Acta Cryst. (1978). B34, 746–752

The Nature of the Bonds Formed by the Transition Metals with Hydrogen, Carbon and Phosphorus

By Linus Pauling

The Linus Pauling Institute of Science and Medicine, 2700 *Sand Hill Road, Menlo Park, California* 94025, *USA*

(*Received* 8 *October* 1976; *accepted* 12 *September* 1977)

The derivations of a set of nine sp^3d^5 bond orbitals and of a set of single-bond covalent radii for enneacovalent transition metals are discussed. Observed values of bond lengths of M—H bonds agree with the sums of these radii and the covalent radius of H, 0·30 Å. This agreement strongly supports the conclusion that the interaction of transition metals and H is that described as formation of a covalent bond. Observed values of bond angles in the groups $-Mn(CO)_5$, $[-Cr(CO)_5]^-$, $-Re(CO)_5$, $[-Mo(CO)_5]^-$, $-Co(CO)_4$, and $[-Fe(CO)_4]^-$ are shown to agree closely with the theoretical values. Curves of bond lengths of transition metals with carbonyl C and P in relation to bond number are formulated and are used, together with arguments involving bond angles, to show that the bonds to P have some double-bond character, with the bond number usually somewhat less than for the bonds to the carbonyl groups.

Introduction

In their report on the crystal structure of the orthorhombic form of hydridodicarbonylbis(triphenylphosphine)iridium(I), Ciechanowicz, Skapski & Troughton (1976) discussed some of the evidence for the conclusion that in hydrides of transition metals there is a covalent M—H bond, similar to other covalent bonds. They list the values of M—H bond lengths, and state that 'it is noteworthy that in every case the observed M—H distances are longer than the sum of Pauling's covalent radii.' I point out that all of the compounds listed by them can be described as containing enneacovalent transition-metal atoms. I have recently derived a set of enneacovalent single-bond radii for the transition metals (Pauling, 1975*a*). When these radii, which are the appropriate ones, are used, the calculated M—H bond lengths agree closely with the observed ones, usually to within one standard deviation.

Sets of nine good sp^3d^5 bond orbitals

Hultgren's (1932) thorough treatment of equivalent, orthogonal, cylindrically symmetrical sp^3d^5 hybrid orbitals seemed to show that no more than six were well suited to bond formation. By abandoning the restriction to cylindrical symmetry of the bond orbitals McClure (1970) was able to demonstrate that in fact nine good orbitals can be formed, with strengths 2·9539 to 2·9936, all close to the maximum value 3. The set found by him, said to be the set that gives the maximum value of the sum of the bond strengths, can be described as having one bond orbital with its maximum along the z axis, five equally spaced (approximate fivefold axis) in a cone with polar angle about 76°, and three equally spaced (approximate threefold axis) in a cone with polar angle about 137°. For the nine orbitals there are 21 small bond angles, averaging 74·04°, and 15 large, averaging 133·35°. These values are close to those for best *spd* orbitals, 73·15 and 133·62° (Hultgren, 1932).

The direct solution of the equations for the best set of several hybrid orbitals is quite difficult. However, I found (Pauling, 1975*b*) an easy way of finding approximate solutions to the problem. The value of the bond strength S for two equivalent orthogonal *spd* orbitals with maximum strength 2 in directions at an angle α to one another is given by the equation

$$S(\alpha) = (3 - 6x + 7{\cdot}5x^2) + (1{\cdot}5 + 6x - 7{\cdot}5x^2) \quad (1)$$

in which $x = \cos^2(\alpha/2)$. Another treatment of the problem (Pauling, 1976*a*) led to the equation

$$S(\alpha) = 3\{[0{\cdot}25 - (\cos^2\alpha + 2\cos\alpha - 1)^2/144]^{1/2} + 0{\cdot}5\}^{1/2}. \quad (2)$$

This equation, although much different in form from (1), is equivalent to it. The equations give a curve with maxima, $S = 3$, at 73·15 and 133·62°, low values below 60 and above 150°, and a minimum of 2·9848 at about 101°. I then made the assumption that the defect $3 - S_i$ for orbital i forming several bond angles α_{ij} with other *spd* orbitals of a best set is approximately equal to the sum of the defects corresponding to the several values of α_{ij}, as given by (1) or (2); that is, that

$$S_i = 3 - \sum_j [3 - S(\alpha_{ij})]. \quad (3)$$

This equation gives values of S in rather good agreement with those calculated rigorously. Application

Table 1. *Single-bond radii* (Å) *for transition metals with covalence* 9

Cr	Mn	Fe	Co	Ni
1·26	1·25	1·24	1·23	1·22
Mo	Tc	Ru	Rh	Pd
1·39	1·38	1·37	1·36	1·35
W	Re	Os	Ir	Pt
1·40	1·39	1·38	1·37	1·36

of the equation has shown that there are two other sets of nine *spd* orbitals that are just about as good as those of McClure (1970). One is the tetragonal antiprism with cap (one bond at $\theta = 0°$, four at $\theta = 67°$, four at $\theta = 120°$) and the other is the trigonal prism with caps on the three rectangular faces (three each at $\theta = 45$, 90, and 135°).

