The structures were solved with use of the heavy-atom method. After refinement of the heavy atom, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 5 Å^2 (**1**) and 6 Å^2 (**2**) but not refined. Full least-squares refinement converged to $R(F) = 0.041$ and $R_w(F) = 0.078$ (**1**) and $R(F) = 0.056$ and $R_w(F) = 0.074$ (**2**) ($w = 1/\sigma^2(\text{count}) + (\rho I)^2$ (132 variables for **1** and 262 for **2**). The unit-weight observations were 1.87 for $\rho = 0.08$ (**1**) and 1.74 for $\rho = 0.08$ (**2**). Final difference Fourier maps revealed no significant maxima. Tables III and IV list the atomic positional and thermal parameters for all non-hydrogen atoms with their estimated standard deviations.

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Supplementary Material Available: Listings of atomic positional parameters for hydrogen atoms, observed and calculated structure factors, and thermal parameters for anisotropically refined atoms (U_{ij}) (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Molecular Mechanics of High-Order Bonds

JAN C. A. BOEYENS*

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Molecular mechanics was used to study the characteristics of homonuclear quadruple bonds between Cr, Mo, W, and Re atoms. Derived force constants that are consistent with the M–M stretching frequencies observed in $M_2(CH_3)_8^{4-}$ anions were used to calculate the barriers to rotation about quadruple bonds and to estimate the δ contribution to the Cr–Cr quadruple-bond strength, obtained as 11 kcal/mol. Satisfactory descriptions of the relationships between dimetal quadruple and triple bonds, in terms of their relative flexibilities and steric requirements of the ligands, were obtained.

Introduction

Chemical interaction between neighboring transition-metal atoms in molecules is remarkably diverse and variable, ranging from simple van der Waals interaction to quadruple bonding, which implies the overlap of four orbital pairs at the dimetal center. This variation from 0 to 4 in bond order is not necessarily matched by a parallel variation in observed structural properties, probably because of the extreme flexibility of metal–metal bonds in comparison with the more conventional covalent bonds formed between p-block atoms. Consequently, the experimental study of dimetal centers with high-order bonding often produces results that are in apparent contradiction or are difficult to interpret. The aim of the present work is to identify experimentally observed structural features in dimetal systems, ostensibly at variance with the trends predicted on the basis of bond order only, and to investigate the possibility of accounting for the discrepancies by the method of molecular mechanics. It, more specifically, deals with trends in vibrational frequency, dimetal bond length, and the conformational demands of δ bonding.

It is notoriously difficult to understand the variability of observed M–M vibrational frequencies, as for instance in compounds containing quadruply bonded dimolybdenum, conveniently formulated as $\mathrm{M}\overset{4}{-}\mathrm{M}$. In particular, one finds quadruple bonds between metal atoms in two basically different types of environment, exemplified by molybdenum carboxylates and terminally substituted dimolybdenum species, respectively. Metal–metal bonds of the first kind are bridged by bidentate ligands whereas only terminal ligands are present in compounds of the second kind. Although the bond order is the same in the two situations, one finds an average shift of about 30–90 cm^{-1} in stretching frequency ($\bar{\nu}$) between the two types,[1] $\bar{\nu}$ being uniformly less for unsupported bonds. A tentative explanation is provided by the calculation[2] that carboxylate-type bridging causes mixing of vibrational modes, but this is not clearly supported by experiment.[3]

Observed dimetal bond lengths offer a special interpretational challenge in that the observed ranges for different bond orders overlap almost at random.[4] A baffling example of this phenomenon emerges from a comparison of the W–W bond lengths in the propanoate $W_2(O_2CEt)_4$ and the axially substituted propanoate $W_2(O_2CEt)_4 \cdot 2CH_2Ph$, respectively. Despite the different bond orders of $\mathrm{W}\overset{4}{-}\mathrm{W}$ and $\mathrm{W}\overset{3}{-}\mathrm{W}$ and apart from the axial ligands in the triply bonded species, the two molecules have virtually identical structures.[5]

