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Application of a Universal Force Field to Metal Complexes

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The ability of a universal force field (UFF) to reproduce the structures of a variety of metal-containing molecules is examined. M–C bond distances are well reproduced, and errors in M–Y polar covalent bond distances are generally less than 0.05 Å. Use of half-integer bond orders to take into account π back-bonding and the *trans* influence leads to errors of less than 0.05 Å in bond distances for these complexes. Errors on the order of 0.15 Å remain for high-valent-metal to halogen bond distances.

I. Introduction

Molecular mechanics is used routinely to look at the structures and conformational energetics of organic and biological molecules because of fairly complete, specific force fields for these classes of compounds. The same cannot be said about transition metal-containing molecules, because of the large number of elements and the diversity of both geometries and oxidation states. Despite the limitation of highly element-specific transition metal force fields, many applications of molecular mechanics to transition metal complexes have been reported.

There have been several reviews on the application of molecular mechanics to metal complexes.[1] The coordination stereochemistry of group VIII chelates has been particularly well studied by molecular modeling.[1a,c] Included are investigations of the conformations, stereochemistry, and structures of Co(II) and Co(III) complexes,[2,3] studies of Ni(II) macrocycles,[4] investigations of Fe(II) chelates,[5] and analysis of binuclear metal complexes of macrocyclic Schiff base ligands.[6] Other recent work on classical coordination compounds includes the simulation of trigonally strained (hexaamine)chromium(III) complexes[7] and studies of the deformability of Cu(II) complexes[8a–d] and other classical coordination complexes.[8e] Molecular mechanics has also been used to study the influence of steric interactions on the length of low-order[9a] and high-order[9b] metal–metal bonds.

Applications of molecular mechanics to bioinorganic chemistry include a number of papers describing the use of molecular modeling techniques to examine *cis*-diammineplatinum(II) anticancer drugs and their interaction with DNA.[10] In addition, studies of vanadyl–adenine complexes and bleomycin have appeared.[11]

Recent molecular mechanics investigations of organometallic complexes include several studies of iron cyclopentadienyl complexes[12] and an actinide cyclopentadienyl complex,[13] as well as investigations of chromium and iron carbonyl phosphines.[14] Quite recently a force field for linear metallocenes was reported.[15] Homogeneous catalysis by organometallic compounds has also been examined by molecular mechanics: two examples are the catalytic asymmetric hydroformylation by Pt complexes[16] and hydrogenation by (phosphine)rhodium(I) catalysts.[17a,b] Force fields for metal carbonyl clusters have also been reported.[17c,d]

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Despite the growing number of applications of molecular mechanics to transition metal complexes, efforts directed at developing a general force field capable of describing the large number of transition metal elements and the diversity of both geometries and oxidation states have been rare. In this paper we describe the application of a new force field not only to classical coordination complexes but also to combinations of biological, organic, inorganic main group, and transition metal complexes. Although this force field may not be as accurate, at this early stage of development, as a force field fit to specific combinations of atoms, here we demonstrate the viability and usefulness of a general approach.

Several steps in this direction have been described in the literature. Recently, Landis and co-workers reported a new set of angular functional forms for the diverse coordination environments of transition metal complexes.[18] Parameters for specific metals of biological importance were provided in the paper describing the Dreiding force field.[19] A parametric approach for modeling inorganic solids using atomic constants has been described.[20] Finally, the MMX force field has been outlined, though specific parameters and benchmark results were not provided.[21]

The present force field has been developed from first principles using general rules for estimating force field parameters based on simple relations from the literature. We refer to this new force field as a universal force field (UFF). The force field was described in detail in the first paper of this series;[22] here we only outline the approach and summarize the results for organic and main group compounds in section II. In section III we describe the calculational details. The results for metallo complexes are discussed in section IV, and overall observations are provided in section V.