The molecule $Os_4O_4(CO)_{12}$ (Bright, 1970) is a good example showing enneacovalence of a transition metal. The four Os atoms lie at the four corners of a tetrahedron with the four O atoms at the corners of the inverse tetrahedron. Each O atom becomes tercovalent by transferring an electron to an Os atom, which then has nine electrons and is enneacovalent, forming three single bonds with the adjacent O atoms and three double bonds with the C atoms of the three attached carbonyl groups. In many molecules of this sort, such as dicobalt octacarbonyl, there are bonds between pairs of transition-metal atoms. I used the observed M—M bond lengths in molecules of this sort in formulating a set of values of enneacovalent single-bond radii (Pauling, 1975*a*), given in Table 1.

Bonds between transition metals and hydrogen

The best example of an enneacovalent transition metal is the Re atom in dipotassium enneahydridorhenate, K_2ReH_9 (Abrahams, Ginsberg & Knox, 1964) [also the Tc atom in dipotassium enneahydridotechnetate, K_2TcH_9 (Ginsberg, 1964)]. Two electrons have been transferred from the K atoms to the Re atom, giving it nine valence electrons. They are used in forming nine single covalent bonds with the nine H atoms, which lie at the corners of a trigonal prism with capped prismatic sides. The observed mean Re—H bond length is 1·68 (1) Å, which agrees to within one standard deviation with the sum of the bond radius for Re from Table 1, 1·39 Å, and the accepted covalent radius for H, 0·30 Å.

A comparison of calculated and observed bond lengths for the seven M—H bonds listed by Ciechanowicz *et al.* (1976) is given in Table 2, together with a recent value (the last in the table). The agreement provides strong support of Ibers's (1965) conclusion that the interaction of the transition metal and H is that described as formation of a covalent bond. It is pertinent that no use was made of observed M—H bond lengths in formulating the set of enneacovalent radii.

The treatment of *spd* orbitals described above has been applied also in the discussion of bond lengths for multiple, including quadruple, M—M bonds (Pauling, 1975*a*), of bond angles (Pauling, 1975*b*, 1976*b*), of the M—M bond lengths in cluster complexes (Pauling, 1976*c*), and of the bond lengths in the elementary transition metals (Pauling, 1977).

Bond angles in some transition-metal carbonyls

The calculation of bond angles in a molecule such as $HMn(CO)_5$ requires a discussion of the nature of the bonds between the transition metal and the carbonyl group. The structure with a double bond, $M{=}C{=}O$, corresponds to zero formal charge on both C and O, whereas that with a single bond, $M{-}C{\equiv}O^+$, involves transfer of an electron from the O to the metal atom. Resonance between these two structures would stabilize the molecule by bringing the resultant charge close to zero, the partial positive charge on the O atom being neutralized by the negative charge corresponding to the partial ionic character of the bonds, as determined by

Table 2. *Comparison of observed* M—H *bond lengths with the sums of covalent radii*

Compound	Method	Bond length (Å)	Sum of radii (Å)	Reference
K_2ReH_9	Neutron	1·68 (1)	1·69	Abrahams, Ginsberg & Knox (1964)
$RhH(CO)(PPh_3)_3$	X-ray	1·60 (12)	1·67	La Placa & Ibers (1965)
$RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$	X-ray	1·70 (5?)	1·67	Ibekive, Kilbourn, Raeburn & Russell (1969)
$RuHCl(PPh_3)_3$	X-ray	1·68 (7)	1·67	Skapski & Troughton (1968)
β-$HMn(CO)_5$	Neutron	1·60 (1·6)	1·55	La Placa, Hamilton, Ibers & Davidson (1969)
$CoH(N_2)(PPh_3)_3$	X-ray	1·64 (11) and 1·67 (12)	1·53	Davis, Payne & Ibers (1969)
$IrH(CO)_2(PPh_3)_2$	X-ray	1·64 (5)	1·67	Ciechanowicz, Skapski & Troughton (1976)
$RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$	X-ray	1·66 (5)	1·66	Hoffman, Yoshida, Okano, Otsuka & Ibers (1976)

the difference in electronegativity of the bonded atoms. For $HMn(CO)_5$ we write a structure in which there are two single-bonded carbonyls, $-C\equiv O^+$. This structure places nine valence electrons on manganese (Mn^{2-}), permitting it to be enneacovalent. The difference in electronegativity of Mn (1·5) and C (2·5) corresponds to 22% ionic character for each covalent Mn—C bond (Pauling, 1960). Thus, for eight bonds to C 1·76 electrons are transferred from Mn to C (and then to O, because of the partial ionic character of the C—O bonds), leaving the Mn atom with only a very small negative charge, in agreement with the electroneutrality principle.

