the ease of electrophilic substitution in the C_4H_4 ring [27]. Reeves and coworkers have pointed out that vari-

TABLE 5

ATOMIC CHARGES. STANDARD GEOMETRY

	Cr	Mn	Fe	Co	Ni
M	0.540	0.553	0.614	0.445	0.223
C(H)	−0.030	−0.070	−0.135	+0.133 Central −0.326 Terminal	−0.095
H	0.004	−0.010	−0.034	−0.008	0.021
C(O)	0.013	0.047	0.076	0.080	0.050
O	−0.141	−0.098	−0.055	−0.042	−0.088
A	−0.158	−0.398	−0.676	−0.560	−0.107
$(CO)_3$	−0.386	−0.155	0.062	0.115	−0.117

TABLE 6

ATOMIC CHARGES. EXPERIMENTAL GEOMETRY

	Cr	Mn	Fe	Co	Ni
M	0.486	0.599	0.629	0.478	0.301
C(H)	−0.022	−0.086	−0.145	−0.150	−0.094
H	0.009	0.003	−0.020	0.004	0.011
C(O)	0.010	0.047	0.065	0.057	0.037
O	−0.110	−0.055	−0.073	−0.050	−0.089
A	−0.078	−0.412	−0.660	−0.430	−0.145
$(CO)_3$	−0.407	−0.188	+0.031	−0.048	−0.156

ous experiments have shown the iron tricarbonyl to be an electron releasing group; this is reflected in the positive charges on the carbonyls in η^4-$C_4H_4Fe(CO)_3$ [28] *. Pettit has also shown that η^4-$C_4H_4Fe(CO)_3$ can stabilise an adjacent carbonion ion due to C—C interaction; this suggests a negatively charged C_4H_4 ring in agreement with the CNDO results [29].

While the general trend in A charges is the same in both the SCCC and CNDO/2 cases, the metal charge trends differ with the CNDO/2 charges increasing from Cr to Fe and then decreasing while the SCCC charges are in the order Cr > Fe > Mn > Ni > Co. However the variations in metal charges are small. The trends in carbonyl charges are similar using both CNDO/2 and SCCC methods, with the carbonyls in the centre of the series being most positive and with decreasing charges towards Cr and towards Ni. Thus even though the absolute value of the charges differs using the CNDO/2 and SCCC approximations, in general, trends are the same.

4. *Orbital populations.* Further insight into the electronic structure of these complexes is provided by the orbital populations (Tables 7 and 8). Again the differences between the standard and experimental values are slight. In general, the CNDO/2 metal s population (0.5 to 0.64) is greater than the SCCC results

TABLE 7

ORBITAL POPULATIONS. STANDARD GEOMETRY

		Cr	Mn	Fe	Co	Ni
M	s	0.506	0.541	0.582	0.618	0.640
	p	0.182	0.210	0.240	0.286	0.290
	d	4.767	5.696	6.564	7.651	8.847
C(O)	s	1.495	1.507	1.518	1.589	1.579
	p_σ	1.076	1.074	1.065	1.037	1.034
	p_π	1.417	1.372	1.343	1.314	1.343
O	s	1.690	1.690	1.690	1.695	1.692
	p_σ	1.445	1.453	1.462	1.498	1.498
	p_π	3.007	2.956	2.904	2.856	2.900

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* ESCA measurements of some iron tricarbonyl complexes [30] have indicated that the oxygen carbonyl atoms have a positive character in such compounds in disagreement with CNDO/2 results for η^4-$C_4H_4Fe(CO)_3$.

TABLE 8

ORBITAL POPULATIONS. EXPERIMENTAL GEOMETRY

		Cr	Mn	Fe	Co	Ni
M	s	0.523	0.542	0.578	0.597	0.628
	p	0.192	0.201	0.237	0.262	0.274
	d	4.800	5.657	6.555	7.663	8.788
C(O)	s	1.496	1.486	1.505	1.611	1.578
	p_σ	1.075	1.074	1.067	1.038	1.038
	p_π	1.420	1.393	1.365	1.305	1.354
O	s	1.691	1.689	1.681	1.691	1.688
	p_σ	1.444	1.444	1.476	1.500	1.504
	p_π	3.010	2.977	2.899	2.889	2.896

