Journal of Organometallic Chemistry, 213 (1981) 35—43
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METAL—METAL AND METAL—LIGAND BOND STRENGTHS IN METAL CARBONYL CLUSTERS *

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(Received January 5th, 1981)

Summary

The assignment of energies to the metal—metal bonds of metal carbonyl clusters, using the bond length (d)-enthalpy (E) relationships of the form $E = Ad^{-4.6}$, is discussed. Clusters of the manganese, iron and cobalt subgroups are considered. The method affords enthalpies for the cluster bonds lower than previous treatments, and implies that the metal—ligand bonds become stronger as the cluster nuclearity increases.

Introduction

Skeletal electron counting schemes developed to rationalize the shapes of boron clusters have proved of some use in predicting or accounting for the shapes of certain intermediate-sized metal carbonyl clusters [1,2] and have prompted discussion of the respects in which metal clusters resemble, or differ from, their boron analogues [3—13]. The present paper, which amplifies arguments outlined briefly in a previous publication [14], is concerned with the question of whether the skeletal bonding in metal carbonyl clusters that superficially resemble boron clusters is really as weak as the boron analogy appears to imply.

The problem is exemplified by the series of octahedral metal carbonyl clusters, of which $Rh_6(CO)_{16}$ [15], $H_2Ru_6(CO)_{18}$ [16], $[HRu_6(CO)_{18}]^-$ [17], $[HOs_6(CO)_{18}]^-$ [18], $[Os_6(CO)_{18}]^{2-}$ [18], $[Co_6(CO)_{14}]^{4-}$ [19],

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* Dedicated to the memory of Professor Paolo Chini.

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$[Co_4Ni_2(CO)_{14}]^{2-}$ [20], $[Ni_6(CO)_{12}]^{2-}$ [21], $Ru_6(CO)_{17}C$ [22] and $[Fe_6(CO)_{16}C]^{2-}$ [23] are examples, that contain 86 valence shell electrons, just two electrons too many to allow their bonding to be described in terms of 2-centre electron pair metal—metal bonds along each of their twelve octahedral edges, with each metal atom assigned a full complement of eighteen valence shell electrons. A localized bond treatment of their skeletal bonding thus requires eleven metal—metal bonds to resonate among the twelve edges, conferring on each edge a metal—metal bond order of $\frac{11}{12}$, i.e. 0.92. The borane analogy on the other hand treats these clusters as *closo* systems like $B_6H_6^{2-}$, i.e. clusters in which the six skeletal atoms are held together by seven skeletal bond pairs. Although these are usually regarded as delocalized throughout the whole of the cluster skeleton, their number corresponds to an average edge bond order of $\frac{7}{12}$, i.e. 0.58, less than two-thirds of the bond order implied by the 2-centre bond description. Here we point out that the metal—metal distances normally found in metal carbonyl clusters tend to be comparable to, or greater than, the metal—metal distances in the bulk parent metals, suggesting that the bond orders in the cluster are therefore like or lower than the bond orders in the parent metals which, for a close-packed (c.p.) lattice, cannot exceed $\nu/12$, where ν is the number of valence shell electrons, i.e. $\nu = 8$ for Fe, Ru and Os; $\nu = 9$ for Co, Rh and Ir etc. These bond orders are lower than the 2-centre bonding description implies. We also elaborate arguments by which the enthalpies of disruption of metal carbonyls into metal atoms and carbon monoxide molecules can be assigned to bond enthalpy terms that reflect the lengths of their metal—metal and metal—ligand bonds, so affording some insight into the strength of the metal—metal and metal—ligand bonding and, where sufficiently accurate structural information is available, into the affinity of the ligands for different types of site, e.g. terminal or bridging [24].

