CNDO/2 Study of the Isoelectronic Series of Complexes Dicarbonyl(dinitrogen)- and Dicarbonyl-η-benzenechromium, -η-cyclopentadienylmanganese, -η-cyclobutadieneiron, and -trismethylenemethane-iron obtained by the Matrix-isolation Technique

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The electronic structure of the isoelectronic series of $[ML(CO)_2(N_2)]$ and $[ML(CO)_2]$ complexes [ML = Cr-(η-C_6H_6), Mn(η-C_5H_5), Fe(η-C_4H_4), or Fe{$C(CH_2)_3$}] has been investigated within a CNDO/2 formalism, using both experimental and standard geometries. The computed trends for CO and N_2 bond strengths in the complexes, as measured by Wiberg indices, charge distributions, and orbital populations, are well correlated with the experimental CO and N_2 stretching frequencies and energy-factored stretching force constants, *i.e.* Cr < Mn < Fe and $[ML(CO)_2] < [ML(CO)_2(N_2)] < [ML(CO)_3]$. The computed total energies of the $[ML(CO)_2]$ complexes suggest that in all cases a tilted geometry is preferred, *i.e.* the plane of the L ligand is not perpendicular to the $M(CO)_2$ plane. New CNDO/2 calculations have been carried out for [Fe{$C(CH_2)_3$}$(CO)_3$] which is shown to fit in well with other $[ML(CO)_3]$ complexes.

THE challenge of the novel structures of binary metal carbonyl and metal dinitrogen species, $M(CO)_n$ and $M(N_2)_m$, observed by matrix-isolation spectroscopy, has provided the impetus for theoretical studies of coordinatively unsaturated fragments.[1,2] Thus Burdett[1] has rationalised the geometries of some transition-metal complexes and Elian and Hoffmann[2] have studied the ability of $M(CO)_n$ fragments to interact with other ligands.

Previously we have described[3] an investigation of the electronic structure of the isoelectronic series of $[ML(CO)_3]$ complexes [ML = Cr(η-C_6H_6), Mn(η-C_5H_5), Fe(η-C_4H_4), Co(η-C_3H_5), or Ni(η-C_2H_4)] and of [Cr(η-C_6H_6)$_2$] within an extended CNDO/2 formalism using both experimental and standard geometries. From this work it was concluded that either experimental or standard geometries may be used to consider the trends occurring within this series of related molecules since the computed trends for bond strengths and stretching frequencies (as measured by Wiberg indices) and for reactivity (as measured by charge distribution) are well correlated with experimental trends. In this paper we describe the application of the CNDO/2 method to the isoelectronic series of $[ML(CO)_2(N_2)]$ and $[ML(CO)_2]$ complexes (ML = Cr(η-C_6H_6), Mn(η-C_5H_5), Fe(η-C_4H_4), or Fe{$C(CH_2)_3$}] which have been characterised by matrix-isolation spectroscopy.[4] New CNDO/2 calculations are also included for [Fe{$C(CH_2)_3$}$(CO)_3$] which has been shown by other CNDO/2[5] and electron-diffraction[6] studies to have the methylene carbons displaced towards

TABLE 1

Energy-factored CO-stretching force constants (k/N m^{-1}), estimated OC–M–CO bond angles (θ/°), and CO Wiberg indices (W.i.) for $[ML(CO)_3]$, $[ML(CO)_2(N_2)]$, and $[ML(CO)_2]$ complexes

	[Cr(η-C_6H_6)$(CO)_3$]			[Cr(η-C_6H_6)$(CO)_2(N_2)$]	[Cr(η-C_6H_6)$(CO)_2$]	
	Ar	CH_4	N_2	N_2	Ar	CH_4
k	1 528.5	1 514.1	1 517.1	1 487.9	1 476.8	1 455.7
θ	88.6	85.6	87.4	86.0	a	102.4
W.i.[b]		2.231		2.227	1.963	
	[Mn(η-C_5H_5)$(CO)_3$]			[Mn(η-C_5H_5)$(CO)_2(N_2)$]	[Mn(η-C_5H_5)$(CO)_2$]	
	Ar	CH_4	N_2	N_2	Ar	CH_4
k	1 580.5	1 569.9	1 575.1	1 535.2	1 518.0	1 501.6
θ	93.5	93.0	94.7	93.6	99.6	101.6
W.i.[b]		2.286		2.278	2.091	
	[Fe(η-C_4H_4)$(CO)_3$]			[Fe(η-C_4H_4)$(CO)_2(N_2)$]	[Fe(η-C_4H_4)$(CO)_2$]	
	Ar	CH_4	N_2	N_2	Ar	CH_4
k	1 635.0	1 621.6	1 627.6	1 596.6	1 570.4	1 556.3
θ	95.5	97.3	96.5	96.8	102.1	101.3
W.i.[b]		2.394		2.402	2.181	
	[Fe{$C(CH_2)_3$}$(CO)_3$]			[Fe{$C(CH_2)_3$}$(CO)_2(N_2)$]	[Fe{$C(CH_2)_3$}$(CO)_2$]	
	Ar	CH_4	N_2	N_2	Ar	CH_4
k	1 655.3	1 648.5	1 646.9	1 622.8	1 598.2	1 585.5
θ	95.5	92.1	94.8	94.8	107.7	100.9
W.i.[b]		2.403		2.407	2.223	