I take as the nine bond orbitals of manganese in $HMn(CO)_5$ an idealized set with one orbital, to H, along the z axis ($\theta = 0°$), five at $\theta = 73·15°$, and three at $\theta = 133·62°$. These values of the polar angle θ are those corresponding to the best *spd* bond orbitals, with strength 3·0000 (Pauling, 1931). The McClure (1970) set has 21 angles near 73·15°, with average 74·04°, and 15 near 133·62°, with average 133·35°. Another good set (Pauling, 1975*b*) has bonds directed toward the corners of a square antiprism with one square capped. It has 20 angles near 73·15°, average 72·10°, and 16 near 133·62°, average 131·44°. If one of the corners of the capped square is taken on the z axis, there are five orbitals at an average of $\theta = 73·24°$ and three at $\theta = 137·59°$. For the McClure (1970) set the corresponding values of θ are 76·51 and 137·11°. The calculated values of these angles (McClure, 1970; Pauling, 1975*b*) are estimated to be reliable to about ±1°. In order to avoid any arbitrariness in carrying out calculations of bond angles, I shall use the ideal values 73·15 and 133·62°, unless the hybridization problem is one that can be rigorously treated.

Let there be a single-bonded ligand, such as H in $HMn(CO)_5$, at $\theta = 0$, another ligand, which forms a bond with bond number n with the central atom, in the opposite axial position, $\theta = 180°$, and several other ligands in an approximately equatorial belt, with polar angle θ to be calculated. I assume that θ can be taken to be the weighted mean of the five orbitals at $\theta = 73·15°$ and $3 - n$ at 133·62°. A test of this assumption is to place n equal to 1, for which symmetry considerations require θ to equal 90°. The calculated value, 90·43°, is close enough to suggest that there will be no great error in the other calculated values.

If we assume for $HMn(CO)_5$ that the bond number for the axial carbonyl is the same as that for each of the four equatorial carbonyls, the bonds to these four would be formed with use of four fifths of the eight Mn orbitals used in Mn—C bonding; that is, 6·4 orbitals, five at 73·15° and 1·4 at 133·62°. The average of these values, 86·4°, is the predicted value of the $H-Mn-C_{eq}$ bond angle given by this simple calculation. We are thus led, by consideration of the bond angles of best *spd* orbitals, to the conclusion that for the $-M(CO)_5$ group the angle between the single bond and the bonds to the equatorial carbonyls should have a value close to 86·4°. This agrees well with observation, as is seen from Table 3. The average of the experimental values for 23 complexes is 85·6°, average deviation 1·3°.

Table 3. *Values of the bond angle* $A-M-C_{eq}$ *for octahedral* $AMn(CO)_5$ *and* $ARe(CO)_5$ *and closely related groups*

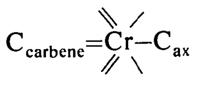
Molecule	Average bond angle (°)	Reference
$HMn(CO)_5$	82·9	La Placa, Hamilton, Ibers & Davidson (1969)
$H_3CMn(CO)_5$	85·3	Seip & Seip (1970)
$[Mn(CO)_5]_2$	86·8	Dahl & Rundle (1963)
$[Mn(CO)_5]_2$	86·6	Almenningen, Jakobsen & Seip (1969)
$CHFCFMn(CO)_5$	86·0	Einstein, Luth & Trotter (1967)
$[(CH_3)_3Si]_3SiMn(CO)_5$	87·4	Nicholson, Simpson & Robinson (1973)
$(CH_3)_3SnMn(CO)_5$	84·4	Bryan (1968)
$(C_6H_5)_3SnMn(CO)_5$	86·7	Weber & Bryan (1967)
$(CO)_4CoSn(C_6H_5)_2Mn(CO)_5$	86·3	Birjukov, Solodova & Struchkov (1968)
$Br_3GeMn(CO)_5$	84·5	Gapotchenko *et al.* (1970)
$(CO)_5CrAs(CH_3)_2Mn(CO)_5$	87·3	Vahrenkamp (1972)
$(CO)_4Fe[Mn(CO)_5]_2$	86·6	Agron, Ellison & Levy (1967)
$Hg[Mn(CO)_5]_2$	84·3	Katcher & Simon (1972)
$C_{15}N_3H_{11}Cd[Mn(CO)_5]_2$	82·9	Clegg & Wheatley (1973)
$C_6H_5C(OCH_3)Mn_2(CO)_9$	85·4	Huttner & Regler (1972)
$CH_2CHCHCH_2Mn_2(CO)_8$	88·0	Sasse & Ziegler (1972)
$H_3CRe(CO)_5$	84	Rankin & Robertson (1976)
$H_3SiRe(CO)_5$	86	
$H_3GeRe(CO)_5$	83	
$(CH_3)_3SiRe(CO)_5$	85·1	Couldwell, Simpson & Robinson (1976)
$[(CH_3)_3Si]_3SiRe(CO)_5$	88	
$\{[(C_6H_5)_3P]_2N\}_2^+[Cr_2(CO)_{10}]^{2-}.CH_2Cl_2$	86·8	Handy, Ruff & Dahl (1970)
$\{[(C_6H_5)_3P]_2N\}_2^+[Mo_2(CO)_{10}]^{2-}.CH_2Cl_2$	85·5	
Average	85·6	

