Osmium–carbonyl distances within the $HOs_3Re(CO)_{15}$ molecule are self-consistent [Os(2)–C(1) = 1.901 (25) Å, Os(2)–C(2) = 1.915 (28) Å, Os(2)–C(3) = 1.897 (15) Å; average 1.904 Å]. There is no significant difference between the bond lengths determined for axial and equatorial sets of osmium–carbonyl vectors and the mean value is in reasonable agreement with the values reported for $Os_3(CO)_{12}$[1] [Os–CO(axial) = 1.946 (6) Å (average) and Os–CO(equatorial) = 1.912 (7) Å (average)]. It should be noted, however, that disorder renders all bond lengths and angles rather imprecise in the current $HOs_3Re(CO)_{15}$ structure.

Distances around M(1) and M(1)″ are, of course, subject to large errors because of the disorder of $Os(CO)_3H$ and $Re(CO)_4$ moieties and the concomitant low occupancies of the C(5A)–O(5A) and C(5B)–O(5B) sites. The resulting metal–carbonyl distances [M(1)–C(4) = 1.912 (19) Å, M(1)–C(5A) = 1.981 (26) Å, and M(1)–C(5B) = 1.720 (53) Å] are, nevertheless, consistent with representing the mean of terminal osmium–carbonyl and rhenium–carbonyl bond lengths.

Finally, we note that the sites of the disordered carbonyl ligands, C(5A)–O(5A) and C(5B)–O(5B), are just far enough apart to be resolved satisfactorily. Separations are 0.893 (67) Å for C(5A)···C(5B) and 1.174 (63) Å for O(5A)···O(5B).

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Registry No. $HOs_3Re(CO)_{15}$, 12565-76-3.

Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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(6) Assuming the validity of the 18-electron rule, the number of outer valence electrons required for a cluster of N_1 metal atoms mutually linked by a total of N_2 two-electron bonds is given by the expression $(18N_1 - 2N_2)$. A "64-electron" tetranuclear species thus requires four metal–metal bonds, a "62-electron" species requires five metal–metal bonds, and a "60-electron" species requires six metal–metal bonds. See: H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973); P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976)–especially Table VI, p 338.

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Molecular Orbital Theory of Organometallic Compounds. 14. Calculation of the ^{13}C NMR Paramagnetic Shielding in Tricarbonylarenemetals

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^{13}C NMR paramagnetic shielding constants are calculated for the isoelectronic series benzenetricarbonylchromium, cyclopentadienyltricarbonylmanganese, cyclobutadienetricarbonyliron, allyltricarbonylcobalt, and ethylenetricarbonylnickel, using the self-consistent charge and configuration molecular orbital method and the Pople–Karplus equation. Correlation between the observed downfield shifts for the carbonyl ligands and the upfield shifts of the carbon atoms in the hydrocarbon ligands with the calculated σ^p values is noted without the need to consider σ^d. The importance of the various terms in the Pople–Karplus expression is shown.

In previous parts in this series,[1] it was shown that self-consistent charge and configuration molecular orbital theory (SCCCMO method) is successful in correlating a wide range of experimental quantities such as infrared stretching frequencies, force constants, ionization potentials, photoelectron spectra, bond dissociation energies, and, even in cases of very similar transition states, relative reactivities of dissociative carbonyl substitution reactions with theoretical quantities, such as orbital energies and overlap populations.

Although there is an extensive literature concerning the ^{13}C NMR spectra of organometallic complexes,[2] a wide variety of explanations for the nature of the observed shifts has been given and this rather confusing state of affairs is aptly summarized in a recent note by Evans and Norton[3] who quote from one of the first papers in the field[4] that "No convincing explanation of these results within the framework of the current approximate theory has been found" then continue "such pessimism unfortunately is still warranted a decade later".

Following Saika and Slichter[5] the shielding constant of any atom may be divided into the sum of three terms: a diamagnetic term (σ^d), a paramagnetic term (σ^p), and contributions due to electron circulation in distant parts of the molecule (σ') which include effects such as interatomic ring currents. Strictly speaking, both the paramagnetic and diamagnetic terms involve integrals centered not only on the atom of interest but also integrals involving the interaction of orbitals on the atom in question with orbitals on distant atoms so that the further division into local and distant terms is rather artificial. It is often stated that the paramagnetic term (σ^p) dominates the ^{13}C NMR shielding constant but this is incorrect. σ^d is frequently of greater magnitude than σ^p but it is relatively insensitive to changes in electronic structure for a series of related molecules.[6] In the case of distant atoms, the effect on σ^d would be expected to be small but this view has been challenged recently by Evans and Norton[3] who propose that σ^d should be calculated from the simple formula of Flygare and Goodisman[7]