A quadruple bond is theoretically stabilized by δ overlap, which demands eclipsing of terminal ligands across the unbridged bond, despite the steric strain expected for this arrangement. The δ contribution should therefore be sufficient to overcome the steric barrier to rotation[6] and to stabilize the eclipsed conformation relative to the sterically more favorable staggered conformation. The compound $Re_2Cl_4(PEt_3)_4$, with a dimetal bond order of 3 however, also has eclipsed geometry, but certainly not stabilized by δ overlap. Eclipsing across the triple bond is therefore not due to electronic factors and can only be of steric origin. Simple steric arguments should therefore clearly distinguish between the two types of eclipsed conformation in order to support the theory of δ bonding.

It is proposed to analyze the interpretational problems described above by the methods of molecular mechanics as recently applied[7] to rationalize structural trends in dimetal systems of low bond order. This will provide a direct quantitative estimate of all intermolecular steric interactions and by implication a means of identifying electronic effects.

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* Address correspondence to the Department of Chemistry, University of the Witwatersrand, Johannesburg, 2001 South Africa.

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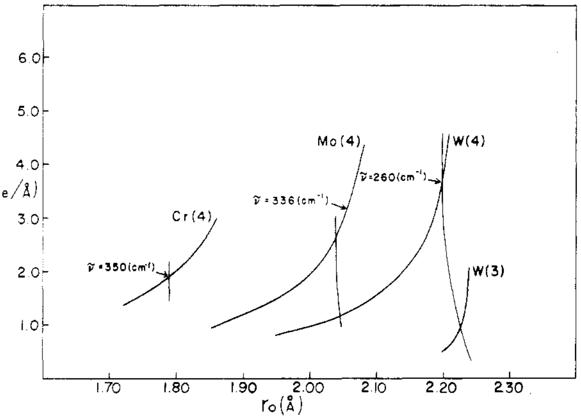

Figure 1. Molecular mechanics solution curves $\{k,r_0\}$ for high-order dimetal bonds. Curves sloping to the right refer to unbridged bonds, and those sloping to the left refer to dimetal bonds supported by bridging ligands.

Computational Strategy

In view of the extreme variability of observed stretching frequency of dimetal bonds,[1] it is almost impossible to obtain transferable force constants for metal–metal bonds from spectroscopic measurements not supported by full normal-coordinate analyses. This complicates the formulation of a suitable force field, required for the analysis of these systems by molecular mechanics. In molecular mechanics electronic properties of a molecule are specified bond-by-bond to define a molecular force field, usually in terms of a harmonic strain-free value, p_0, for each possible distortion. To model steric factors, nonbonded interaction potentials are added to the electronic force field and the total strain is minimized as a function of all atomic coordinates. For a molecule like a metal carboxylate the force field for all interactions, but the metal–metal bond, can be defined in terms of well-established transferable values from the literature. Suitable values of force constant and characteristic bond length, r_0, for the metal–metal bond can then be obtained by trial and error. A likely value for r_0, e.g., is assumed and k is adjusted until a combination (k, r_0) is found to reproduce the observed structure after energy minimization. This is repeated for a range of values of r_0 to define a solution set $\{k,r_0\}$, which can conveniently be represented graphically as in Figure 1. In order to obtain unique transferable values one looks for different solution sets pertaining to the same bond order and intersecting at a single point. To achieve this, it is necessary to identify bonds of the same order in sterically different environments. In the present case, compounds with and without bridging ligands suggest themselves as appropriate classes for comparison. Once the parameters for a given bond order have been determined, they are used without further adjustment in all further calculations involving those bonds.