[a] Low conversion into [Cr(η-C_6H_6)$(CO)_2$] in argon matrices precluded an accurate determination of θ from the experimental intensity ratio $I_{sym}/I_{antisym}$. [b] For $[ML(CO)_3]$[3] and $[ML(CO)_2(N_2)]$ W.i. (experimental geometry) and for $[ML(CO)_2]$ W.i. (tilted geometry) values are reported.

the iron atom. Hückel-type calculations on a range of polyene-ML_3 transition-metal complexes, including [Fe{$C(CH_2)_3$}$(CO)_3$], have also been reported.[7]

EXPERIMENTAL

The [$ML(CO)_2$] species [ML = Cr(η-C_6H_6), Mn(η-C_5H_5), Fe(η-C_4H_4), or Fe{$C(CH_2)_3$}] were formed by u.v. photolysis of [$ML(CO)_3$] complexes in argon and methane matrices and [$ML(CO)_2(N_2)$] complexes were observed on u.v. photolysis in nitrogen matrices at 12 K.[4] The various species were detected by i.r. spectroscopy and from the i.r. frequencies the energy-factored force constants (k) in the various matrices were calculated (Table 1). The OC–M–CO angles (θ, Table 1) were calculated by averaging the integrated intensities under the symmetric and antisymmetric vibrations and using the expressions $I_{\text{sym}}/I_{\text{antisym}} = [3\cot^2(\theta/2) - 1]/4$ for $ML(CO)_3$ complexes and $I_{\text{sym}}/I_{\text{antisym}} = \cot^2(\theta/2)$ for $ML(CO)_2$ complexes.

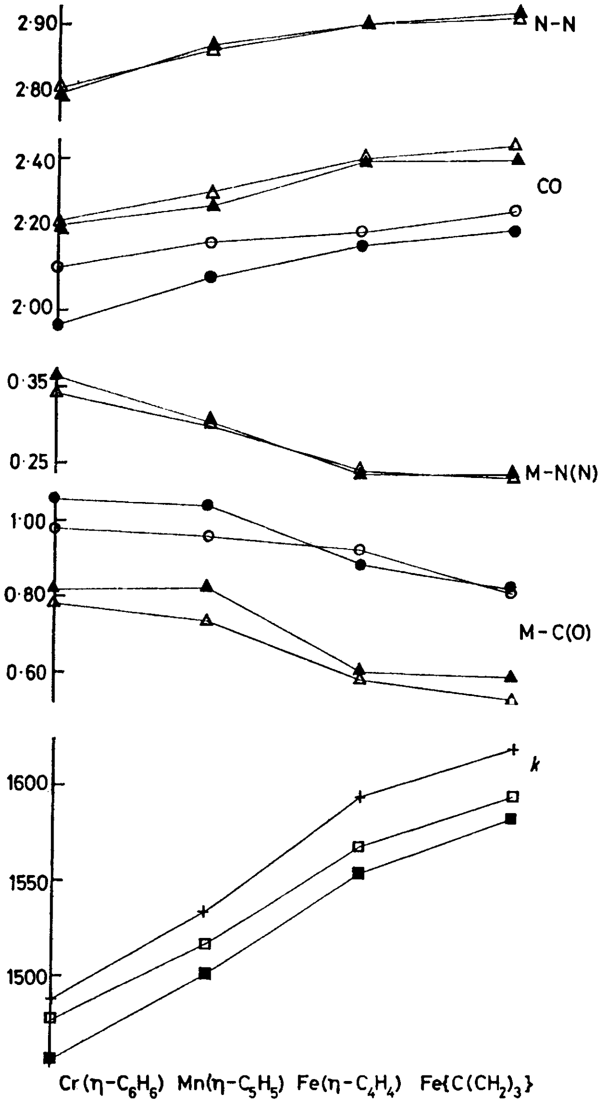

FIGURE 1 Wiberg indices and energy-factored CO stretching force constants (k in N m^{-1}) for [$ML(CO)_2(N_2)$] and [$ML(CO)_2$] complexes: (△) [$ML(CO)_2(N_2)$] with standard geometry; (▲) [$ML(CO)_2(N_2)$] with experimental geometry; (○) [$ML(CO)_2$] with untilted geometry; (●) [$ML(CO)_2$] with tilted geometry; (+) [$ML(CO)_2(N_2)$] in N_2; (□) [$ML(CO)_2$] in Ar; and (■) [$ML(CO)_2$] in CH_4