$$\sigma^d = \sigma^d(\text{free atom}) + (e^2/3mc^2) \sum_{\alpha} (Z_\alpha/r_\alpha)$$

and so transition-metal atoms will then cause very large increases in σ^d (i.e., upfield shifts in NMR spectra) of the order of 100–400 ppm for normal interatomic distances. Acceptance of this view by Vrieze and co-workers for a series of *trans*-$PtCl_2XY$ and *trans*-$PtBr_2XY$ ($X = C_2H_4$, CO; Y = 4-R-py) complexes[8] necessitated the assumption that the σ^p term for the ethylenic carbon atoms must be downfield to the extent of 300 ppm in magnitude!

However, there are a number of objections to the use of the above formula to calculate σ^d in organometallic systems. Firstly, the formula was developed and endorsed only for simple diatomic molecules of first-row elements[9] but no similar justification has been given for compounds of transition metals; secondly, if the formula were applicable, then σ^d in a series of organometallic molecules should increase markedly as the metal atom varies in the sequence first transition series < second transition series < third transition series. For example, application of the above formula to calculate σ^d for the carbonyl carbon atom in the sequence $M(CO)_6$ (M = Cr, Mo, W) leads to approximate values for σ^d of 120, 210, and 370 ppm compared with the experimental screening constants of 212, 202, and 192 ppm (positive downfield relative to internal Me_4Si), respectively. It is very unlikely that a corresponding (and opposing) increase in σ^p will occur for the CO ligand within the above series, thereby giving the much closer spaced screening constants observed (range 20 ppm). Thirdly, in the case of π complexes of fused ring ligands and biphenyls, the Flygare–Goodisman formula predicts significant upfield shifts for exocyclic carbon atoms and carbon atoms in adjacent fused rings, whereas, in fact, the opposite effect is observed, i.e., that such carbon atoms show very small upfield shifts or even downfield shifts in contrast to the large upfield shifts (30 ppm) of the carbon atoms of the ring π bonded to the metal atom.[10,11] Finally, a calculation of ^{13}C chemical shifts by an INDO finite perturbation method for the series CH_4, C_2H_6, C_2H_4, and C_2H_2 showed that variations in chemical shifts in this series are dominated by variations in the one-center paramagnetic term and that, although the numerical value of the one-center diamagnetic term is large, contributions from two-center terms are negligible.[12] For these reasons, we feel that the Flygare–Goodisman formula cannot be used to calculate σ^d for organometallic systems and that trends in the chemical shifts of carbon atoms in ligands bonded to transition elements can be discussed adequately in terms of the paramagnetic term (σ^p) which must, of course, include interaction terms between the orbitals centered on the carbon atom in question and orbitals on distant nuclei, especially, the transition-metal atom.

Turning our attention to observed shifts of organometallic systems, we may distinguish to a first approximation between σ-bonded and π-bonded ligands. In the former case, we are primarily interested in the carbonyl group which when bonded to a transition metal generally experiences a *downfield* shift, whereas π-bonded ligands such as ethylene, cyclopentadienyl, benzene, etc., show marked upfield shifts.[2] Earlier workers discussed these effects qualitatively assuming that the dominant paramagnetic term was given by the Pople–Karplus equation[13]

$$\sigma^p = -(K/\Delta E)\langle r^{-3}\rangle_{2p}\Sigma Q_{AB}$$

where ΔE is an average excitation energy, $\langle r^{-3}\rangle_{2p}$ is the expectation value of the inverse cubed radius of the 2p orbitals, and the Q terms involve bond-order/density matrix terms. For example, Gansow and co-workers[14] suggested that for a range of complexes $LM(CO)_5$ [M = Mo, W; L = $P(OR)_3$, PR_3, etc.], as the ability of L to π bond with M decreases, the $(\Delta E)^{-1}$ term and the increased π bonding to carbon should cause increased shielding, whereas the $\langle r^{-3}\rangle_{2p}$ term would give decreased shielding. However, Braterman and co-workers[15] suggested that changes in C–O bond polarity (which affect both $\langle r^{-3}\rangle_{2p}$ and Q_{AB} with the r term dominant) occur because attached electronegative groups decrease π-bond polarity leading to upfield shifts; alternatively if M–CO π bonding increases, the $(\Delta E)^{-1}$ term may dominate, thereby giving downfield shifts. Thus, obviously, it is very difficult to assess qualitatively the various factors influencing the chemical shifts of σ-bonded ligands.