Results and Discussion

The structures of the homologous anions $M_2(CH_3)_8^{4-}$ (M = Cr, Mo, W) have all been determined with sufficient accuracy[8-10] to constitute a basis for comparison of the different $M\overset{4}{-}M$ bonds. In particular, the relative amounts of steric strain can be compared directly by simulation of the observed structures through molecular mechanics. Details of the computational model and program have been described before.[7] Force field parameters not defined before, and used in the present study, are summarized in Table I. The solution sets $\{k,r_0\}(M\overset{4}{-}M)$ for the three anions are represented graphically as curves with positive slope in Figure 1. Unique solutions followed from a similar analysis of three authentic quadruply bonded bridged metal dimers of known structure. The three compounds considered in the calculations are $Cr_2[MeNC(Ph)NMe]_4$,[11] $Mo_2[pyNC(O)CH_3]_4$,[12] and $W_2[O_2CEt]_4$.[13] The corresponding solution curves have negative slopes and intersect the curves of the octamethyl anions, to yield the unique solutions

$$k(\mathrm{Cr;\ Mo;\ W})/\mathrm{mdyn\ Å^{-1}} = 1.87;\ 2.75;\ 3.65$$

$$r_0(\mathrm{Cr;\ Mo;\ W})/\mathrm{Å} = 1.79;\ 2.04;\ 2.20$$

The values of harmonic force constant that would yield the frequencies observed[14,15] for the unbridged species are indicated by arrows to the solution curves of the unbridged compounds. The close agreement with the calculated points of intersection strongly suggests that the harmonic approximation is valid for unbridged metal–metal bonds, but not for bridged bonds. The calculations are relatively insensitive to small changes in k and r_0, suggesting that the derived force constants have standard deviations of about 5%. It seems reasonable to assume that the same holds for $Re\overset{4}{-}Re$ bonds. The force constant for the dirhenium quadruple bond was therefore calculated directly from $\tilde{\nu}$ = 275 cm^{-1} as k = 4.15 mdyn/Å. The observed[6] structure of the $Re_2(CH_3)_8^{2-}$ anion is

Table I. Force Field Parameters for Interacting Pairs of Atoms[a]

atoms	a	b	c	k	r_0	ref (k)
Cr–C				2.08	2.18	19
Mo–C				1.96	2.27	19
W–C				2.36	2.31	19
Re–C				1.5	2.19	
Re–Cl				0.7	2.20	
Re–P				0.7	2.40	
Re···Re[b]	38.36	2.38	6.6			
Re···Cl	325.9	2.99	10.75			
Re···P	479.6	3.09	8.44			
Re···C	272.1	3.21	3.70			
Re···H	1.392	2.02	2.31			
Cl···Cl	2180.6	3.75	17.5			
Cl···P	2367.6	3.87	13.75			
Cl···C	1801.2	4.02	6.02			
Cl···H	322.8	3.91	2.44			

[a] Bonding interactions are described by k (mdyn/Å) and r_0 (Å). Nonbonded interactions are described by the potential $U = a\exp(-br) - c/r^6$, where r is the interatomic distance, a is in units (u) of 10^{-11} erg/molecule ≡ kcal mol^{-1}/144, b is in units of Å^{-1}, and c is in units of u Å^6. [b] Re and W atoms have been assigned the same parameters in nonbonded interactions, corresponding to a van der Waals radius of 2.6 Å.

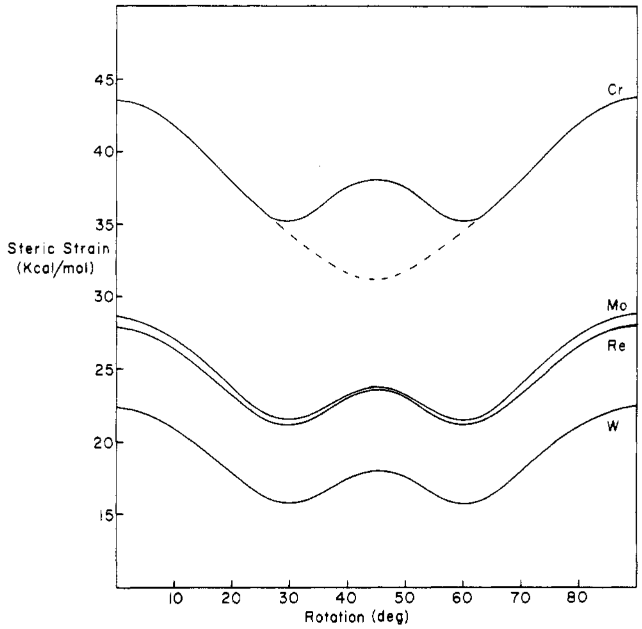

Figure 2. Angular variation of steric strain in quadruply bonded octamethyl dimetal ions. The extrapolated broken curve corresponds to spherically symmetrical ligands.