The CNDO/2 formalism as developed by Labarre and his co-workers[8,9] was used for the calculations which were carried out on the IBM 360/50 computer at University College, Dublin.

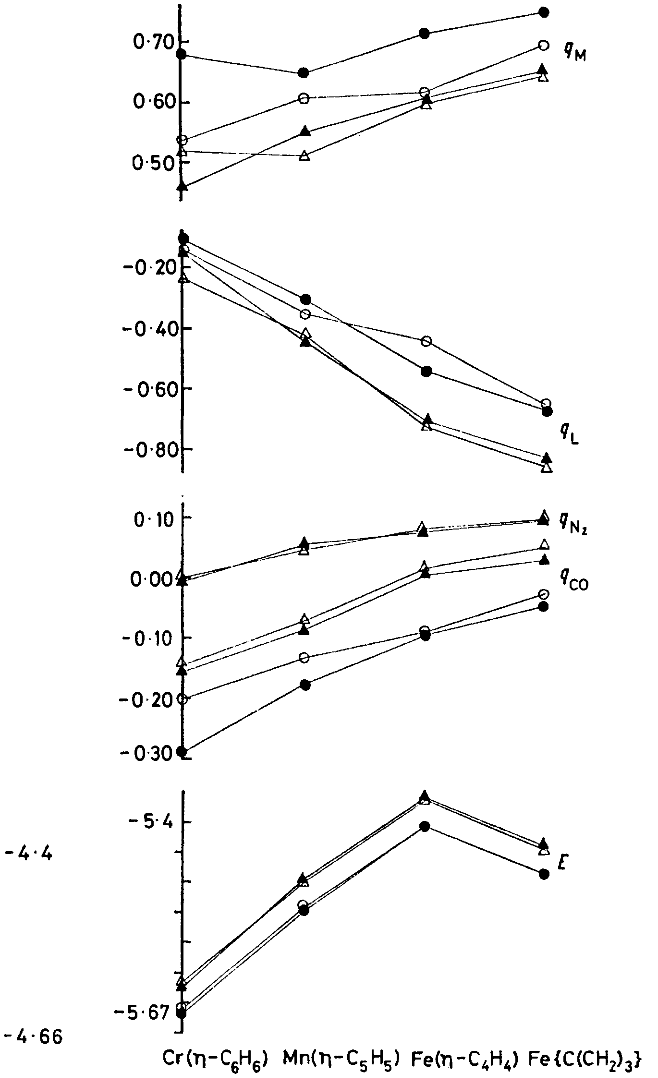

FIGURE 2 Charge distributions (q) and total energies ($E/10^{16}$ J) in [$ML(CO)_2(N_2)$] and [$ML(CO)_2$] complexes: (△) [$ML(CO)_2(N_2)$] with standard geometry; (▲) [$ML(CO)_2(N_2)$] with experimental geometry (-5.4 to -5.67×10^{-16} J); (○) [$ML(CO)_2$] with untilted geometry; and (●) [$ML(CO)_2$] with tilted geometry (-4.4 to -4.66×10^{-16} J)

For the [$ML(CO)_2(N_2)$] series the standard geometries used were an extension of those used for the [$ML(CO)_3$] series,[3] namely r[M–C(H)] = 2.1, r(C–C) = 1.40, r(C–H) = 1.08, r[M–C(O)] = 1.85, r(C–O) = 1.15, r(M–N) = 1.90, r(N–N) = 1.19 Å, and OC–M–CO = OC–M–N_2 = 90° in all cases except for the trismethylenemethane complex (see below). Geometries based on the experimental geometries of [$ML(CO)_3$][10-12] were also considered for the [$ML(CO)_2(N_2)$] series with M–N and N–N bond distances as used for the standard geometry calculations.