The relationship between bond energies and bond lengths

Since the early work of Pauling [25], various empirical relationships have been used to estimate the energies of bonds from their lengths. While there is general qualitative agreement that when two atoms are directly bonded to each other, the greater the internuclear distance between them, the weaker that bond is expected to be, and the lower its bond order, there is nevertheless no generally accepted quantitative relationship linking bond energies (E) to bond lengths (d). Among those relationships that have found extensive use are the following:

$E = Ad^{-k}$ [26—31]

$E = Ad^{-2} + B$ [32]

$E = A - Bd + Cd^2$ [33]

$E = Ad - Bd^2 + Cd^3 - Dd^4$ [34,35]

$E = A + Bd + Cd^{-2} + Dd^3 + Fd^{-4} + Gd^5$ [36]

$E = A - Bd$ [25,37,38]

(in these equations, A, B, C, D, F, G and k are constants)

Of these equations, we use the first, $E = Ad^{-k}$, in the present work because it is the simplest expression that satisfactorily correlates a wide range of data. For example, a straight line of slope ($-k$) -3.3 is obtained by plotting log E against log d for carbon—carbon single, double and triple bonds, and for bonds of intermediate bond orders, i.e. for bonds spanning an energy range of from ca. 340—840 kJ mol^{-1} and a length range of from 155—120 pm [39]. Data for carbon—oxygen bonds afford a similar linear plot of slope ca. -5 [24], while metal—oxygen bonds give linear plots of slopes that vary with the metal and lie in the range -2 to -7. Over the short range of metal—metal distances for which the length-energy relationship is needed in applications to clusters, virtually any of the above equations could be used without affecting significantly the energies calculated, and we show elsewhere the compatibility of our results with the use of a length-energy equation of the last type, i.e. $E = A - Bd$, provided that the range of bond lengths (d) considered is small.

As the values of the constants A and k in the equation $E = Ad^{-k}$ may be expected to vary with the system, they need to be established for each metal in turn before clusters of that metal can be treated. Our method of calculating A and k exploits the fact that many metals are known in both a close-packed modification — hexagonal (h.c.p.) or cubic (c.c.p.) — and in a body-centered cubic (b.c.c.) form of very similar atomization enthalpy. Consideration of the interatomic distances in the two forms allows the values of A and k to be calculated as follows.

In c.p. structures, individual atoms are surrounded by twelve nearest neighbours at a distance $d_{\text{c.p.}}$. If one assumes that all the bonding interactions can be regarded as localized between nearest neighbours, and that bonding to second or outer coordination sphere atoms can therefore be neglected, then the process of atomisation effectively involves breaking six metal—metal bonds per metal atom.

Hence, $\Delta H_{\text{atomisation}} = 6E(\text{M—M})_{\text{c.p.}}$

In a body-centred cubic structure, each metal atom is surrounded by eight nearest neighbours at a distance $d_{\text{b.c.c.}}$, with a further six next-nearest neighbours only slightly further away, located over the centres of the cube faces, at a distance $2d_{\text{b.c.c.}}/\sqrt{3}$, i.e. $1.155d_{\text{b.c.c.}}$, close enough to bond directly to the central atom, which thus may be regarded as bonding strongly to eight and rather less strongly to a further six neighbours. Assigning all the enthalpy of atomisation of such a structure to the cleavage of these fourteen bonds means that, on average, four bonds of length $d_{\text{b.c.c.}}$ and three of length $1.155d_{\text{b.c.c.}}$ have to be broken per metal atom. For metals that are known to form both c.p. and b.c.c. lattices, there is only a very small energy difference between them — their atomisation enthalpies are effectively identical. We can therefore write:

$$\Delta H_{\text{atomisation}} = 6E(\text{M—M})_{\text{c.p.}} = 4E(\text{M—M})_{\text{b.c.c.}} + 3E'(\text{M—M})_{\text{b.c.c.}}$$

where $E(\text{M—M})_{\text{b.c.c.}}$ and $E'(\text{M—M})_{\text{b.c.c.}}$ are the bond enthalpy terms for the two types of bond (to nearest neighbours and next nearest neighbours, respectively) in the b.c.c. structure. Hence, replacing $E(\text{M—M})$ by $A[d(\text{M—M})]^{-k}$, we obtain:

$$\Delta H_{\text{atomisation}} = 6A[d_{\text{c.p.}}]^{-k} = 4A[d_{\text{b.c.c.}}]^{-k} + 3A[1.155d_{\text{b.c.c.}}]^{-k}$$

The value of k for a particular metal can thus be calculated if $d_{\mathrm{c.p.}}$ and $d_{\mathrm{b.c.c.}}$ are known. Interestingly, k appears to vary little from metal to metal, since the ratio $d_{\mathrm{c.p.}}/d_{\mathrm{b.c.c.}}$ varies little from metal to metal. For example, for iron this ratio is ca. 1.0171, for chromium ca. 1.0172, and for titanium ca. 1.0177 [40]. Moreover, the values of $d_{\mathrm{c.p.}}$ and $d_{\mathrm{b.c.c.}}$ are not known with sufficient precision for these slight differences to be regarded as significant. We have therefore used the average value of 1.017 to calculate k (ca. 4.6), and in calculating bond enthalpy terms in the present work, we have used this value of k for all the metals considered irrespective of whether both close-packed and body-centered cubic structures are known.