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reproduced well by using (k, r_0) = (4.15, 2.11 Å). One can be confident that all of the calculated parameters for the M$\overset{4}{-}$M bonds are of the correct order of magnitude and hence suitable for the calculation of barriers to rotation in the corresponding compounds.

The torsional parameter used to render the eclipsed conformation energetically favored (2.4 kcal/mol) was replaced by an artificial incremental parameter[16] to drive the rotation around the metal–metal bond, sampling the equilibrium steric strain at each position. The results are shown in Figure 2. In each case the potential energy has a maximum at ϕ = 0, viz. the eclipsed conformation. This shows conclusively that an electronic factor, i.e. δ bonding, is responsible for the stabilization of the observed conformation. Potential minima are observed at ϕ = 30 and 60°, and not at 45°. The explanation to this lies in the fact that the potential energy curve essentially reflects interaction between hydrogen atoms on methyl groups. These have local threefold symmetry, which is superimposed on the fourfold symmetry of the anion. The compromise is a local submaximum at 45°. However, the difference in potential energy, ΔU = 8.5, 7.5, and 6.5 kcal/mol for Cr, Mo (Re), and W, respectively, defines a lower limit for the δ contribution to the quadruple-bond strength.

The local maximum at 45° would clearly not occur for spherically symmetrical ligand atoms like Cl and Br. As shown by extrapolation of the curve for dichromium, one predicts a somewhat deeper minimum for the octachloro- or -bromo complexes; i.e., $\Delta U \simeq$ 12.5 kcal/mol. It is intriguing to note that apart from the octamethyl and one related compound, no other unbridged dichromium compounds have been synthesized, and in particular no halogeno complexes of the type $Cr_2X_8{}^{4-}$. It is tempting to ascribe this to the higher energy required for stabilizing the compounds with structureless ligands. This would also fix an upper limit to the δ contribution, which hence appears to be about 11 kcal/mol for Cr$\overset{4}{-}$Cr bonds. This is not sufficient to stabilize the eclipsed conformation, and monomeric compounds are formed instead. Whereas steric factors are clearly less demanding for the other metals, quadruply bonded chloro, bromo, and other compounds abound.

To clarify the relationship between M$\overset{4}{-}$M and M$\overset{3}{-}$M bonds, the axially substituted analogue, $W_2[O_2CEt]_4{\cdot}2CH_2Ph$, of the propanoate already described was analyzed. Whereas the two compounds were found to have identical structures, apart from the benzyl groups, it is not surprising also to find that their molecular mechanics solution curves coincide. The appropriate solution for the triple bond was obtained by computing also the solution curve for the unbridged tungsten dimer $W_2(CH_2SiMe_3)_6$. The observed structure[17] was correctly modeled by specifying r_0(W–C) =2.17 Å and strain-free bond angles, θ_0(W–W–C; C–W–C) (90°; 120°). The solution curve is also shown in Figure 1. The surprising result of the identical cores in the carboxylates of W$\overset{4}{-}$W and W$\overset{3}{-}$W is now readily explained. The carboxylate framework, as noted before,[7] is sterically cohesive and compresses metal–metal bonds toward a natural bite distance that varies with M–O bond length. Definition of strain-free parameters in terms of the gas-phase geometry of propanoic acid, as determined by microwave spectroscopy,[18] gives a bite distance of 2.18 Å at a W–O bond length of 2.085 Å. This is an almost ideal bite for W$\overset{4}{-}$W bonds, which are compressed very slightly, from r_0 = 2.20 Å to the observed 2.19 Å. Because of its lower force constant (k = 1.0 mdyn/Å), the W$\overset{3}{-}$W bond is more flexible and easily compressed from r_0 = 2.23 Å to accommodate the propanoic bite at 2.19 Å.