For the $[ML(CO)_2]$ series standard geometries were used for all the molecules except that r[M–C(O) = 1.68, r(C–O) = 1.19 Å, and OC–M–CO = 100° were used, which are close to the experimental parameters for $[Co(\eta\text{-}C_5H_5)(CO)_2]$ [r(Co–C) = 1.675, r(C–O) = 1.194 Å by electron diffraction[13] and OC–Co–CO = 98.6 and 96° by electron diffraction[13] and i.r. solution[14] studies]. Values for OC–M–CO in matrices are close to 100° (Table 1). Two conformations of $[ML(CO)_2]$ were considered: (*i*) untilted, in which the plane of the hydrocarbon ring was perpendicular to the plane of the $M(CO)_2$ moiety; (*ii*) tilted, in which the plane of the ring was tilted 60° out of the $M(CO)_2$ plane. These conformations were considered because Hofmann,[15] on the basis of eigenvalue arguments, has shown that a tilted (pyramidal) geometry for $[Mn(\eta\text{-}C_5H_5)(CO)_2]$ is preferred over the untilted (planar) one.

For $[Fe\{C(CH_2)_3\}(CO)_3]$ two geometries were considered, the experimental geometry[6] obtained by electron diffraction and a second one with the standard geometry for the $Fe(CO)_3$ fragment (see above). For $[Fe\{C(CH_2)_3\}(CO)_2(N_2)]$ the standard and experimental geometries were based on the parent tricarbonyl molecule and for $[Fe\{C(CH_2)_3\}(CO)_2]$ the geometries used for the $Fe\{C(CH_2)_3\}$ and $Fe(CO)_2$ fragments were considered.

RESULTS AND DISCUSSION

Wiberg Indices.—A comparison of the CO Wiberg indices[16] with the energy-factored CO-stretching force constants is shown in Figure 1, from which it is seen that the standard and experimental CO Wiberg indices differ little. Thus either standard or experimental values are adequate for discussing the trends. Similarly, both the tilted and untilted values show the same trends. The increase in both CO-stretching force constants and Wiberg indices is clear from Figure 1 and the results are summarised in Table 1.

TABLE 2

$2p_\pi$ Orbital populations (free-ligand data in parentheses) and total energies ($\times 10^{-16}$J) for $[ML(CO)_2(N_2)]$ (experimental geometry) and $[ML(CO)_2]$ (tilted geometry) complexes

		$[Cr(\eta\text{-}C_6H_6)(CO)_2(N_2)]$	$[Cr(\eta\text{-}C_6H_6)(CO)_2]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2]$
$2p_\pi$ Population					
C	(1.162)	1.429	1.539	1.400	1.461
O	(2.838)	3.009	3.021	2.981	2.926
N *	(2.0)	2.079		2.074	
N′ *	(2.0)	2.090		2.028	
Total energy		−5.642	−4.634	−5.487	−4.484
		$[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$	$[Fe(\eta\text{-}C_4H_4)(CO)_2]$	$[Fe\{C(CH_2)_3\}(CO)_2(N_2)]$	$[Fe\{C(CH_2)_3\}(CO)_2]$
$2p_\pi$ Population					
C	(1.162)	1.362	1.423	1.331	1.431
O	(2.838)	2.896	2.932	2.906	3.046
N *	(2.0)	2.077		2.080	
N′ *	(2.0)	1.990		1.972	
Total energy		−5.369	−4.363	−5.439	−4.432

* M–N–N′.

The N–N Wiberg indices increase across the series from Cr to Fe corresponding to the increase in ν(NN), the values being 2 148.4, 2 175.3, 2 206.8, and 2 219.1 cm^{-1} respectively. The M–N(N) Wiberg indices are small, especially for the iron complexes, indicating a lack of stability for these particular complexes.

The values of the standard and experimental C–O Wiberg indices for $[Fe\{C(CH_2)_3\}(CO)_3]$, 2.436 and 2.403 respectively, fit into the general trends for the $[ML(CO)_3]$ series[3] and the corresponding M–C(O) values, 0.540 and 0.595 respectively, also obey the expected trend.

The increasing values of Wiberg indices and CO stretching force constants across the series from Cr to Fe suggest that in going across the series π back bonding becomes less in all cases. It is noteworthy that in the $[ML(CO)_2]$ complexes the M–C(O) Wiberg indices are appreciable and this is well correlated with greater M–C π back bonding than for the $[ML(CO)_3]$ series, in accordance with the charge on the metal being distributed over two CO groups for $[ML(CO)_2]$ compared to three CO groups for $[ML(CO)_3]$. The decrease in the values of C–O and N–N Wiberg indices in going from free CO (2.602) and free N_2 (3.0) to the complexes $[ML(CO)_3]$ and $[ML(CO)_2(N_2)]$ is less for N_2 than for CO and this may be interpreted as indicating less perturbation of the N_2 on complex formation and hence weaker bonding to the metal. In the $[ML(CO)_2(N_2)_2]$ series the C–O Wiberg indices fall between those for the $[ML(CO)_3]$ and $[ML(CO)_2]$ series showing that N_2, as a ligand, is less effective for π back bonding.