In the case of π-bonded ligands, upfield shifts are invariably observed, but it is now even more difficult to assess qualitatively the effect of bonding on the three terms in the above equation and, consequently, other qualitative approaches have been suggested.[2] For example, attempts have been made to use ^{13}C shifts in π-bonded ligands to estimate charges on the rings by extrapolation from isolated ring systems where the ^{13}C shift has been related to the charge on an sp^2 carbon atom.[16] Thus, in the tricarbonylarenemetals in which upfield shifts of about 30 ppm (relative to the pure atom) are observed in the sequence W > Cr > Mo it was concluded that about one electron was transferred to the benzene ring,[17] but this approach when applied to ferrocene gives a charge distribution of $(C_5H_5)^{-1.8}{}_2Fe^{+3.6}$, which is obviously ridiculous.[2] Alternatively, the upfield shifts may be interpreted in terms of rehybridization in the complexed ring,[17] but the low-temperature neutron-diffraction work of Coppens shows no evidence to support this.[18] More detailed studies of a range of monosubstituted tricarbonylarenechromiums[19] and of the series[20] $[(CH_3)_nC_6H_{6-n}Mn(CO)_3]^+$ confirm the upfield shift of the arene carbon resonances and of the downfield shift of the carbonyl carbon resonances. We now consider the application of the SCCCMO method to the above problem.

Method

The self-consistent charge and configuration molecular orbital method (SCCCMO) of this paper used an atomic orbital basis set employing the Richardson functions for the metal orbitals[21,22] and Clementi and Raimondi functions[23] for all other atoms. The Wolfsberg–Helmholz approximation was used for the off-diagonal H terms ($k = 1.75$)[24] and the VOIP's for the diagonal H terms.[25] Experimental geometries were chosen in all cases except nickel where ideal geometry was assumed.[26-29] A number of molecular orbital calculations have been reported for $C_6H_6Cr(CO)_3$,[30-32] $C_5H_5Mn(CO)_3$,[33] $C_4H_4Fe(CO)_3$,[34] and $C_3H_5Co(CO)_3$.[35] In a previous note,[36] we reported results for the present series, $AM(CO)_3$, taking into account only the π orbitals of the ring moiety A, while, more recently, one of us reported a CNDO study of the series.[37] $\sum Q_{AB}$ values were calculated using the method of Pople and Karplus while the $\langle r^{-3}\rangle_{2p}$ values ($=\xi^3/3$, where ξ = orbital exponent) were calculated by modifying the neutral carbon atom exponent to allow for the charges on the carbon atoms. Calculation of the ΔE values will be discussed later. Separate SCCCMO calculations were performed on the isolated carbon monoxide and benzene ligands, using experimental geometries.[38,39]

Table I. Metal, Ligand (A), and Carbonyl Charges

		Cr	Mn	Fe	Co	Ni
q_M	*a*	0.600	0.511	0.410	0.333	0.242
	b	0.182	0.123	0.143	0.085	0.113
	c	0.540	0.553	0.614	0.445	0.223
q_A	*a*	−0.133	−0.157	−0.123	−0.095	−0.144
	b	0.572	0.566	0.193	0.301	0.032
	c	−0.158	−0.398	−0.676	−0.560	−0.107
q_{CO}[d]	*a*	−0.156	−0.118	−0.095	−0.079	−0.033
	b	−0.251	−0.231	−0.113	−0.129	−0.049
	c	−0.129	−0.052	0.021	0.038	−0.039

[a] SCCC ($\sigma + \pi$). [b] SCCC (π).[36] [c] CNDO.[37] [d] Average values.

Table II. M–C(O) Bond Properties (average values per CO)

		Cr	Mn	Fe	Co	Ni
Overlap pop	*a*	0.254	0.247	0.228	0.230	0.235
Overlap pop	*b*	0.392	0.360	0.287	0.219	0.213
Wiberg index	*c*	0.807	0.797	0.602	0.538	0.563

[a] $\sigma + \pi$. [b] π.[36] [c] CNDO.[37]

Table III. C–O Bond Properties (average values per CO)

		Cr	Mn	Fe	Co	Ni
Overlap pop	*a*	0.709	0.723	0.748	0.743	0.757
π^*	*b*	0.356	0.326	0.208	0.199	0.136
Wiberg index	*c*	2.231	2.286	2.394	2.396	2.365

[a] $\sigma + \pi$. [b] π.[36] [c] CNDO.[37]

Results and Discussion

In view of the use of an atomic orbital basis set and hence the inclusion of both σ and π orbitals of the ring moiety, it is useful to compare the present results with those obtained previously (a) by the SCCCMO method including π orbitals only[36] and (b) by the CNDO method.[37] Table I gives this comparison for metal charge, ligand (A) charge, and carbonyl charge. Table II gives the M–C(O) Mulliken overlap populations for the SCCC and the Wiberg indices for the CNDO calculations while Table III gives the C–O Mulliken overlap population for the ($\sigma + \pi$) SCCC calculation, the π^* orbital population for the π SCCC, and the C–O Wiberg indices for the CNDO calculations.