This treatment incidentally eliminates one of the anomalies in a common treatment of body-centred cubic structures, in which the atomisation enthalpy is assigned to the cleavage of only the eight first coordination sphere bonds, the six slightly longer bonds being ignored. In assigning bond enthalpy terms $E(\mathrm{M{-}M})_{\mathrm{b.c.c.}}$ to the shortest bonds in a body-centred cubic structure, our treatment requires the atomisation enthalpy to be divided by 5.55, not 4. (Division of $\Delta H_{\mathrm{atomisation}}$ by four would make the body-centred cubic lattice bonds of length $d_{\mathrm{b.c.c.}}$ 50% stronger than those of length $d_{\mathrm{c.p.}}$ in the close-packed lattice, even though the latter, as just seen, are only ca. 1.7% longer than the former).

Results and discussion

Using published values of the interatomic distances [41] and of the atomisation enthalpies [42—44] of the metals of the iron, cobalt and nickel subgroups, we have calculated bond enthalpy terms $E(\mathrm{M{-}M})$ kJ mol^{-1} for the bonds in the metals themselves, and the value of A, the constant in the equation $E(\mathrm{M{-}M}) = A[d(\mathrm{M{-}M})]^{-4.6}$ (Table 1). The data show the familiar increase in $E_{\mathrm{c.p.}}$ with increasing atomic number within each sub-group, and the decrease in $E(\mathrm{M{-}M})$ in the sequence Fe > Co ~ Ni which incidentally underlines the fact that the

TABLE 1

THE LENGTH AND STRENGTH OF THE BONDS IN METALS OF THE IRON, COBALT AND NICKEL SUBGROUPS

Metal	$d_{\mathrm{c.p.}}$ [a] (pm)	$E(\mathrm{M{-}M})$ [b] (kJ mol^{-1})	Ref. [c]	$A \times 10^{-13}$ [d]
Fe	248.2	75.2	42	0.780
Ru	265.0	108.5	43	1.522
Os	267.5	131.7	43	1.928
Co	250.6	71.4	42	0.755
Rh	269.0	92.9	44	1.396
Ir	271.4	110.9	44	1.735
Ni	249.2	71.6	42	0.757
Pd	275.1	63.0	42	1.050
Pt	277.5	94.0	42	1.633

[a] Interatomic distances from ref. 41 relate to c.p. lattices except in the case of Fe (b.c.c.). [b] $E(\mathrm{M{-}M})_{\mathrm{c.p.}} = \Delta H_{\mathrm{atomisation}}/6$; $E(\mathrm{Fe{-}Fe})_{\mathrm{b.c.c.}} = \Delta H_{\mathrm{atomisation}}/5.55$.. [c] Source of $\Delta H_{\mathrm{atomisation}}$. [d] $A = [E(\mathrm{M{-}M}) \times [d(\mathrm{M{-}M})]^{4.6}$ pm$^{4.6}$ kJ mol^{-1}.

extra electrons in the valence shells of the latter two elements are not increasing the bond order relative to that of iron. The trends in E(M—M) are understandably reflected by the manner in which A varies with M. The variations in A show that, for bonds of a particular length, that between two osmium atoms is the strongest of the set considered, while those between cobalt or nickel atoms are the weakest.

The equations $E(\text{M—M}) = A[d(\text{M—M})]^{-4.6}$ have in turn been used to calculate the energies of the metal—metal bonds in a series of metal carbonyl clusters for which the enthalpies of formation [43,45—47] and interatomic distances [48—57] are known. For example, in the dinuclear carbonyls $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$, metal—metal bond enthalpy terms have been assigned solely on the length of the one metal—metal bond each contains, regardless of whether the bond in question is bridged by carbonyl groups (as in the case of $Fe_2(CO)_9$ [50]) or not. The three metal—metal bonds in the triangular trinuclear clusters $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and the six metal—metal bonds in the tetranuclear species $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ have been treated similarly.