II. Force Field

Development of a Full Periodic Table Force Field. Parameters and functional forms are the vital infrastructure of molecular mechanics and dynamics force fields. In order to facilitate studies of a variety of atomic associations, for example those of bioinorganic and organometallic complexes, we have developed a new force field using general rules for estimating force field parameters based on simple relations. This set of fundamental parameters is based only on the element, its hybridization, and its connectivity. We refer to this new force field as a universal force field (UFF).[22]

The parameters used to develop the first-generation UFF force field include a set of hybridization-dependent atomic bond radii, a set of hybridization angles, van der Waals parameters, torsional and inversion barriers, and a set of effective nuclear charges. The elements in the universal force field periodic table are the atom types: atoms of the same type may only be similar chemically and physically, yet as is the norm, they are treated identically in the force field. As reported,[22] UFF has 126 atom types. A five-character mnemonic label is used to describe the atom types. The first two characters correspond to the chemical symbol; an underscore appears in the second column if the symbol has one letter (e.g.: N_ is nitrogen; Rh is rhodium). The third column describes the hybridization or geometry: 1 = linear, 2 = trigonal, R = resonant, 3 = tetrahedral, 4 = square planar, 5 = trigonal bipyramidal, 6 = octahedral. Thus N_3 is tetrahedral nitrogen while Rh6 is octahedral rhodium. The fourth and fifth columns are used as indicators of alternate parameters such as formal oxidation state: Rh6+3 indicates an octahedral rhodium formally in the +3 oxidation state, e.g. $Rh(NH_3)_6^{3+}$. H_b indicates a bridging hydrogen as in B_2H_6. O_3_z is an oxygen suited for framework oxygens of a zeolite lattice. P_3_q is a tetrahedral four-coordinate phosphorus used to describe organometallic coordinated phosphines, e.g. $(Ph_3P)_2PtCl_2$.

In molecular mechanics the potential energy of an arbitrary geometry for a molecule is written as a superposition of various two-body, three-body, and four-body interactions. The potential energy is expressed as a sum of valence or bonded interactions and nonbonded interactions:

$$E = E_R + E_\theta + E_\phi + E_\omega + E_{vdW} + E_{el}$$

The valence interactions consist of bond stretching (E_R) and angular distortions. Included as angular distortions are bond angle bending (E_θ), dihedral angle torsion (E_ϕ), and inversion terms (E_ω). The nonbonded interactions consist of van der Waals (E_{vdW}) terms and electrostatic (E_{el}) terms.

Bond Stretch. The first-generation UFF describes the bond stretch interaction either as a harmonic oscillator

$$E_R = {}^1/_2 k_{IJ}(r - r_{IJ})^2 \tag{1a}$$

or as the Morse function

$$E_R = D_{IJ}[e^{-\alpha(r-r_{IJ})} - 1]^2 \tag{1b}$$

where k_{IJ} is the force constant in units of (kcal/mol)/Å^2, r_{IJ} is the standard or natural bond length in angstroms, D_{IJ} is the bond dissociation energy (kcal/mol), and

$$\alpha = \left[\frac{k_{IJ}}{2D_{IJ}}\right]^{1/2} \tag{1c}$$

The Morse function is a more accurate description since it implicitly includes anharmonic terms near equilibrium (r_{IJ}) and leads to a finite energy (D_{IJ}) for breaking bonds. As with the Dreiding force field,[19] for calculations using the Morse stretch the dissociation energy (D_{IJ}) is set to $n \times 70$ kcal/mol where n is the bond order between centers I and J. This simplification affects neither bond distances nor force constants. The calculations reported here use the harmonic stretch form (eq 1a). The natural bond length r_{IJ} is assumed to be the sum of atom-type-specific single-bond radii, a bond order correction, and an electronegativity correction:

$$r_{IJ} = r_I + r_J + r_{BO} + r_{EN} \tag{2}$$

The initial observation of, and subsequent understanding of, many important structural effects in chemistry arose by comparing "standard" bond distances (from a summation of covalent radii) with experimental bond distances. These structural-electronic effects include electronegativity, resonance, metal–ligand π bonding, metal–ligand π back-bonding, and the *trans* influence. A force field capable of fully predicting molecular structure must reproduce these effects. In order to account for these effects and to exploit the wealth of literature data expressed in terms of covalent radii and bond orders, a Pauling type[23] bond order correction r_{BO} is used to modify the single-bond radii

$$r_{BO} = -\lambda(r_I + r_J)\ln(n) \tag{3}$$

where the proportionality constant $\lambda = 0.1332$ was determined for the set propane, propene, and propyne simultaneously with

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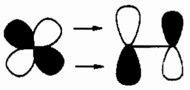
Table I. Dependence of M–C Bond Distance (Å) on M–C Bond Order

	bond order		
compd	1	2	exptl
$Cr(CO)_6$	2.026	1.838	1.918[a]
$Mn(CH_3)(CO)_5$	2.061	1.869	1.860[b]
$Fe_2(CO)_9$	2.027	1.839	1.836[c]
$(CO)_4Fe(R_2Sb_2)$	2.024	1.836	1.801[d]
$(Cp)(C_2H_5)(PPh_3)(CO)Fe^{II}$	2.000	1.815	1.719[e]