(0.3 to 0.4). The CNDO/2 metal p populations are also much larger (0.18 to 0.29) vs. (0.09 to 0.15). The ab initio population in η^6-$C_6H_6Cr(CO)_3$ is $d^{4.447}$ $s^{-0.189}$ $p^{-0.314}$ [15]. These negative orbital populations are worry features of the ab initio "single ζ" technique. The populations on the metals for the CNDO/2 calculations indicate an increase in p population across the series. The SCCC results are similar (with the exception of Co). However the metal p populations have different trends, since the CNDO/2 populations increase and the SCCC results show a general decrease across the series. The CNDO/2 and SCCC trends in metal d populations are the same. In the case of the carbonyl C and O p_σ and p_π contributions are distinguishable since the coordinates were chosen in such a way that a carbonyl group was along a coordinate axis. The s population of O differs little across the series being approximately 1.69 in all cases. The oxygen p_σ population increases across the series from 1.44 to 1.50, while the p_π population decreases from 3.01 to 2.86 (standard) or 2.89 (experimental), before increasing to 2.90 for the nickel complex. Thus the p_π variation is the largest, and its decrease across the series causes the O charges to decrease generally in absolute value across the series. Thus the early members of the series can be represented M=C=O while the later members have more of M—C≡O. Thus the orbital populations also correlate with the experimental trend in ν(CO) values which increase across the series.

5. Total energy, ionization potential and dipole moment. From the total energies in Tables 9 and 10 it is seen that the experimental geometry does not have the lowest energy in all cases. In his CNDO calculations on η^3-$C_3H_5Co(CO)_3$ Clarke used the criterion of "bond indices" to optimize the angles of tilt [19]. Previously it has been seen that the experimental geometries have the larger M—C(O) Wiberg indices. The calculated dipole moments peak in the middle of the series corresponds to the large negative A charges and somewhat positive carbonyl charges for the corresponding complexes. In fact the calculated direction of the dipole changes since the chromium complex has a dipole due essentially to electrons drifting to the carbonyl groups while with the Mn, Fe and Co complexes the CNDO/2 results indicate electron drift to the hydrocarbon moiety. The experimental dipole moment of η^6-$C_6H_6Cr(CO)_3$ is approximately 0.5 D [17] and this differs from the CNDO/2 value.

The ionization potentials in Tables 9 and 10 are based on Koopmans' theo-

TABLE 9

TOTAL ENERGY AND EXPERIMENTALLY MEASURABLE PARAMETERS. STANDARD GEOMETRY

	Cr	Mn	Fe	Co	Ni
TE (a.u.)	−131.404	−128.025	−125.292	−125.687	−125.593
μ(D)	0.850	2.965	7.590	7.684	1.464
IP (a.u.)	0.277	0.350	0.285	0.303	0.253
	0.277	0.351	0.286	0.373	0.296
	0.309	0.353	0.418	0.430	0.307

rem. In all cases the three highest occupied molecular orbitals are essentially metal orbitals. The ab initio calculations give the uppermost levels of η^6-C_6H_6-$Cr(CO)_3$ at −0.3091 a.u. (17*e*) and −0.4068 a.u. (17a_1) where the former has 51% and the latter 79% Cr 3*d*. The CNDO/2 results indicate that the two highest occupied levels are degenerate (*e* type) with 60% and the next level has 75% metal 3*d* character. In their study of the photoelectron spectra and electronic structure of a series of manganese tricarbonyls Whitesides and coworkers [18] calculate the highest molecular orbitals in η^5-$C_5H_5Mn(CO)_3$ to be at −0.3437 a.u. (degenerate) and −0.3485 a.u. which are metal non-bonding orbitals. These agree with the CNDO/2 results where, for example, the experimental degenerate levels at −0.360 a.u. have approximately 60% and the next level at −0.368 a.u. has 75% Mn 3*d* character.

B. The dibenzene chromium

(η^6-$C_6H_6)_2Cr$ was considered using various geometries: (a) the experimental geometry of Ibers [12] and (b) that of Jellinek [13] (c) that used for η^6-C_6H_6-$Cr(CO)_3$ [8] where a second benzene group replaced the tricarbonyl moiety and finally (d) that of Bailey and Dahl [14] where the CO groups were also replaced. The results are given in Table 11 for the total energy, Wiberg indices and bicentric energies.