For the octahedral cluster $Rh_6(CO)_{16}$, we have assumed the cluster bonding to consist of twelve metal—metal bonds of length 278 pm along the octahedral edges, ignoring the longer cross-cluster interactions on the grounds that comparably long second coordination sphere interactions in the bulk metals were ignored in our derivation of the length-energy equation $E = Ad^{-4.6}$. If these three cross-cluster interactions between *trans* pairs of metal atoms are included in the skeletal bonding, their length ($\sqrt{2} \times$ the octahedral edge length, i.e. 393 pm) implies that each should be assigned an enthalpy term E(M—M) of ca. 16 kJ mol^{-1}, boosting the total energy assigned to the cluster bonding by 5%.

The average enthalpy contribution assignable to the bonding of each carbonyl ligand in these clusters, D(M—CO) (Table 2) was calculated from the known enthalpy changes for the disruption of these clusters into metal atoms

TABLE 2

METAL—METAL AND METAL—LIGAND BOND ENTHALPY TERMS FOR METAL CARBONYLS OF KNOWN DISRUPTION ENTHALPY

Metal carbonyl	$\Delta H_{\text{disrupt}}$ [a] (kJ mol^{-1})	Ref.	d(M—M) (pm)	Ref.	E(M—M) (kJ mol^{-1})	D(M—CO) (kJ mol^{-1})	% [b]
$Mn_2(CO)_{10}$	1068	43	292	48	35	103	3
$Re_2(CO)_{10}$	2029	43	304	49	80	195	4
$Fe(CO)_5$	585	43	—	—	—	117	0
$Fe_5(CO)_9$	1173	43	252	50	70	123	6
$Fe_3(CO)_{12}$	1676	43	256, 268	51	65, 52	126	10
$Ru_3(CO)_{12}$	2414	43	285	52	78	182	10
$Os_3(CO)_{12}$	2690	45	288	53	94	201	11
$Co_2(CO)_8$	1160	43	252	54	70	136	6
$Co_4(CO)_{12}$	2121	46	249	55	74	140	21
$Rh_4(CO)_{12}$	2648	43	273	55	86	178	20
$Rh_6(CO)_{16}$	3874	47	278	56	80	182	25
$Ir_4(CO)_{12}$	3051	43	268	57	117	196	23

[a] $\Delta H_{\text{disrupt}}$ is the enthalpy change for the gas-phase process $M_x(CO)_y \rightarrow x\text{M} + x\text{CO}$. [b] % is the percentage of the disruption enthalpy attributed to the metal—metal bonding i.e. $100\ \Sigma E(\text{M—M})/\Delta H_{\text{disrupt}}$.

and carbon monoxide molecules, $\Delta H_{\text{disrupt}}$:

$$M_x(CO)_y(g) \rightarrow xM(g) + y(CO)(g)$$

$$\Delta H_{\text{disrupt}} = \Sigma E(M{-}M) + yD(M{-}CO)$$

The term $D(M{-}CO)$ is an average value for all the ligands associated with a particular cluster $M_x(CO)_y$, and is expected to be lower than the enthalpy term, $E(M{-}C)$, assignable to the metal—carbon bond (or bonds) by which the ligand is bound to the cluster, since the disruption process involves not only the expenditure of energy on the cleavage of these metal—carbon bonds, but also a gain in energy by the carbon monoxide molecules, which have weaker carbon—oxygen bonds when coordinated than when uncoordinated.

The experimental errors in the published thermochemical and structural data, and the assumptions made in our treatment are such that detailed analysis of the data in Table 2 would be inappropriate. However, a few qualitative generalisations can be made. Our method assigns only a small percentage (final column of Table 2) of the disruption enthalpy to cleavage of the metal—metal bonds in these clusters, ca. 5% for dinuclear clusters $M_2(CO)_y$, ca. 10% for trinuclear clusters, and ca. 20% for tetranuclear clusters. Obviously, as the cluster nuclearity increases, the percentage of the disruption enthalpy attributable to the metal—metal bond necessarily increases, in part because the number of metal—metal bonding interactions increases disproportionately, but also because the number of carbonyl ligands per metal atom, and so the relative contribution due to $\Sigma D(M{-}CO)$, decreases.

