Molecular-orbital Treatment of the Relative Strengths of Metal–Carbon Bonds in Substituted Metal Carbonyls

By **Derek W. Smith,** School of Science, University of Waikato, Hamilton, New Zealand

Relative M–C bond orders in metal carbonyl derivatives $M(CO)_nX_{6-n}$ have been determined from extended Hückel calculations. The results are in agreement with experimental determinations of M–C bond strengths; the M–C bond order increases with increasing subsitution, and CO groups *trans* to substituents are predicted to be more strongly bound than CO groups *trans* to other CO groups. The relative stabilities of geometrical isomers are correctly predicted. The theoretical basis for the conventional qualitative rationalisations of these phenomena is explored.

STRUCTURAL and spectroscopic studies of transition-metal carbonyls and their derivatives suggest that the M–CO bond shortens with increasing substitution by ligands X, which are usually poorer π acceptors and better σ donors than CO. Moreover, M–CO bonds which are *trans* to an X substituent in octahedral systems $M(CO)_nX_{6-n}$ are apparently shorter than M–CO bonds which are *trans* to other CO groups. For $n = 3$ or 4, the geometrical isomer having the greater number of CO groups *trans* to X groups is more often encountered. Table 1 lists some structural data which illustrate these points. Spectroscopic data [1-4] suggest that C–O bonds *trans* to other CO groups are stronger than C–O bonds *trans* to X substituents, consistent with structural studies. In trigonal-bipyramidal systems $M(CO)_nX_{5-n}$ the CO groups prefer equatorial positions.[5-7]

TABLE 1

Structural data (Å) for some $[Cr(CO)_nX_{6-n}]$ molecules

Compound	Cr–C distance		Ref.
	trans to CO	*trans* to X	
$[Cr(CO)_6]$	1.909(3)		*a*
$[Cr(CO)_5(PPh_3)]$	1.880(4)	1.844(4)	*b*
$[Cr(CO)_5\{P(OPh)_3\}]$	1.896(4)	1.861(4)	*b*
$[Cr(CO)_4(dppe)]$ [c]	1.884(7)	1.831(7)	*d*
$[Cr(CO)_4\{P(OPh)_3\}_2]$	1.878(6)		*e*
$[Cr(CO)_3(PH_3)_3]$		1.838(7)	*f*
$[Cr(CO)_3(apd)]$ [g]		1.817(8)	*h*

[a] A. Whitaker and J. W. Jeffrey, *Acta Cryst.*, 1967, **B23**, 977. [b] H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, 1969, **91**, 4326. [c] dppe = 1,2-Bis(diphenylphosphino)-ethane. [d] M. J. Bennett, F. A. Cotton, and M. D. LaPrade, *Acta Cryst.*, 1971, **B27**, 1899. [e] H. S. Preston, J. M. Stewart. A. T. Plastas, and S. O. Grim, *Inorg. Chem.*, 1972, **11**, 161. [f] G. Huttner and S. Schell, *J. Organometallic Chem.*, 1973, **47**, 383. [g] apd = 3-Azapentane-1,5-diamine. [h] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

The qualitative rationalisation of these observations is well established. In octahedral systems, a maximum of three π-bonding molecular orbitals (m.o.s) can be constructed. Thus it is asserted [4] that the M–C π-bond order in $M(CO)_6$ is 0.5, increasing to 1.0 in $M(CO)_3X_3$, where there are three filled π-bonding m.o.s and three M–CO bonds in an 18-electron system. It is further argued that a CO group *trans* to a substituent is more strongly bonded than one *trans* to another CO group, since two *trans*-CO groups necessarily share the same *d* orbitals for π bonding. This simple and useful argument can be justified by considering group overlap integrals. If, in an octahedral system, a bonding m.o. is formed by π overlap of a metal t_{2g} orbital with a single CO π-antibonding m.o., the group overlap integral G_π is simply equal to S_π, the diatomic overlap integral. For the overlap of two π-antibonding m.o.s of *trans*-CO groups with the same metal *d* orbital, G_π is equal to $2^{\frac{1}{2}}S_\pi$, and not to $2S_\pi$. It is easy to show by such arguments that mutually *cis* CO groups enjoy more π overlap with metal *d* orbitals than *trans*-CO groups. However, overlap integrals are not strictly additive quantities. If it is assumed that the stabilisation afforded by a filled bonding m.o. is proportional to the square of the group overlap integral, the distinction between CO groups *cis* and *trans* to substituents is lost. There are sound reasons for preferring this 'squared-overlap' assumption. Kettle [8] showed, using perturbation theory, that the strength of an M–CO π bond is proportional to k^2, where $G_\pi = kS_\pi$, provided that the overlap is small and the energy separation between the overlapping orbitals is great. Moreover, any simple assumptions made about the relations between m.o. energies and overlap integrals must satisfy boundary conditions in limits of accidental degeneracy. The 'squared-overlap' approximation satisfies these, but other simple relations do not (see Appendix). Kettle [8] noted the interesting result that the sum of the squared group overlap-integral coefficients k^2 between metal *d* orbitals and CO π orbitals in $M(CO)_mX_n$ is always equal to $2m$, irrespective of geometry. The electronic stabilisation energy (for 18-electron systems) per M–C bond arising from π overlap is constant, and all M–C bonds have the same squared π overlap. Thus the structural features discussed above cannot be explained.