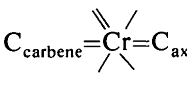
A problem closely similar to that of the $-M(CO)_5$ group is that of the $-M(CO)_4$ group with one axial and three equatorial carbonyls. When there is a single bond between the other axial ligand A and the metal atom there must be double bonds between M and each of the carbonyl C atoms. Thus, six orbitals are needed for the bonds to the three equatorial carbonyls, and the angle $A-M-C_{eq}$ is calculated to be $(5 \times 73{\cdot}15° + 133{\cdot}72°)/6 = 83{\cdot}23°$. This value agrees well with the average value for the eight compounds in Table 4, 82·7° (mean deviation 2·7°).

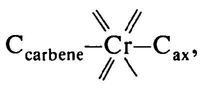
It is interesting that the difference between the calculated values of the $A-M-C_{eq}$ angle for $A-M(CO)_4CO$ and $A-M(CO)_3CO$ is 3·2°, and that between the average observed values (Tables 3 and 4) is 2·9°. The agreement to within 10% gives increased confidence in the theory.

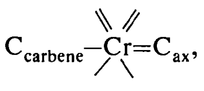
Angles for a carbene ligand

When A is a carbene its bond with M is a formal double bond. In $C_5H_5(CH_3O)CCr(CO)_5$ (Mills & Redhouse, 1968), $CH_3[(C_2H_5)_2N]CCr(CO)_5$ (Connor & Mills, 1969), and $CH_3(C_6H_5S)CCr(CO)_5$ (Hoare & Mills, 1972) the average values of the angle $C_{carbene}-Cr-C_{eq}$ are 92·3, 91·8 and 90·0°, respectively, with average 91·4°. For the structure A the calculated value of this angle is 96·8°, and for B it is (by symmetry) 90°. With random distribution of the double bonds to the five carbonyls these two structures contribute in the ratio 6:4, which gives 94·1° as the expected value for the angle if the carbene–metal bond is a true double bond. In each of these molecules, however, there is resonance with structures, such as $H_3C-\ddot{O}{=}\overset{|}{C}-Cr(CO)_5$, in which an electron has been transferred to the metal atom from O, N or S, and the carbene–metal bond is a single bond. The observed bond lengths for O, N and S to the carbene C are 1·33, 1·31 and 1·69 Å respectively. The decreases from the single-bond values 1·43, 1·47 and 1·81 Å correspond to an average bond number of 1·4; that is, to 40% contribution of the structures with $C_{carbene}-M$ (C and D) and 60% contribution of those with $C_{carbene}{=}M$ (A and B). For C and D, calculated values of $C_{carbene}-M-C_{eq}$ are 90 and 83·23°, with the mean 85·9° for random resonance of the double bonds among the carbonyls. The calculated value of the angle is accordingly $0{\cdot}6 \times 94{\cdot}1° + 0{\cdot}4 \times 85{\cdot}9° = 90{\cdot}81°$, in approximate agreement with the observed average value, 91·4°.


A


B


C


D

I am planning to discuss bond angles for $M(CO)_2$, $M(CO)_3$, and other $M(CO)_4$ groups in another paper.

Bonds to phosphorus

The assumption that the $A-M$ bond is a single covalent bond is, of course, reasonable for A = H or C of a methyl group. For A = Si, Ge, Sn and As it is also rather reasonable, in that for these heavier atoms multiple bonds are less stable than single bonds. P, however, has a greater tendency to form multiple bonds and also to assume a quinquecovalent transargonic structure. With a bond from A to M with more double-bond character than that from M to the axial carbonyl (about 50%) the angle $A-M-C_{eq}$ would be greater than 90°. The observed average values of $P-Cr-C_{eq}$ of 91·6° for $(C_6H_5)_3PCr(CO)_5$ (Plastas, Stewart & Grim, 1973) and 91·7° for $C_{23}H_{17}PCr(CO)_5$ (Vahrenkamp & Nöth, 1973) thus indicate a value a little greater than 1·5 for the P–Cr bond. In the trigonal bipyramidal molecules $(C_6H_5)_2HPFe(CO)_4$ (Kilbourn, Raeburn & Thompson, 1969) and $(CH_3P)_2[Fe(CO)_4]_2$ (Jarvis, Mais, Owston & Thompson, 1968)