A very slight increase in $D(M{-}CO)$ with increasing cluster nuclearity is also apparent in Table 2. For example, compare the values of $D(M{-}CO)$ for $Fe(CO)_5$ (117 kJ mol^{-1}), $Fe_2(CO)_9$ (123 kJ mol^{-1}), and $Fe_3(CO)_{12}$ (126 kJ mol^{-1}). Though these differences have to be regarded as statistically insignificant, the trend is in the direction that allows rationalisation in terms of stronger binding of ligands when fewer are attached to, and therefore competing for the bonding capacity of, one metal atom. At least, the effect draws into question the assumption that is normally made, indeed that has to be made to allow the data to be processed, i.e. that the strength of attachment of carbon monoxide to a particular metal atom does not vary with the nuclearity of the metal cluster considered [43]. In future, it is clear that allowance needs to be made for variation in the strength of binding of ligands as the cluster nuclearity increases [58], though the extent of the variation is unlikely to be so great as to make carbonyl clusters inappropriate models for metal surfaces.

Our estimate of the proportion of the disruption enthalpy that should be assigned to the metal—metal bonding is significantly lower (by ca. 10—35%, depending on the cluster) than that of previous methods, which, however, in some systems required long bonds to be treated as stronger than short bonds [14,43]. Indeed, it is possible that our method slightly over-emphasizes the importance of the metal—ligand bonding. Nevertheless, we feel that a bond length-based bond enthalpy treatment is preferable for systems in which significant variations in bond length, not accountable by 2-centre electron-pair bond schemes, are found.

It has recently been pointed out [59] that a factor our treatment fails to take into account is the manner in which the metal coordination number changes on going from a bulk metal, particularly a close-packed metal lattice, to a metal carbonyl cluster. In effect, a metal atom may be expected to bond more strongly to each of its few neighbours in a cluster than it does to each of its many neighbours in the bulk metal, even when the neighbours are at a similar distance in both cluster and metal. Interestingly, the relationship E(C—C) = Ad(C—C)$^{-3.3}$ applicable to carbon—carbon bonds in typical organic systems holds for a range of carbon coordination numbers from 2 in alkynes to 4 in alkanes, and this, coupled with our method of making allowance for the second coordination sphere interactions in b.c.c. metal lattices, suggested that coordination number effects could be ignored in an approximate treatment such as the present one. A planned future refinement will explore the effect of coordination number.

The self-consistency of our method is not, however, in question, and allows thermochemical parameters to be predicted from structural data. In Table 3 we list the interatomic distances and predicted bond enthalpy terms E(Os—Os) and D(Os—CO), and disruption enthalpies $\Delta H_{\text{disrupt}}$ for the process

$$\mathrm{Os}_x(\mathrm{CO})_y(\mathrm{g}) \rightarrow x\mathrm{Os}(\mathrm{g}) + y(\mathrm{CO})(\mathrm{g})$$

for the osmium carbonyl clusters $Os_5(CO)_{16}$ [60], $Os_6(CO)_{18}$ [61] and $Os_7(CO)_{21}$ [62]. In treating these clusters, we have ignored cross-cluster, second coordination sphere bonding interactions, which if allowed for would increase $\Delta H_{\text{disrupt}}$ by less than 1%.

The relationship $E(\mathrm{Os—Os}) = 1.928 \times 10^{13} [d(\mathrm{Os—Os})]^{-4.6}$ that we have used to calculate the metal—metal bond enthalpy terms in Table 3 incidentally affords values that do not differ significantly from those calculated using the linear relationship $E(\mathrm{Os—Os}) = 588 - 1.72d(\mathrm{Os—Os})$.

To conclude: our assessment of the strength of the cluster bonds in metal carbonyl clusters suggests that they are as weak as the borane analogy implies.

TABLE 3

PREDICTED METAL—METAL AND METAL—LIGAND BOND ENTHALPY TERMS, AND ENTHALPIES OF DISRUPTION, OF THE OSMIUM CARBONYL CLUSTERS $Os_5(CO)_{16}$, $Os_6(CO)_{18}$ AND $Os_7(CO)_{21}$.