In general, all three methods give similar *trends* (Tables I, II, III) which is an encouraging result and supports our general philosophy concerning the use of semiempirical MO theory for correlating trends in chemical behavior in a series of related molecules. Nevertheless, there are differences and the inclusion of both ring σ and π orbitals leads to less charge transfer from the ring to the carbonyl groups than obtained when only the ring π orbitals are considered. In all cases, the CNDO charges give closer agreement with the SCCCMO ($\sigma + \pi$) charges than with the SCCCMO (π only) ones. Correlation between observed infrared carbonyl stretching frequencies, ν(CO), and the C–O bond properties is excellent in the three calculations and, similarly, the previous correlation noted between kinetic activity for carbonyl substitution with the M–C(O) overlap population and with metal charge q_M holds for the SCCCMO ($\sigma + \pi$) calculations of this paper. We are confident, therefore, that the method used here provides a good correlation between experiment and theory for the $AM(CO)_3$ series and so may be used as a basis for discussion of the ^{13}C NMR shifts in this series.

^{13}C NMR Shifts. As explained above, we shall assume that σ^d and σ' are effectively constant in the series $AM(CO)_3$ and so relate the observed ^{13}C NMR shifts to changes in the paramagnetic term σ^p only. In the latter case, only rotationally allowed transitions contribute to σ^p, which is a useful simplifying factor especially for the carbonyl ligands where it permits a completely unambiguous correlation of observed downfield shifts (Tables IV, V, VI).

Table IV. Carbonyl ^{13}C Shielding in $AM(CO)_3$ (average values)

	Cr	Mn	Fe	Co	Ni
ΣQ_{AB}	1.347	1.331	1.333	1.333	1.341
$\langle r^{-3}\rangle_{2p}$	1.293	1.301	1.304	1.307	1.316
$(\Delta E)^{-1}$	0.418	0.391	0.389	0.527	0.388
σ^p	−702.8	−653.6	−652.8	−886.4	−661.0
δ(exptl)	−233.3[a]	−225.1[b]	−209.0[c]		

[a] From ref 19. [b] From ref 40. [c] From ref 41.

Table V. Arene ^{13}C Shielding in $AM(CO)_3$ (average values)

	Cr	Mn	Fe	Co	Ni
ΣQ_{AB}	1.470	1.478	1.409	1.402	1.397
$\langle r^{-3}\rangle_{2p}$	1.279	1.273	1.274	1.277	1.268
σ^p	−303.1	−303.3	−289.4	−288.6	−285.6
δ(exptl)	−93.5[a]	−82.7[b]	−61.0[c]		

[a] From ref 19. [b] From ref 40. [c] From ref 41.

Table VI. ^{13}C Shielding in CO and C_6H_6

	CO	C_6H_6
ΣQ_{AB}	1.616	1.558
$\langle r^{-3}\rangle_{2p}$	1.312	1.283
$(\Delta E)^{-1}$	0.292	0.167
σ^p	−597.7	−322.3
δ(exptl)	−181.3[a]	−128.0[b]

[a] From ref 42. [b] From ref 19.