One final problem concerns the eclipsed geometry observed[19] for $Re_2Cl_4(PEt_3)_4$ in the absence of δ bonding to stabilize the observed arrangement. Without trying to find the characteristic (k, r_0) pair for Re$\overset{3}{-}$Re, it was observed that the calculated strain remains constant along the solution curve. To allow for the possibility of some δ bonding, the steric strain was analyzed by using (k, r_0) = (3.5 mdyn/Å, 2.15 Å). The calculated strain as a function of rotation around the central bond is shown in Figure 3. It leaves no doubt about the cause of the observed conformation, confirming previous suggestions[20] that fully staggered triethylphosphine groups represented the minimum-strain arrangement. It is interesting to note that the structure as refined by molecular mechanics does not have $\bar{4}$ symmetry. It has Cl–Re–Re–P torsion angles alternating between +0.13 and –0.07° around the central bond. This is averaged out by the observed disorder and probably has some bearing on the exact nature thereof.

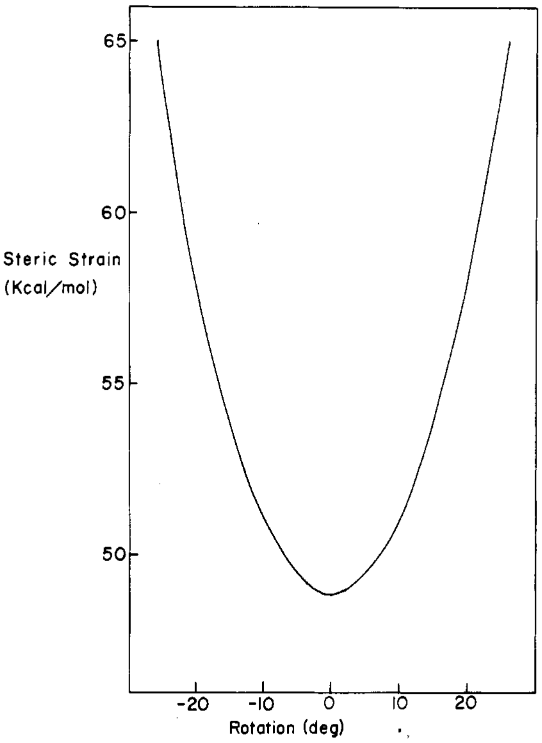

Figure 3. Steric strain in $Re_2Cl_4(PEt)_4$ as a function of twist angle.

Table II. A Selection[1] of M–M Stretching Frequencies and Observed Bond Lengths

complex	d(M–M)/Å	$\bar{\nu}$/cm^{-1}
$Mo_2(CH_3)_8{}^{4-}$	2.148	336
$Mo_2(O_2CCH_3)_4$	2.093	406
$Mo_2[pyNC(O)CH_3]_4$	2.037	416
$Mo_2(O_2CCF_3)_4{\cdot}2py$	2.129	367

Conclusion

These results demonstrate the steric origin of several puzzling features in the chemistry of high-order dimetal centers and suggest a firm value for the δ contribution to the strengths of chemical bonds. Although the variability of vibrational frequency is not explained, some evidence pertaining to this problem does emerge. It is noted that the force constants obtained only by internal comparison of structural data for M$\overset{4}{-}$M systems are in fair accord with the spectroscopic properties of the unbridged dimers, assuming localized harmonic M–M vibrations. The substantial shifts caused by bridging ligands seem to suggest some coupling, as suggested by partial normal-coordinate analysis.[2] The origin of this coupling could be the steric cohesion of carboxylate-like bridging frameworks. Where this is weakened by axial ligation one finds a corresponding reduction of the spectral shift. These

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trends are demonstrated qualitatively by the selection of vibrational frequencies shown in Table II. It is noted that the observed frequencies for Re$\overset{4}{-}$Re, which occur over a narrow range,[1] do not include any fully bridged molecules without axial ligands. A detailed examination of these effects should be a fruitful area for future application of molecular mechanics to the study of dimetal systems.