Table 4. *Values of the angle $A-M-C_{eq}$ for trigonal bipyramidal ACo(CO)$_4$ and closely related groups*

Molecule	Average bond angle (°)	Reference
$H_3SiCo(CO)_4$	81·7	Robiette *et al.* (1968)
$F_3SiCo(CO)_4$	85·4	Berry *et al.* (1970)
$Cl_3SiCo(CO)_4$	85·2	Robinson & Ibers (1967)
$In[Co(CO)_4]_3$	83·3	Robinson & Schussler (1973)
$[(C_2H_5)_4N]^+[Br_2In\{Co(CO)_4\}_2]^-$	84·6	Cradwick (1971)
$(C_6H_5)_3PAuCo(CO)_4$	78·3	Blundell & Powell (1971)
$C_{17}H_{23}As_3AgCo(CO)_4$	78·1	Blundell & Powell (1971)
$BrSn[Co(CO)_4]_3$	87·0	Ball & Hall (1973)
$[\{(C_6H_5)_3P\}_2N]^+[HFe(CO)_4]^-$	80·9	Smith & Bau (1973)
Average	82·7	

the average values of P—Fe—C_{eq} are 88·2 and 89·1°, respectively, which indicate that the bond number for the P—Fe bonds is a little less than 1·5, probably about 1·4 by interpolation between 90° for n = 1·5 and 86·4° for n = 1.

Examples of enneacovalence

The extent to which the idea of enneacovalence of the transition metals can be applied in the interpretation of the formulas and structures of their compounds can be indicated by some examples.

Co, Rh and Ir have nine outer electrons and can accordingly be enneacovalent without transfer of any electrons to or from other atoms. Examples are the eight compounds A—$Co(CO)_4$ listed in Table 4, in which the Co atom forms a single bond with A and four double bonds with the carbonyl groups.

For Fe, Ru, and Os an electron must be transferred to the transition-metal atom to give it enneacovalence, as in the anion $[HFe(CO)_4]^-$. Often, the electron comes from an electron-donating ligand, such as a single-bonded carbonyl or phosphine; an example is $Fe(CO)_5$, in which the average amount of double-bond character for the Fe—C bond is 80%. Another example is $Os_4O_4(CO)_{12}$ (mentioned in an earlier section of this paper), in which an electron is transferred from each O atom to an Os atom.

For Mn, Tc, and Re two additional electrons are required for enneacovalence, as in the anions $[TcH_9]^{2-}$ and $[ReH_9]^{2-}$. In the compounds A—$Mn(CO)_5$ and A—$Re(CO)_5$ listed in Table 3 two singly-bonded carbonyl groups contribute the two electrons, so that the bonds to the carbonyl atoms have 60% double-bond character. Similarly, three electrons are required for enneacovalence for Cr, Mo and W. For the last two compounds in Table 3 one electron per Cr or Mo comes from the charge on the anion and the other two from two singly-bonded carbonyls; the bonds to carbonyl in these $[-Cr(CO)_5]^-$ and $[-Mo(CO)_5]^-$ groups accordingly also have 60% double-bond character, whereas in $Cr(CO)_6$ and $Mo(CO)_6$ they have only 50%.