[a] Jost, A.; Rees, B. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *B31*, 2649. [b] Hellwege, K.-H. *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Berlin, 1976; Vol. 7, p 325. [c] Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800. [d] Cowley, A. H.; Norman, N. C.; Pakulski, M.; Bricker, D. L.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 8211. [e] Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Organomet. Chem.* **1987**, *320*, C19.

the C_3, C_2, and C_1 radii. The single-bond covalent distance is included in the correction to provide the correct metric throughout the periodic table.

An early discussion of the concept of "carbonyl back-bonding" by Cotton and Wing[24] was based on a comparison of ideal covalent M–C single-bond distances with the substantially shorter experimental bond distances in metal carbonyls. The short experimental bond distances were attributed to increased M–C bond order due to back-bonding from the filled metal dπ orbitals into the empty C–O π^* orbitals (**1**). This effect is amply demonstrated by the structural results for the set of carbonyl complexes studied in this work. A bond order of 2 is used to account for this back-bonding, though a bond order of $1^1/_2$ is more appropriate for carbonyls experiencing a *trans* influence (discussed below). Calculated metal–carbon bond distances using bond orders of 1 and 2 are collected in Table I and compared to the experimental values. It is interesting that experimental C–O distances do not vary substantially from the free CO distance of 1.129 Å for terminal carbonyl ligands, despite the increase in M–C bond order. The forward coordination of the carbon lone pair, which is antibonding with respect to the C–O bond, and back-donation into the π^* orbitals of CO must be nearly canceling, resulting in a net bond order of nearly 3 for the C–O bond. Detailed discussions of the individual structures are provided in section IIIC.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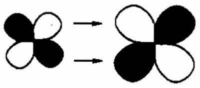
Phosphines also participate in "back-bonding"[25] with filled dπ orbitals at metal centers utilizing either low-lying empty dπ orbitals on phosphorus (**2**) or low-lying σ^* orbitals also centered at phosphorus (**3**). A bond order of 2 is used to account for this back-bonding, though a bond order of $1^1/_2$ is more appropriate for phosphines experiencing a *trans* influence (discussed below).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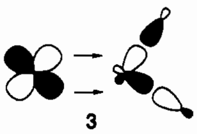
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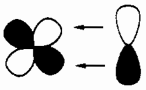
Table II. Dependence of M–P Bond Distance (Å) on M–P Bond Order

	bond order			
	1	1.5	2	exptl
		mer-$Br_3(PMe_2Ph)_3Rh^{III}$		
P1	2.481	2.371	2.288	2.392[a]
P2	2.481	2.364	2.281	2.296
		$(PMe_3)_4Cu^I$ Cation		
P	2.341	2.231	2.154	2.261[b]
		mer-$Br_2(C_2H_5)(PMe_3)_3Ir^{III}$		
P1	2.485	2.368	2.281	2.263[c]
P2	2.490	2.366	2.280	2.344
		$Cl(L_2)(Me)Pt^{II}$		
P1	2.441	2.316	2.229	2.233[d]
P2	2.436	2.315	2.227	2.322
		$(Cp)(C_2H_5)(PPh_3)(CO)Fe^{II}$		
P	2.367	2.246	2.159	2.186[e]

[a] English, R. B. *Cryst. Struct. Commun.* **1979**, *8*, 167. [b] Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208. [c] Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. [d] Payne, N. C.; Stephan, D. W. *J. Organomet. Chem.* **1982**, *228*, 203. [e] Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Organomet. Chem.* **1987**, *320*, C19.

Calculated metal–phosphorus bond distances using bond orders of 1, $1^1/_2$, and 2 are collected in Table II and compared to the experimental values. Detailed discussions of the individual structures are provided in section IIIC.

For high-valent complexes, halides and alkoxides participate in π bonding[25] with empty π orbitals on the metal center (**4**)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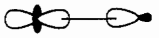
We have not accounted for this effect in the force field. Because of this π bonding and the multiple electronegative substituent effect discussed in the main group paper,[26] these bond distances are systematically overestimated in the UFF force field.

The bonding between high-valent (Lewis acidic) metals and donor ligands such as amines, ethers, or phosphines is dative, and so, as for the main group compounds,[26] a bond order of $^1/_2$ is appropriate here.