Clearly, a m.o. theory is needed for substituted metal carbonyls which goes beyond the simple perturbation

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[1] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[2] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1.

[3] L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

[4] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[5] J. R. Shapley and J. A. Osborn, *Accounts Chem. Res.*, 1973, **6**, 305.

[6] M. R. Churchill and K.-K. G. Lin, *J. Amer. Chem. Soc.*, 1974, **96**, 76.

[7] S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 770.

[8] S. F. A. Kettle, *J. Chem. Soc.* (*A*), 1966, 420.

treatment. Molecular-orbital calculations have been made on these systems at various levels of approximation, ranging from the SCCC model,[9] through more elaborate non-empirical treatments [10–12] to *ab initio* SCF calculations.[13] None of these provides an intelligible explanation of the relative strengths of M–C bonds in carbonyl derivatives since they start from the observed geometry. The extended Hückel approach has recently returned to favour as a framework for calculation of the equilibrium geometries of metal carbonyl fragments $M(CO)_x$.[14–17] This work emphasises the importance of σ bonding and of *d–s* and *d–p* mixing in determining the most stable configurations of such fragments. Elian and Hoffmann [17] go on to suggest that the most stable configurations for substituted carbonyls can be predicted by considering the interaction between the appropriate carbonyl fragment $M(CO)_x$ and σ-donor groups, using empty hybrid acceptor orbitals on the metal. Thus they predict (as does Burdett [14]) that a d^6 $M(CO)_4$ species should have C_{2v} rather than D_{4h} symmetry; but since the acceptor orbitals lie higher in energy in C_{2v} than in D_{4h} symmetry, they argue that for d^6 $M(CO)_4X_2$ the *trans* isomer should be more stable if the X groups are better σ donors than CO, while the *cis* configuration is favoured if the substituents are poorer σ donors than CO. This conclusion is not supported by the experimental facts; most X groups in substituted metal carbonyls are better σ donors than CO, yet the *cis* configuration seems to be favoured for $M(CO)_4X_2$. None of these extended-Hückel and angular-overlap calculations explains the observed trends in metal–carbon bond lengths.

In the hope of resolving these difficulties, I have made simple extended-Hückel calculations on substituted metal carbonyls. It is suggested that M–CO bond lengths can be related to M–CO π-bond orders; since the model of Elian and Hoffmann,[17] with its emphasis on σ bonding as the dominant factor in determining stereochemistry, fails to account for the experimental geometries of d^6 $M(CO)_4X_2$, it may be that the role of π bonding deserves greater emphasis. We are therefore concerned with the calculation of electronic stabilisation energies arising from the occupancy of π-bonding m.o.s in octahedral $M(CO)_nX_{6-n}$.

The m.o. energies are given by the roots of the determinant (1). The off-diagonal elements H_{ij} are obtained by use of the Wolfsberg–Helmholtz equation (2). In

$$|H_{ij} - G_{ij}E| = 0 \qquad (1)$$

$$H_{ij} = cG_{ij}(H_{ii} + H_{jj})/2 \qquad (2)$$

most extended-Hückel treatments, the diagonal elements are estimated from atomic spectral data and iterative procedures are used to obtain m.o.s which lead to charge distributions compatible with the chosen values of H_{ii} and H_{jj}. Fixed values are adopted for the diagonal elements for simplicity; thus the results have no absolute significance, since they take no account of the identity of the metal or its formal oxidation number; nor can they take into account the effects of electron withdrawal and donation by different types of substituent. The element H_{ii} is taken to be $-80\,000$ cm^{-1} for metal *d* orbitals and $-40\,000$ cm^{-1} for CO π-antibonding m.o.s. The parameter *c* in (2) is set equal to 2.00, and the two-centre overlap integral S_π is taken to be 0.15. Ligand–ligand overlap is neglected, as is overlap involving filled CO π m.o.s. Group overlap-integral coefficients are calculated in the usual way.[18] The substituents are assumed to be engaged only in σ bonding.