As noted from Table 11, the lowest total energy is not obtained for Ibers' and Jellinek's X-ray geometries but for the models built from Schäfer and coworkers' electron diffraction works on η^6-$C_6H_6Cr(CO)_3$. This is not at all surprising for the former geometries may be altered by some packing effect while

TABLE 10

TOTAL ENERGY AND EXPERIMENTALLY MEASURABLE PARAMETERS. EXPERIMENTAL GEOMETRY

	Cr	Mn	Fe	Co	Ni
TE (a.u.)	−131.541	−127.948	−125.212	−125.508	−125.418
μ(D)	1.642	2.787	6.845	3.403	1.221
IP (a.u.)	0.269	0.360	0.300	0.328	0.277
	0.269	0.360	0.301	0.352	0.301
	0.296	0.368	0.411	0.382	0.316

TABLE 11

DIBENZENE CHROMIUM. TOTAL ENERGIES, WIBERG INDICES AND BICENTRIC ENERGIES

	Ibers [12]	Jellinek [13]	Schäfer [8]	Dahl [14]
TE (a.u.)	−103.173	−103.255	−103.409	−103.399
Wiberg indices				
M—C	0.305	0.304	0.290	0.282
C—C	1.298	1.300	1.308	1.313
C—H	0.938	0.934	0.938	0.938
Bicentric energies (a.u.)				
M—C	−0.134	−0.136	−0.140	−0.136
C—C	−1.302	−1.303	−1.306	−1.312
C—H	−0.735	−0.732	−0.731	−0.734

the latter, deduced from measurements in the gas phase, lead logically to molecular structures closer to the one which characterizes isolated $(\eta^6\text{-}C_6H_6)_2Cr$.

A calculation, using the ring geometry of Schäfer et al. on benzene gave C—C and C—H Wiberg indices of 1.446 and 0.959 with corresponding bicentric energies of −1.389 a.u. and −0.750 a.u. Thus on complexing the C—C and C—H bonds are weakened. The C—H Wiberg index and bicentric energy of $\eta^6\text{-}C_6H_6Cr(CO)_3$, using the Schäfer and coworkers geometry, are 0.939 and −0.736 a.u. Thus the C—H bonds are weakened in complexing to form $\eta^6\text{-}C_6H_6Cr(CO)_3$ and further weakened in the dibenzene complex. Similarly the C—C average Wiberg index and bicentric energy for $\eta^6\text{-}C_6H_6Cr(CO)_3$ using the geometry of Schäfer and coworkers are 1.325 and −1.315 a.u. Thus on complexing to form $\eta^6\text{-}C_6H_6\text{-}Cr(CO)_3$ the C—C bonds in benzene are weakened, but by less than, as expected, in the disubstituted complex.

Further results for dibenzenechromium are given in Table 12. It is noted that the differences between the various geometries are small and that the overall electronic distributions are essentially the same. These, in fact, differ appreciably from the ab initio single ζ results, where a charge of +2.66 for chromium was calculated [15]. This is excessive for a nonionic compound. Also the ab

TABLE 12

DIBENZENE CHROMIUM. ATOMIC CHARGES, ORBITAL POPULATIONS AND IONISATION POTENTIALS (KOOPMANS)

	Ibers [12]	Jellinek [13]	Schäfer [8]	Dahl [14]
q_M	0.489	0.469	0.435	0.411
q_C	−0.037	−0.033	−0.035	−0.031
q_H	−0.004	−0.006	−0.001	−0.003
M *s*	0.454	0.457	0.466	0.465
p	0.238	0.251	0.256	0.249
d	4.820	4.822	4.843	4.875
IP (a.u.) degenerate	0.252	0.254	0.242	0.231
	0.300	0.304	0.302	0.290

initio calculations indicate negative population for the $s(-0.295)$ and $p(-0.833)$ orbitals. The ab initio carbon and hydrogen charges also differ from the CNDO/2 values, being -0.45 and $+0.22$ (respectively). The highest ab initio molecular orbital is at -0.2754 a.u. ($4e_{2g}$) and the next is at -0.4142 a.u. ($8a_{1g}$). The CNDO/2 highest orbital is also degenerate followed by a nondegenerate level. In the ab initio case the highest level has 53% metal *d* while the next level has 92% metal *d* components. The CNDO/2 calculations show that the highest level has from 58 to 63% metal *d* contributions, depending on the geometry, and that there is 94% to 95% *d* character in the next highest level. Hillier and coworkers have also considered a self-consistent charge calculation with electron interaction [31] and they initially calculated a configuration of $d^{5.65}\ s^{-0.49}\ p^{-1.78}$. They consider that the negative populations, due to the Mulliken population analysis, indicate that these orbitals do not participate in bonding. The CNDO/2 results do not support this idea. Their final charges are 0.54, -0.06 and $+0.01$ on Cr, C and H (respectively), which are in better agreement with the CNDO/2 calculations than are the ab initio results.

Conclusions

The CNDO/2 results show that standard geometries may be used to study trends in bonding in this series of related compounds. The variations in the calculated results, in general, parallel the experimental data, in particular in the case of cyclobutadienetricarbonyliron whose experimental results show the electrophilic nature of the ring.

In the case of the chromium complexes the CNDO/2 results are more reasonable than are the ab initio single ζ results.

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