The distinction between low-valent (bond order of $1^1/_2$ or 2) and high-valent (bond order $^1/_2$) donor ligands is based on the availability of filled d orbitals to participate in back-bonding. For example, for a low-spin d^6 Cr(0) complex there will be back-bonding but for a high-spin d^3 Cr(III) complex there is only a dative interaction between the metal and the donor ligand.

Amides (NR_2) are capable of bonding to metals either through a purely σ bond (**5**) or through a σ dative bond plus a covalent π bond (**6**). If the former bonding arrangement is present, then a normal covalent bond with a bond order of 1 is correct. If the latter bonding arrangement is operative, then a bond order of $1^1/_2$ or 2 is appropriate. The multiple-bond bonding configuration is also characterized by a planar M–NR_2 fragment. Metal to nitrogen distances for a set of five high-valent multiple-bonded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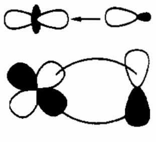
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(25) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 474. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163. Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Y. A. *Coord. Chem. Rev.* **1975**, *17*, 1.

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Table III. Dependence of M–N Bond Distance (Å) on M–N Bond Order for Metalloamides

bond	bond order 1.5	bond order 2	exptl
	$((SiMe_3)_2N)_3Sc^{III}$		
Sc–N	2.035	1.953	2.049[a]
	(2,5-dimethylpyrroyl)$_4$Zr^{IV}		
Zr–N(av)	2.086	2.005	2.079[b]
	$((SiMe_3)_2N)_3(O)Nb^{V}$		
Nb–N(av)	2.025	1.944	2.020[c]
	$(CMe_3N)(Me_2N)_3Ta^{V}$		
Ta–N1	2.079	1.995	1.99[d]

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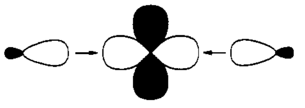
metal amide complexes are collected in Table III with bond orders of 1$^1/_2$ and 2 and compared to experiment. With the exception of the Ta complex, planar or near planar amides are well described with a bond order of 1$^1/_2$.

An additional structural-electronic effect for transition metal complexes is the *trans* influence,[25] which is a measure of the extent to which a ligand weakens the M–L bond for a ligand *trans* to itself. Such bond weakening often results in an increase in bond length for the *trans* ligand. The origin of this effect is thought to be electronic: ligands that are mutually *trans* in square planar and octahedral complexes must compete for a stabilizing interaction with an empty metal σ orbital (**7**) and for stabilizing filled dπ orbitals through back-bonding (**8**). The ligand orbital capable of forming the stronger bond interacts with the metal orbital preferentially, causing the ligand *trans* to this bond to weaken and hence lengthen. Three of the phosphine complexes in Table II demonstrate the *trans* influence.[25] A good example is *mer*-$Br_3(PMe_2Ph)_3Rh(III)$.[27] Here P2 is *trans* to another phosphine and P1 is *trans* to a bromine; the experimental Rh–P2 bond distance is 0.1 Å longer than the Rh–P1 distance because phosphines are stronger *trans*-influencing ligands than halides. In addition, the Rh–Br2 bond (*trans* to a phosphine) is 0.07 Å longer than the Rh–Br1 bond (*trans* to bromine). The present UFF force field does not automatically account for the *trans* influence though fractional bond orders are used to include this effect for phosphines. A bond order of 2 is used for M–P bonds without a significant *trans* influence such as the Rh–P1 bond. A bond order of 1$^1/_2$ is used for M–P bonds where a significant *trans* influence should be present, such as the Rh–P2 bonds. The smaller, though significant, effect on Rh–Br bond lengths is not accounted for in the present force field. Work to systematically include this ground-state structural effect in the force field is being carried out.