Acknowledgment. I am grateful to Professor F. A. Cotton for the hospitality extended while this work was carried out in his laboratory and for alerting me to many of the problems treated here and also to the University of the Witwatersrand for granting me a year's sabbatical leave.

Registry No. Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7; Re, 7440-15-5.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Synthesis of New Hybrid Phosphine Amine and Phosphine Amide Compounds. Preparation of a Series of New Phosphine Amido Chelate Complexes of Palladium(II) and Platinum(II) and Their Reactions with Bases and Brønsted Acids

DAVID HEDDEN and D. MAX ROUNDHILL*

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The phosphine amine and phosphine amide compounds *o*-$Ph_2PC_6H_4NHCH_2Ph$ (PNHBz), *o*-$Ph_2PC_6H_4CH_2NHPh$ (PCNHPh), *o*-$Ph_2PC_6H_4NHC(O)Ph$ (PNH(CPhO)), and *o*-$Ph_2PC_6H_4C(O)NHPh$ (P(CO)NHPh) have been synthesized and characterized. The reaction of PNH(CPhO) or P(CO)NHPh with $PtCi_4^{2-}$ or $PdCl_4^{2-}$ gives *trans*-$PtCl_2L_2$ or -$PdCl_2L_2$ (L = PNH(CPhO) or P(CO)NHPh)) where L is bonded monodentately through phosphorus. Treatment of these complexes with bases can be used to synthesize the N-bonded amido complexes *cis*- and *trans*-$M(P(CO)NPh)_2$ (M = Pd, Pt) and *cis*-$Pt(PN(CPhO))_2$. The amido complexes react with HCl to give $MCl_2(PNH(CPhO))_2$ and $MCl_2(P(CO)NHPh)_2$ (M = Pd, Pt). Structures are deduced by a combination of IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR techniques.

The coordination chemistry of chelate ligands having mixed functionality types has received extensive study. An important aspect of this work is the development of hybrid ligands where one arm of the chelate is a tertiary phosphine that will selectively coordinate to group 8–10[22] elements of the second- and third-row transition metals.[1] These functionalized phosphines have been used as chelate ligands in complexes where it is desirable to have a hinging chelate arm available for ready substitution.[2] Alternatively the concept has been used to complex functional groups that usually only poorly coordinate[3] or to assemble hybrid ligands for the synthesis of heterobimetallics.[4] With this intramolecular effect, "chelate-assisted oxidative addition" has been induced with C–H,[5] Si–H,[6] N–H,[7] and C–C[8] bonds. In general, these reactions can be considered to be analogous to the well-known orthometalation reactions, where the close proximity between the ortho hydrogen and the transition-metal center enhances the reactivity.[9]

The feasibility of effecting O–H or N–H cleavage by these intramolecular-assisted reactions with functionalized phosphines was apparent after the synthesis of *o*-(diphenylphosphino)phenol[10] and *o*-(diphenylphosphino)aniline.[11] If we pursue the analogy that the ortho-metalation reaction is a good model for N–H activation, we will facilitate the insertion of a metal center into the N–H bond if the amino group has bulky substituents incorporated into the amide or secondary amine.[12] This paper describes the synthesis of our new hybrid phosphine amine and phosphine amide ligands and also the preparation of the phosphine amide complexes with platinum(II) and palladium(II). In addition to the characterization of the amide complexes, this first paper of ours from the project describes the reaction chemistry of the amide and amido complexes with external bases and acids, to effect the interconversion between complexed-amido and free-amide functionalities.

The secondary-amide- and amine-functionalized tertiary phosphines described in this paper are functionalized triphenylphosphines. The syntheses take full advantage of the properties of triarylphosphines, which can be easily modified by known synthetic procedures. Every attempt has been made to develop methods that allow for facile modification of the R substituent in *o*-$Ph_2PC_6H_4NHR$ while the integrity of the remainder of the

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