Having found the energies of the π bonding m.o.s, the electronic stabilisation energies arising from their occupancy can be calculated by taking the difference between the m.o. energy and H_{ii} for the metal *d* orbitals. Relative M–C π-bond orders may then be determined as follows. The π-bond order in the triatomic molecule MCO is arbitrarily assigned the value of 2.000 for a d^4 system where two π-bonding m.o.s (degenerate) are filled. For a substituted carbonyl $M(CO)_nX_{6-n}$ the stabilisation energy is partitioned among the M–C bonds; the π-bond order of a particular M–C bond which has been apportioned a stabilisation energy of ΔE will then be $2(\Delta E/\Delta E_0)$, where ΔE_0 is the stabilisation energy found for MCO. In cases where all M–C bonds are equivalent, the partitioning of the π-electronic stabilisation energy in this manner is straightforward, but it is not immediately obvious how we should partition the electronic stabilisation energy of a filled bonding m.o. which involves non-equivalent CO groups. For example, in the case of $M(CO)_5X$ (C_{4v}), the *e* π-bonding m.o.s involve both equatorial and axial CO groups. The simplest way of apportioning the stabilisation energy arising from the occupancy of an *e* π-bonding m.o. is to divide it equally among the three M–C bonds (two equatorial and one axial) to which it contributes. This assumption is not so naive as it may seem. The application of the considerations discussed in the Appendix to bond orders shows that this simple assumption will uphold the relevant boundary conditions; alternatively, the stabilisation energy can be partitioned in the ratio of the squared group overlap-integral coefficients. Moreover, the bond order between atoms *a* and *b* has been quantitatively related [19] to the bond population r', given by (3), where c_{ai} and c_{bi} are the coefficients

$$r' = \Sigma_i n_i c_{ai} c_{bi} S_{abi} \qquad (3)$$

of atomic orbitals on atoms *a* and *b* in the *i*th m.o. and n_i is the occupation number (0, 1, or 2) of the *i*th m.o. It follows from the form of the secular determinants that,

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[9] D. A. Brown and W. J. Chambers, *J. Chem. Soc.* (*A*), 1971, 2083.

[10] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 1970, **9**, 1053.

[11] M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, **11**, 1619.

[12] A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, 1975, **14**, 247.

[13] B. R. Higginson, D. R. Lloyd, J. A. Connor, and I. H. Hillier, *J.C.S. Faraday II*, 1974, 1418.

[14] J. K. Burdett *J.C.S. Faraday II*, 1974, 1599.

[15] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.

[16] A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.

[17] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[18] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1821.

[19] J. Stals, *Rev. Pure Appl. Chem.*, 1970, **20**, 1 and refs. therein.

for a π-bonding m.o. such as (4), where a metal orbital ϕ_M overlaps with two distinct CO group orbitals ϕ_L and

$$\psi = c_M\phi_M + c_L\phi_L + c_{L'}\phi_{L'} \qquad (4)$$

$\phi_{L'}$, $c_L/c_{L'} = k_{ML}/k_{ML'}$, where the quantities k are the group overlap-integral coefficients. It would thus follow that the contributions to the relevant bond populations from the two group overlap integrals would be in the ratio of the squared group overlap-integral coefficients.

A further difficulty in octahedral compounds having C_{nv} symmetry is the possibility of appreciable *d–p* mixing. There are widely differing views on the importance of metal $(n + l)p$ orbitals in metal carbonyl derivatives;[14,20] *d–p* mixing will be ignored in the hope that it may not be very important.