Compound	d(M—M) (pm)	E(M—M) (kJ mol^{-1})	D(M—CO) (kJ mol^{-1})	$\Delta H_{\text{disrupt}}$ [a] (kJ mol^{-1})	% [b]
$Os_5(CO)_{16}$ [c]	275 (X5)	116	205	4240(50)	23
	288 (X4)	94			
$Os_6(CO)_{18}$ [d]	273 (X1)	120	208	5035(60)	26
	278 (X3)	110			
	280 (X5)	107			
	283 (X3)	102			
$Os_7(CO)_{21}$ [e]	282 (X6)	103	209	5870(70)	25
	285 (X5)	98			
	288 (X4)	94			

[a] $\Delta H_{\text{disrupt}}$ is the predicted enthalpy change for the gas-phase reaction $\mathrm{Os}_x(\mathrm{CO})_y \rightarrow x\mathrm{Os} + y(\mathrm{CO})$.

[b] % is the percentage of the disruption enthalpy attributed to the metal—metal bonding, i.e. 100 $\Sigma E(\mathrm{M—M})/\Delta H_{\text{disrupt}}$.

[c] Ref. 60. [d] Ref. 61. [e] Ref. 62.

Making allowance for the coordination number effect would afford higher cluster bond enthalpy terms, though nevertheless less strong than a bond order of ca. 1.0 would require. Neither the weakness of bonds implied by the borane analogy, nor the strength of bonds implied by the 2-centre electron-pair bond treatment, appears completely appropriate for the bonds in metal carbonyl clusters, though the two approaches appear to define the limits between which metal carbonyl characteristics are to be found, a point made frequently by Professor Chini [3,4,63] to whose memory this paper is dedicated.

Acknowledgement

We thank SRC for financial support.

References

1 K. Wade, Advan. Inorg. Chem. Radiochem., 18 (1976) 1.
2 K. Wade in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, London, 1980, p. 193.
3 P. Chini, G. Longoni and V.G. Albano, Advan. Organometal. Chem., 14 (1976) 285.
4 P. Chini, Gazz. Chim. Ital., 109 (1979) 225.
5 R. Mason and D.M.P. Mingos, MTP Internat. Rev. Sci., Phys. Chem. Ser. 2, 11 (1975) 121.
6 R.W. Rudolph, Accounts Chem. Research, 9 (1976) 446.
7 R.W. Rudolph in R.W. Parry and G. Kodama (Eds.), Boron Chemistry, Pergamon, Oxford and New York, 1980, p. 11.
8 R.J. Gillespie, Chem. Soc. Rev., 8 (1979) 315.
9 J. Lewis and B.F.G. Johnson, Gazz. Chim. Ital., 109 (1979) 271.
10 C.E. Housecroft and K. Wade, Gazz. Chim. Ital., 110 (1980) 87.
11 R.G. Woolley in B.F.G. Johnson (Ed.), Transition Clusters ,Wiley, London, 1980, p. 193.
12 K. Wade in R.W. Parry and G. Kodama (Eds.), Boron Chemistry, Pergamon, Oxford and New York, 1980, p. 23.
13 T.P. Fehlner in R.W. Parry and G. Kodama (Eds.), Boron Chemistry, Pergamon, Oxford and New York, 1980, p. 95.
14 C.E. Housecroft, K. Wade and B.C. Smith, J. Chem. Soc. Chem. Commun., (1978) 765.
15 E.R. Corey, L.F. Dahl and W. Beck, J. Amer. Chem. Soc., 85 (1963) 1202.
16 M.R. Churchill and J. Wormald, J. Amer. Chem. Soc., 93 (1971) 5670.
17 C.R. Eady, B.F.G. Johnson, J. Lewis, M.C. Malatesta, P. Machin and M. McPartlin, J. Chem. Soc. Chem. Commun., (1976) 945.
18 M. McPartlin, C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1976) 883.
19 V.G. Albano, P.L. Bellon, P. Chini and V. Scatturin, J. Organometal. Chem., 16 (1969) 461.
20 V.G. Albano, G. Ciani and P. Chini, J. Chem. Soc. Dalton, (1974) 432.
21 J.C. Calabrese, L.F. Dahl, A. Cavalieri, P. Chini, G. Longoni and S. Martinengo, J. Amer. Chem. Soc., 96 (1974) 2616.
22 A. Sirigu, M. Bianchi and E. Benedetti, Chem. Commun., (1969) 596.
23 M.R. Churchill and J. Wormald, J. Chem. Soc. Dalton, (1974) 2410.
24 C.E. Housecroft, K. Wade and B.C. Smith, J. Organometal. Chem., 170 (1979) C1.
25 L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, N.Y., 1939.
26 C.H.D. Clark, Nature, 143 (1939) 800.
27 H.A. Skinner, Trans. Faraday Soc., 41 (1945) 645.
28 G. Glockler, J. Chem. Phys., 16 (1948) 842.
29 I.D. Brown and R.D. Shannon, Acta Cryst. A, 29 (1973) 266.
30 I.D. Brown, Chem. Soc. Rev., 7 (1978) 359.
31 K. Waltersson, Acta Cryst. A, 34 (1978) 901.
32 W. Gordy, J. Chem. Phys., 15 (1947) 305.
33 G. Glockler, J. Chem. Phys., 21 (1953) 1242.
34 G. Glockler, J. Phys. Chem., 61 (1957) 31.
35 M.P. Bhutra, S.P. Tandon and P.P. Vaishnava, Z. Naturforsch., 30A (1975) 21.
36 V.G. Dashevskii, Zh. Strukt. Khim., 11 (1970) 489.
37 Z.G. Szabo and T.I. Konkoly, Acta Chim. Acad. Sci. Hung., 86 (1975) 127.
38 G. Glockler, Trans. Faraday Soc., 59 (1963) 1080.
39 J.B. Holbrook and B.C. Smith, personal communication.