For all ligands, the $\sum Q_{AB}$ and $\langle r^{-3}\rangle_{2p}$ were calculated as discussed above from the output data from the SCCCMO ($\sigma + \pi$) program and are given in Tables IV and V for both the carbonyl ligand and the A moiety in the complexes, while Table VI gives the results for free CO and benzene. It is the estimation of $(\Delta E)^{-1}$ which presents problems. In the case of the free carbon monoxide ligand ΔE was taken directly from the rotationally allowed transition between the highest occupied molecular orbital, HOMO (5σ), and the lowest unoccupied orbital, LUMO (2π). In the $AM(CO)_3$ series, there is a group of predominantly $M(CO)_3$ orbitals in both the highest occupied and the lowest unoccupied regions, and also in this case ΔE was taken as the HOMO–LUMO separation. The calculated σ^p for the carbonyl ligand are given in Table IV for the $AM(CO)_3$ series while the calculated value for free CO is in Table VI. Assuming σ^d and σ' are effectively constant, it is possible to compare σ^p directly with the experimental shifts (relative to Me_4Si) which have been reported for $C_6H_6Cr(CO)_3$,[19] $C_5H_5Mn(CO)_3$,[40] $C_4H_4Fe(CO)_3$,[41] and free CO.[42] It is gratifying to find that both the downfield shift of the carbonyl carbon atom in these complexes relative to that in free CO and the sequence of shifts within that series are predicted. It is also apparent that the downfield shift is a consequence of the product of the three factors in the Pople–Karplus equation and so qualitative attempts to discuss ^{13}C shifts in complexes in terms of any one of these factors are probably doomed from the start. However, it may be noted that the $(\Delta E)^{-1}$ term predominates. The confusion existing in the literature heretofore is not surprising therefore, and we urge extreme caution in any attempts of this type.

In the case of the A moiety, the position is much more complex because now there is no longer a predominant and unambiguous transition from which one may calculate ΔE as could be done for the carbonyl ligand. Consider the case of $C_6H_6Cr(CO)_3$; discounting the predominantly $M(CO)_3$ orbitals, rotationally allowed transitions between which have already been used to calculate σ^p for the carbonyl carbon, there are a number of rotationally allowed transitions between predominantly A moiety σ and π orbitals, for example, ΔE = 5.10, 5.25, 5.70, and 6.03 eV, and the question arises as to a choice between these transitions and, indeed, how far to extend the range of ΔE values across the complete range of both occupied and unoccupied orbitals. In principle, one may abandon the Pople–Karplus average energy excitation formula and resort to the original formula involving summation over the complete energy manifold,[43] but our attempts to do this gave disappointing results. This, again, is not surprising in view of the known inadequacy of MO methods to calculate excitation energies; indeed in a recent review[44] Ditchfield pointed out that proper use of the basic formulas for calculating σ^p should include integration over continuum states so use of the summation formula may not be feasible for molecules such as $AM(CO)_3$. Secondly, one may choose the calculated transition in $AM(CO)_3$ involving predominantly those A ligand orbitals which correspond most closely with the allowed HOMO → LUMO transition in the free ligand (6.03 eV in the complex compared with 5.94 eV in free benzene). Indeed, if this is done for $C_6H_6Cr(CO)_3$ then σ^p calculated for the complexed benzene is obtained as −301.0 ppm compared with −324.9 ppm for the free ligand so that the calculated upfield shift on complexing is in agreement with the observed shift (−93.5 ppm in $C_6H_6Cr(CO)_3$ vs. −128.0 ppm in free benzene). However, this choice is difficult to sustain in view of the close proximity of other rotationally allowed transitions in $C_6H_6Cr(CO)_3$. Consequently, we consider that the most consistent approach is to use the Pople–Karplus average excitation energy formula and to take a fixed and experimentally reasonable ΔE value for the A ligand in the complete series $AM(CO)_3$. The value of ΔE was taken as approximately the first rotationally allowed transition in free benzene (6.0 eV). The σ^p thus calculated are given in Tables V and VI and may be compared with the experimental values for three of the complexes and for free benzene. Although only fair agreement is obtained between the calculated σ^p values and observed shifts, it is again gratifying to note that, in the case of benzene, an upfield shift for the ligand in the complex compared with the free ligand is predicted as observed.

In conclusion use of SCCCMO theory together with the Pople–Karplus equation for σ^p gives a satisfactory explanation of the observed downfield shifts for the carbonyl ligand in the series $AM(CO)_3$; it also provides a rationalization of the upfield shifts of the carbon atoms in the attached A ligands although calculation of the average excitation energy ΔE is much more difficult. We feel that our results show two things clearly: firstly, that qualitative discussions of ^{13}C shifts are not likely to be successful because of the necessity of taking into account all three terms in the Pople–Karplus formula and, secondly, that the observed shifts in a related series can be correlated in terms of σ^p alone without allowing for variations in the σ^d term which if calculated by the formula of Flygare and Goodisman would be large (>100 ppm for even first-row transition elements).

Registry No. $C_6H_6Cr(CO)_3$, 12082-08-5; $C_6H_5Mn(CO)_3$, 12079-65-1; $C_4H_4Fe(CO)_3$, 12078-17-0; $C_3H_5Co(CO)_3$, 12144-85-3; $C_2H_4Ni(CO)_3$, 56082-48-5; CO, 630-08-0; C_6H_6, 71-43-2; ^{13}C, 7440-44-0.

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