RESULTS AND DISCUSSION

Calculated M–C π-bond orders and CO π-antibonding orbital populations for octahedral d^6 $M(CO)_nX_{6-n}$ species are listed in Table 2. The M–C bond orders follow trends consistent with the experimental results; the π-bond order increases with increasing substitution, and is greater for CO groups *trans* to substituents than for those *trans* to other CO groups. The total π-orbital stabilisation energies (reflected by the sum of the π-bond orders) predict that the C_{2v} (*cis*) isomer of $M(CO)_4X_2$ should be more stable, while C_{3v} geometry is preferred for $M(CO)_3X_3$. The populations of the π-antibonding m.o.s of the CO groups follow the trends expected from vibrational spectra,[1-4] to the extent that approximate C–O force constants reflect the extent of π backbonding.[11]

TABLE 2

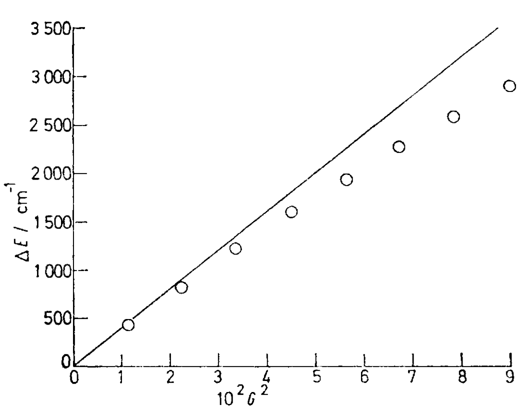
Results of m.o. calculations on substituted metal carbonyls: (a) and (b) refer respectively to CO groups which are *trans* to another CO group or to an X substituent

System	M–C π-bond order	Population of CO antibonding m.o.s
MCO	2.000	0.1589
$M(CO)_6$	1.711	0.1188
$M(CO)_5X$	1.752(a)	0.1241(a)
	1.794(b)	0.1295(b)
$M(CO)_4X_2(D_{4h})$	1.803	0.1306
$M(CO)_4X_2(C_{2v})$	1.794(a)	0.1295(a)
	1.842(b)	0.1360(b)
$M(CO)_3X_3(C_{2v})$	1.842(a)	0.1360(a)
	1.897(b)	0.1442(b)
$M(CO)_3X_3(C_{3v})$	1.889	0.1425
$M(CO)_2X_4(D_{4h})$	1.889	0.1425
$M(CO)_2X_4(C_{2v})$	1.945	0.1507
$M(CO)X_5$	2.000	0.1589

The reasons for the trends in π-bond orders can be found in some quite simple algebra arising from the solution of the secular determinants. Within the approximations, the stabilisation ΔE of a π-bonding m.o. depends on 'squared-overlap' considerations to the extent that it depends only on the value of the sum of the squares of the relevant group overlap integrals, irrespective of how these are distributed over the various ligand-group orbitals with which a *d* orbital may overlap. But ΔE is not directly proportional to G_π^2 except, to a very good approximation, for very small values of G_π. This is illustrated in the Figure, where ΔE is plotted against G_π^2 (or, where appropriate, ΣG_π^2 over all relevant group orbitals). For small values of G_π, the plot is linear, with a gradient of 40 cm^{-1}; in general, the gradient is given by (5), where H_1 and H_2 are the diagonal elements in the secular determinant. If a straight line of this

$$\text{Gradient} = (H_1^2 - H_2^2 - H_1H_2)/(H_1 - H_2) \quad (5)$$

gradient is regarded as representing the stabilisation energy of a bonding m.o. in Kettle's squared-overlap approximation, the deviation from squared-overlap proportionality is always negative irrespective of the choice of parameters in the secular determinants. Moreover, the negative deviation from the straight line increases sharply as G_π increases; further analysis shows this deviation to be proportional to $G_\pi^{3.7}$. Thus if we have a bonding m.o. with a group overlap-integral coefficient of $2^{\frac{1}{2}}$, the stabilisation energy will be less than that afforded by two bonding m.o.s with group overlap-integral coefficients of 1. Given two isomers with the same total squared π overlap, the greater stabilisation energy will be obtained with the isomer in which the squared overlap is more evenly distributed among the m.o.s. In octahedral complexes, the group overlap-integral coefficients for overlaps with CO groups *trans* to substituents are always relatively small and the squared overlap is more economically utilised, leading to higher π-bond orders. Group overlap-integral coefficients increase with the number of CO groups present (and especially with the number of CO groups *trans* to one another), so that, although the total amount of squared overlap per CO group is constant, the stabilisation energy afforded per M–C bond decreases. Hence M–C bond orders increase with increasing substitution.