A test of these considerations is provided by the observed values of the metal—carbonyl bond lengths. Observed average values and the amounts of double-bond character (in parentheses) as given by the above discussion are A—$Co(CO)_4$ 1·74 Å (100%), $[H-Fe(CO)_4]^-$ 1·74 Å (100%); $[(C_4H_9)_3PCo(CO)_3]_2$ 1·75 Å (100%; Ibers, 1968); $Fe(CO)_5$ 1·80 Å (80%), $[Mn(CO)_5]^-$ 1·81 Å (80%); average of several compounds containing the $Fe(CO)_4$ group with Fe forming two single bonds, 1·79 Å (75%); A—$Cr(CO)_5$ 1·83 Å (60%); $Cr(CO)_6$ 1·91 Å (50%; Whitaker & Jeffery, 1967; Jost, Rees & Yelon, 1975); $C_6H_5(OCH_3)C{=}Cr(CO)_5$ 1·88 Å (40%; Mills & Redhouse, 1968), $(C_2H_5)_2NH(CH_3)C{=}Cr(CO)_5$ 1·89 Å (40%; Connor & Mills, 1969); $C_6H_5S(CH_3)C{=}Cr(CO)_5$ 1·91 Å (40%; Hoare & Mills, 1972). These values are shown in Fig. 1, with a curve that approximates them. The curve is calculated by an equation formulated for single-bond:triple-bond resonance (Pauling, 1960, p. 241), with the single-bond distance to the carbonyl C taken as 2·07 Å and the triple-bond distance as 1·63 Å. The upper curve, for M—P bonds, is drawn in the same way through the points 2·45 Å for n = 1 and 2·18 Å for n = 2 {from $H(N)_2Co[P(C_6H_5)_3]_3$ 2·19 Å (Davis, Payne & Ibers, 1969) and $[(C_4Hg)_3P]_2Co(CO)_3$ 2·18 Å (Ibers, 1968)}. These curves have not been corrected for the change in enneacovalent radius from 1·26 Å for Cr to 1·23 Å for Co (which, in fact, is largely neutralized by the correction for the difference in electronegativity). They may be unreliable by 0·01 or 0·02 Å in bond lengths and about 0·05 or 0·10 in bond numbers, but ratios of bond numbers may be in small error, and the bond numbers can be corrected by a factor such as to give the value 9 for covalence of the metal atom.

An example is $(C_6H_5)_2P(H)Fe(CO)_4$ (Kilbourn *et al.*, 1969), with P—Fe = 2·24 and Fe—C = 1·79 Å, which lead to n = 1·60 and 1·75 respectively. For $[(C_2H_5)_3PMn(CO)_4]_2$ (Bennett & Mason, 1968) the values 2·25 and 1·81 Å lead to n = 1·52 and 1·62, respectively, and for $(C_6H_5)_3C_5H_2PCr(CO)_5$ the values 2·37 and 1·84 Å lead to n = 1·15 and 1·57, respectively. In general, the bonds to the carbonyl groups have larger

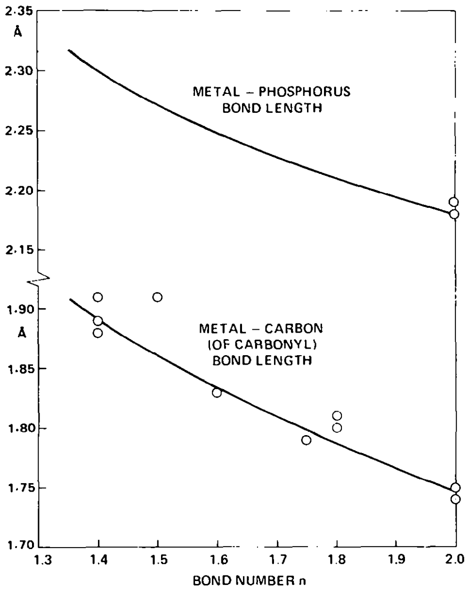


Fig. 1. Curves giving the bond lengths of bonds between the enneacovalent transition metals Cr, Mn, Fe and Co, and P (above) and carbonyl C (below) as functions of the bond number. The refinement of considering the change in radius from 1·26 Å for Cr to 1·23 Å for Co has not been made. The circles are the experimental values mentioned in the text.

values of n than those to P, although usually the difference is only 0·1 or 0·2. The evidence from bond angles supports this conclusion.

The heavier transition metals

The foregoing considerations can be applied also to compounds of the heavier transition metals. Angles in compounds A—Re(CO)$_5$ are given in Table 3. Bond numbers are about the same as for the corresponding lighter congeners; for example, the bond lengths Os—P = 2·36 and Os—C = 1·92 Å in $[(C_6H_5)_3P]_2Os(CO)_3$ (Stalick & Ibers, 1969) lead, with use of the curves of Fig. 1 changed by 0·14 Å to correct for the difference in radius of Os and Fe, to $n = 1·73$ and 1·85, respectively.

Some theoretical treatments of bond lengths and bond angles of compounds of transition metals have been published; for example, those of Bennett & Mason (1965), Berry, Corey, Hagen, MacDiarmid, Saalfeld & Wayland (1970), and Brown, Chambers, Fitzpatrick & Rowlinson (1971). These treatments do not have enough in common with the arguments of this paper and my earlier papers to justify more than mention of them.

I thank Mrs Dorothy Munro, Mrs Ruth Reynolds and Mrs Lynne Wilcox for assistance in checking the literature.

References

Abrahams, S. C., Ginsberg, A. P. & Knox, K. (1964). *Inorg. Chem.* **3**, 558–567.

Agron, P. A., Ellison, R. D. & Levy, H. A. (1967). *Acta Cryst.* **23**, 1079–1086.

Almenningen, A., Jakobsen, G. G. & Seip, H. M. (1969). *Acta Chem. Scand.* **23**, 685–686.