Charge Distribution.—The charges on the metals in $[ML(CO)_2(N_2)]$ and $[ML(CO)_2]$ follow the same trend (Figure 2) as the charges in the $[ML(CO)_3]$ series.[3] The charge on iron in $[Fe\{C(CH_2)_3(CO)_3]$ * also fits into the general trend for $[ML(CO)_3]$.

The charges on L are very negative in all cases and become progressively more negative across the series. Between the series in general the trend in L charges is $[ML(CO)_2] > [ML(CO)_3] > [ML(CO)_2(N_2)]$, which is the same as the M charges.

The charges on the carbonyl group increase across the series in all cases and, as previously, $[Fe\{C(CH_2)_2\}(CO)_3]$ fits in with the general $[ML(CO)_3]$ series trend. Between the series the trend is $[ML(CO)_2] < [ML(CO)_2(N_2)] < [ML(CO)_3]$ in general which is the reverse of the trend of the M–C Wiberg indices. Thus the CO charges are cor-

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* Charge distributions (q) and $2p_\pi$ populations in $[Fe\{C(CH_2)_3\}(CO)_3]$ for standard and experimental geometries respectively were: $q_M = 0.657, 0.669$; $q_L = -0.825, -0.780$; $q_{CO} = 0.056, 0.037$; $q_{C(O)} = 0.092, 0.088$; $q_O = -0.036, -0.051$; C $2p_\pi$ population = 1.320, 1.334; O $2p_\pi$ population = 2.887, 2.909.

related with the force constants and with traditional back-bonding concepts.

Orbital Populations.—The $2p_\pi$ orbital populations (Table 2) show trends: (*i*) there is a general decrease in the C and O $2p_\pi$ populations across the series, as was seen[3] in the $[ML(CO)_3]$ series; (*ii*) the position of $[Fe\{C(CH_2)_3\}(CO)_3]$ fits into the general trends, with the exception of the oxygen $2p_\pi$ population, using experimental geometry; (*iii*) the N $2p_\pi$ populations using both standard and experimental geometries have a minimum with Mn, while the N′ $2p_\pi$ population decreases right across the series.

For oxygen the more negative charge and larger $2p_\pi$ population for the chromium complex is indicative of greater back bonding in the early members of the series. Also for nitrogen a large N′ $2p_\pi$ population corresponds to more negative charge as suggested by lower NN frequencies for the early members of the series. From the $2p_\pi$ populations of the free ligand it is seen that C gains π density on complexing, particularly in the $[ML(CO)_2]$ cases, and least so in $[ML(CO)_3]$ in general. Oxygen also gains in $2p_\pi$ electrons on complexing and again the order is as expected being greater for Cr complexes which have the lowest CO frequencies and force constants.

Energetics.—The total energies (Figure 2) show that in all cases the tilted geometries have the lowest energies and are, on this basis, preferred (Table 2). However, previously[3] it was found that for some members of the $[ML(CO)_3]$ series the standard geometries were lower in energy than the experimental ones; thus it is inferred that energy minimisation may not always give the preferred geometries in complexes of the type under consideration. In the $[ML(CO)_2(N_2)]$ series it is also apparent that in most cases the standard energies are lower.

A consideration of the eigenvalues near the highest-occupied and lowest-unoccupied molecular orbitals, h.o.m.o. and l.u.m.o., for a conformation with tilt angles of 0, 30, and 60° does not give a definite preference for any tilt angle since no overall pattern in the eigenvalue variations occurs. The h.o.m.o. for $[Cr(\eta\text{-}C_6H_6)(CO)_2]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_2]$ goes through a minimum but for the iron complexes the untilted h.o.m.o. has the lowest energy. Hofmann,[17] using extended-Hückel calculations, has found that in $[ML(CO)_2]$ complexes the preferred conformation for the chromium and magnanese complexes is the tilted one but for the iron complex the untilted conformation is preferred.

Conclusion.—The results of CNDO/2 calculations show that for all members of the series the calculated data are well correlated with experimental data and between the series $[ML(CO)_2]$, $[ML(CO)_3]$, and $[ML(CO)_2(N_2)]$ there is also general agreement. In particular, the results for $[ML(CO)_2]$, whether the L group is tilted or not, are well correlated, while the smaller differences between $[ML(CO)_3]$ and $[ML(CO)_2(N_2)]$ are not so clearly differentiated. More detailed results are available as Supplementary Publication No. SUP 22398 (8 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.