40 J. Donohue, The Structures of the Elements, Wiley, New York, 1974.

41 L.E. Sutton (Ed.), Tables of Interatomic Distances, Supplementary Volume, Chem. Soc. Spec. Publ., Vol. 18, Chemical Society, London, 1965.

42 J. Chao, JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan; U.S. Dept. of Commerce, Nat. Bur. Standards, Institute for Applied Technol., 1965, 1968.

43 J.A. Connor, Topics Current Chem., 71 (1977) 71.

44 G. Pilcher, MTP Internat. Rev. Sci. Phys. Chem. Ser. 2, Vol. 10, (1975) 45.

45 J.A. Connor, H.A. Skinner and Y. Virmani, Faraday Symp. Chem. Soc., 8 (1973) 18.

46 D.L.S. Brown, J.A. Conor, H.A. Skinner, C.P. Demain, M.L. Leung, J.A. Martinho-Simoes and M.T. Zafarani, J. Organometal. Chem., 142 (1977) 321.

47 D.L.S. Brown, J.A. Connor and H.A. Skinner, J. Chem. Soc. Faraday I, 71 (1975) 699.

48 L.F. Dahl and R.E. Runcle, Acta Cryst., 16 (1963) 419.

49 J.C. Hileman, D.K. Huggins and H.D. Kaesz, Inorg. Chem., 1 (1962) 933.

50 F.A. Cotton and J.M. Troup, J. Chem. Soc, Dalton, (1974) 800.

51 F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 4155.

52 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.

53 M.R. Churchill and B.G. DeBoer, Inorg. Chem., 16 (1977) 878.

54 G.G. Sumner, H.P. Klug and L.E. Alexander, Acta Cryst., 17 (1964) 732.

55 F.A. Cotton, F.H. Carre and B.A. Frenz, Inorg. Chem., 15 (1976) 380.

56 E.R. Corey, L.F. Dahl and W. Beck, J. Amer. Chem. Soc., 85 (1963) 1202.

57 C.H. Wei, G.R. Wilkes and L.F. Dahl, J. Amer. Chem. Soc., 89 (1967) 4792.

58 J.A. Connor in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, London, 1980, p. 345.

59 R.G. Wooliey in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, London, 1980, p. 607.

60 B.F.G. Johnson, C.R. Eady, J. Lewis, B.E. Richart and G.M. Sheldrick, J. Chem. Soc. Chem. Commun., (1976) 271.

61 R. Mason, K.M. Thomas and D.M.P. Mingos, J. Amer. Chem. Soc., 95 (1973) 3802.

62 C.R. Eady, B.F.G. Johnson, J. Lewis, R. Mason, P.B. Hitchcock and K.M. Thomas, J. Chem. Soc. Chem. Commun., (1977) 385.

63 P. Chini, J. Organametal. Chem., 200 (1980) 37.