Ball, R. D. & Hall, D. (1973). *J. Organomet. Chem.* **52**, 293–295.

Bennett, M. J. & Mason, R. (1965). *Nature (London)*, **205**, 760–762.

Bennett, M. J. & Mason, R. (1968). *J. Chem. Soc. A*, pp. 75–81.

Berry, A. D., Corey, E. R., Hagen, A. P., MacDiarmid, A. G., Saalfeld, F. E. & Wayland, B. B. (1970). *J. Am. Chem. Soc.* **92**, 1939–1945.

Birjukov, B. P., Solodova, O. P. & Struchkov, Yu. T. (1968). *Russ. J. Struct. Chem.* **9**, 228–239.

Blundell, T. L. & Powell, H. M. (1971). *J. Chem. Soc. A*, pp. 1685–1690.

Bright, D. (1970). *Chem. Commun.* pp. 1169–1170.

Brown, D. A., Chambers, W. J., Fitzpatrick, N. J. & Rowlinson, R. M. (1971). *J. Chem. Soc. A*, pp. 720–725.

Bryan, R. F. (1968). *J. Chem. Soc. A*, pp. 696–703.

Ciechanowicz, M., Skapski, A. C. & Troughton, P. G. H. (1976). *Acta Cryst.* B**32**, 1673–1680.

Clegg, W. & Wheatley, P. J. (1973). *J. Chem. Soc. Dalton Trans.* pp. 90–94.

Connor, J. A. & Mills, O. S. (1969). *J. Chem. Soc. A*, pp. 334–340.

Couldwell, M. C., Simpson, J. & Robinson, W. T. (1976). *J. Chem. Soc. Dalton Trans.* pp. 714–719.

Cradwick, P. D. (1971). *J. Organomet. Chem.* **27**, 251–260.

Dahl, L. F. & Rundle, R. E. (1963). *Acta Cryst.* **16**, 419–426.

Davis, B. R., Payne, N. D. & Ibers, J. A. (1969). *Inorg. Chem.* **8**, 2719–2728.

Einstein, F. W. B., Luth, H. & Trotter, J. (1967). *J. Chem. Soc. A*, pp. 89–93.

Gapotchenko, N. I., Alekseev, N. V., Antonova, A. B., Anisimov, K. N., Kolobova, N. E., Ronova, I. A. & Struchkov, Yu. T. (1970). *J. Organomet. Chem.* **23**, 525–530.

Ginsberg, A. P. (1964). *Inorg. Chem.* **3**, 567–568.

Handy, L. B., Ruff, J. K. & Dahl, L. F. (1970). *J. Am. Chem. Soc.* **92**, 7312–7326.

Hoare, R. J. & Mills, O. S. (1972). *J. Chem. Soc. Dalton Trans.* pp. 653–656.

Hoffman, P. R., Yoshida, T., Okano, T., Otsuka, S. & Ibers, J. A. (1976). *Inorg. Chem.* **15**, 2462–2466.

Hultgren, R. (1932). *Phys. Rev.* **40**, 891–907.

Huttner, G. & Regler, D. (1972). *Chem. Ber.* **105**, 1230–1244.

Ibekive, S. D., Kilbourn, B. T., Raeburn, V. A. & Russell, D. R. (1969). *Chem. Commun.* pp. 433–434.

Ibers, J. A. (1965). *Ann. Rev. Phys. Chem.* **16**, 375–392.

Ibers, J. A. (1968). *J. Organomet. Chem.* **14**, 423–428.

Jarvis, J. A. J., Mais, R. H. B., Owston, P. G. & Thompson, D. T. (1968). *J. Chem. Soc. A*, pp. 622–628.

Jost, A., Rees, B. & Yelon, W. B. (1975). *Acta Cryst.* B**31**, 2649–2658.

Katcher, M. L. & Simon, G. L. (1972). *Inorg. Chem.* **11**, 1651–1657.

Kilbourn, B. T., Raeburn, U. A. & Thompson, D. T. (1969). *J. Chem. Soc. A*, pp. 1906–1909.

La Placa, S. J., Hamilton, W. C., Ibers, J. A. & Davidson, A. (1969). *Inorg. Chem.* **8**, 1928–1935.

La Placa, S. J. & Ibers, J. A. (1965). *Acta Cryst.* **18**, 511–519.

McClure, V. E. (1970). *Localized and Equivalent Orbitals*, PhD Dissertation, Univ. of California, San Diego.

Mills, O. S. & Redhouse, A. D. (1968). *J. Chem. Soc. A*, pp. 642–647.

Nicholson, B. K., Simpson, J. & Robinson, W. T. (1973). *J. Organomet. Chem.* **47**, 403–412.

Pauling, L. (1931). *J. Am. Chem. Soc.* **53**, 1367–1400.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Pauling, L. (1975*a*). *Proc. Natl Acad. Sci. USA*, **72**, 3799–3801.