Plot of m.o. stabilisation energy against G_π^2. The straight line of gradient 40 cm^{-1} represents the stabilisation energies as predicted by 'squared-overlap' proportionality

It should be noted that the nature of the curve in the Figure could be predicted from the binomial expansion

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[20] P. S. Braterman, *Structure and Bonding*, 1972, **10**, 57.

of the secular determinant discussed in the Appendix to ref. 15. This analysis uses a rather different type of determinant from mine, however; the off-diagonal terms are essentially perturbation matrix elements which are set proportional to the overlap integral and contain no term in E.

The simple qualitative rationalisations which depend on counting overlap integrals can be justified by some elementary algebraic inequalities. If, as I have suggested, π bonding is optimised by even sharing of the available squared overlap, it can be shown that the situation having the maximum total (unsquared) overlap is favoured. For example, if $a^2 + b^2 = 2c^2$, it is easy to show that $2c > a + b$. Further, if $a > b > c > d$, and if $a^2 + d^2 = b^2 + c^2$, then $b + c > a + d$. Thus the conventional rationale of M–C bond lengths in substituted carbonyls is essentially correct, although the underlying theory is rather more subtle. Moreover, these inequalities emphasise the point that my results do not depend on our choice of parameters (provided that the relevant metal and ligand orbitals lie at negative energy, and that the metal d orbitals lie lower than the CO π-antibonding orbitals) and the trends in our calculated π-bond orders are indeed general.

A weakness in this model is in the neglect of the effects of the substituents on the values of the diagonal elements in the secular determinants. Clearly, a ligand which behaves as a good σ donor and a poor π acceptor will make H_{ii} for the metal d orbitals less negative, and increase the π interaction with the CO groups. This effect alone would lead to an increase in the M–C π-bond order with increasing substitution, although it would not explain the different bond lengths in, for example, $M(CO)_4X_2$ (C_{2v}), nor would it account for the relative stabilities of isomers. I am presently looking into the question of how far the variation in M–C bond lengths with increasing substitution results simply from the increased availability of electron density at the metal for π-back donation to the CO groups. I have also extended the calculations to d^8 trigonal-bipyramidal systems $M(CO)_nX_{5-n}$. Difficulties arise here with σ–π mixing, but it can be predicted that CO groups should prefer equatorial positions in the coordination sphere. I do not report these results in detail here since Rossi and Hoffmann[16] have dealt thoroughly with this topic.

APPENDIX

Consider an octahedral complex MX_5Y, where both X and Y can function as π acceptors. In C_{4v} symmetry, π-bonding m.o.s are obtained labelled b_2 and e; the former arises from the overlap of d_{xy} with equatorial ligand orbitals, while the latter involves overlap of d_{xz} and d_{yz} with both equatorial and axial ligands. The group overlap-integral coefficient for overlap of d_{xy} with the b_2 combination of equatorial X groups is 2; for the e m.o.s, the corresponding coefficients for equatorial X and axial X and Y are respectively $2^{\frac{1}{2}}$, 1, and 1. If a simple approximation is made relating m.o. stabilisation energies to group overlap-integral coefficients it must be ensured that, in the limit where Y is very nearly equivalent to X and the microsymmetry approaches O_h, the b_2 and e bonding m.o.s become accidentally degenerate.

Assuming direct proportionality between m.o. stabilisation energies and group overlap integrals, the relations (A.1) and (A.2), may be proposed, where c_x and c_y are the proportionality constants appropriate to X and Y. These

$$\Delta E(b_2) = 2c_x \tag{A.1}$$

$$\Delta E(e) = 2^{\frac{1}{2}}c_x + c_y + c_x \tag{A.2}$$

expressions obviously fail in the limit of accidental degeneracy. If, on the other hand, it is proposed that m.o. stabilisation energies are proportional to the squares of group overlap-integral coefficients k, equations (A.3)—(A.5) are obtained, which lead to degeneracy of b_2 and e in the

$$\Delta E = \sum_i k_i^2 c_i \tag{A.3}$$

$$\Delta E(b_2) = 4c_x \tag{A.4}$$

$$\Delta E(e) = 2c_x + c_x + c_y \tag{A.5}$$

limit where $X \equiv Y$ and $c_x = c_y$. In (A.3) the summation is made over all group orbitals of the appropriate symmetry. Working through other examples should convince the reader that the 'squared-overlap' approximation is generally successful in predicting accidental degeneracies of this kind.

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