Pauling, L. (1975*b*). *Proc. Natl Acad. Sci. USA*, **72**, 4200–4202.

Pauling, L. (1976*a*). *Proc. Natl Acad. Sci. USA*, **73**, 274–275.

Pauling, L. (1976*b*). *Proc. Natl Acad. Sci. USA*, **73**, 1403–1405.

Pauling, L. (1976*c*). *Proc. Natl Acad. Sci. USA*, **73**, 4290–4293.

Pauling, L. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 2614–2615.
Plastas, H. J., Stewart, J. M. & Grim, S. O. (1973). *Inorg. Chem.* **12**, 265–272.
Rankin, D. W. H. & Robertson, A. (1976). *J. Organomet. Chem.* **105**, 331–340.
Robiette, A. G., Sheldrick, G. M., Simpson, R. N. F., Aylett, B. J. & Campbell, J. M. (1968). *J. Organomet. Chem.* **14**, 279–285.
Robinson, W. T. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 1208–1213.
Robinson, W. T. & Schussler, D. P. (1973). *Inorg. Chem.* **12**, 847–854.
Sasse, H. E. & Ziegler, M. L. (1972). *Z. Anorg. Allg. Chem.* **392**, 167–172.
Seip, H. M. & Seip, R. (1970). *Acta Chem. Scand.* **24**, 3431–3432.
Skapski, A. C. & Troughton, P. G. H. (1968). *Chem. Commun.* pp. 1230–1231.
Smith, M. B. & Bau, R. (1973). *J. Am. Chem. Soc.* **95**, 2388–2389.
Stalick, J. K. & Ibers, J. A. (1969). *Inorg. Chem.* **8**, 419–423.
Vahrenkamp, H. (1972). *Chem. Ber.* **105**, 1486–1496.
Vahrenkamp, H. & Nöth, H. (1973). *Chem. Ber.* **106**, 2227–2235.
Weber, H. P. & Bryan, R. F. (1967). *Acta Cryst.* **22**, 822–836.
Whitaker, A. & Jeffery, J. W. (1967). *Acta Cryst.* **23**, 977–984.

Acta Cryst. (1978). B**34**, 752–758

High-Temperature Phases of $SrZrO_3$

By M. Ahtee

Department of Physics, University of Helsinki, Siltavuorenpenger 20 D, SF00170 Helsinki 17, Finland

A. M. Glazer

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, England

and A. W. Hewat

Institut Laue–Langevin, Grenoble, France

(*Received* 16 *August* 1977; *accepted* 30 *September* 1977)

The high-temperature structures of $SrZrO_3$ have been determined by neutron powder profile refinement, and the phase transitions described by the condensation of soft vibrational modes. At 900°C, $SrZrO_3$ is tetragonal, $I4/mcm$, with an O octahedron antiphase tilt of 6·5° about [001], intermediate between those found in the isomorphous phases of $SrTiO_3$ below 110 K and $KMnF_3$ below 184 K. At 760°C the structure is orthorhombic *Bmmb* with almost equal b_0 and c_0 axes, and not tetragonal. In addition to the antiphase tilt, now 8·5° about [001], there is an in-phase tilt of 3·1° about [010]. Yet a third tilt, antiphase about [100] and identical to that about [001], is introduced at room temperature. This series of transitions indicates that the sequence of condensation of soft modes from the high-temperature cubic phase is R_{25}, M_3 and finally R_{25} again. In addition, the two latter transitions are first order, and are accompanied by a condensation from the X-point of the Brillouin zone, which produces atomic displacements. The unusually anisotropic thermal ellipsoids provide some additional evidence for the existence of low-frequency vibrational modes.

Introduction

Carlsson (1967) has studied the high-temperature phase transitions in $SrZrO_3$ by differential thermal analysis and X-ray diffraction. He found the following sequence of phase transitions:

$$\text{orthorhombic} \underset{700\,^{\circ}\mathrm{C}}{\rightarrow} \underset{c/a<1}{\text{tetragonal}} \underset{830\,^{\circ}\mathrm{C}}{\rightarrow} \underset{c/a>1}{\text{tetragonal}} \underset{1170\,^{\circ}\mathrm{C}}{\rightarrow} \text{cubic.}$$

In an earlier paper (Ahtee, Ahtee, Glazer & Hewat, 1977) the structure of $SrZrO_3$ at room temperature was reported, solved by the neutron powder profile refinement technique (Rietveld, 1969; Hewat, 1973). In this paper we report the structures of the two high-temperature phases at 760 and 900°C and also consider the possible soft modes associated with the corresponding transitions.

Data collection

Neutron diffraction measurements were made on the D1A high-resolution powder diffractometer on the high-