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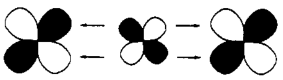

8

The concept of electronegativity,[23] another structural-electronic effect, arose from discrepancies between "standard" bond distances and observed bond distances; as such, an electronegativity correction is an important part of an atom-based force field. The electronegativity correction r_{EN} of O'Keeffe and Brese[28]

$$r_{EN} = \frac{r_I r_J(\sqrt{\chi_I} - \sqrt{\chi_J})^2}{\chi_I r_I + \chi_J r_J} \tag{4}$$

is used directly with the previously reported GMP electronegativity set.[29]

The bond stretching force constants are atom based and are obtained from a previously reported generalization of Badger's rules.[30]

Angular Distortions: Bend and Torsion. General Fourier expansions (see eq 5) are employed in the universal force field to describe all angular distortions

$$E_\gamma = K\sum_{n=0}^{m} C_n \cos(n\gamma) \tag{5}$$

because the expansions can be constructed (1) to have derivatives that are singularity free, (2) to have the appropriate distortions for the large-amplitude motions found in molecular dynamics simulations, and (3) to permit the C_n coefficients to be straightforwardly chosen to satisfy appropriate, physically justified, boundary conditions.

In UFF, the angle bend term is described with a small cosine Fourier expansion in θ:

$$E_\theta = K_{IJK}\sum_{n=0}^{m} C_n \cos(n\theta) \tag{6}$$

where the coefficients C_n are chosen to satisfy appropriate boundary conditions, including that the function have a minimum at the natural bond angle θ_0.

For linear, trigonal planar, square planar, and octahedral coordination environments, two-term Fourier expansions are used each with an $n = 0$ term C_0 and an $n = 1$, 3, 4, or 4 term, respectively. Thus eq 6 simplifies to eq 7. These terms are

$$E_\theta = \frac{K_{IJK}}{n^2}[1 - \cos(n\theta)] \tag{7}$$

precisely the same terms as are used in the SHAPES force field[18] for these symmetric/periodic coordination environments.

For the general nonlinear case, for example for water, the bend function should have a minimum with $E_\theta = 0$ at $\theta = \theta_0 = 104.5°$, the second derivative at θ_0 equal to the force constant, and a maximum at 180°. This leads to a three-term Fourier expansion (for the general nonlinear case)

$$E_\theta = K_{IJK}[C_0 + C_1\cos(\theta) + C_2\cos(2\theta)] \tag{8}$$

with the three expansion coefficients defined in eq 9.

$$C_2 = \frac{1}{4\sin^2(\theta_0)} \qquad C_1 = -4C_2\cos(\theta_0)$$

$$C_0 = C_2[2\cos^2(\theta_0) + 1] \tag{9}$$

The angle bend force constants are generated using a previously reported angular generalization of Badger's rules.[30] Basically, the functional form of the bond stretch is assumed to extent to the I and K atoms of a angle bend for polyatomics.

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The torsional terms for two bonds IJ and KL connected via a common bond JK is described with a small cosine Fourier expansion in ϕ:

$$E_{\phi} = K_{\mathrm{IJKL}}\sum_{n=0}^{m} C_n \cos(n\phi_{\mathrm{IJKL}}) \qquad (10)$$

where K_{IJKL} and the coefficients C_n are determined by the rotational barrier V_{ϕ}, the periodicity of the potential, and the equilibrium angle. For a given central J–K bond all torsions about this bond are considered, with each torsional barrier being divided by the number of torsions present about this J–K bond. The present torsional periodicities and minima are the same as those described in the recently published Dreiding force field[19] with modifications to the torsional barriers V_{ϕ} to account for periodic trends.

van der Waals and Electrostatic Interactions. Nonbonded interactions (van der Waals forces) are included in the universal force field. A Lennard-Jones 6–12 type expression is used:

$$E_{\mathrm{vdW}} = D_{\mathrm{IJ}}\left[-2\left(\frac{x_{\mathrm{IJ}}}{x}\right)^{6} + \left(\frac{x_{\mathrm{IJ}}}{x}\right)^{12}\right] \qquad (11)$$

where D_{IJ} is the well depth in kcal/mol and x_{IJ} is the van der Waals bond length in Å. The 6–12 Lennard-Jones form is chosen over an exponential-6 form (discussed below) for its numerical stability—the exponential-6 form blows up for small internuclear separations. The UFF Lennard-Jones van der Waals parameters were developed within the conceptual framework of the exponential-6 form. This functional form is physically based on a short-range exponential repulsion arising from Pauli orthogonalization and the long-range $1/r^6$ induced dipole–induced dipole dispersive attraction:

$$E_{\mathrm{vdW}} = Ae^{-Bx} - C_6/x^6 \qquad (12)$$

The repulsion exponent B was developed from a consideration of the physical basis of the repulsive term, that is the repulsive interaction between pairs of closed shells. This repulsive interaction to first order is proportional to the overlap between the wave functions squared. The dispersion terms C_6 were taken as proportional to the upper bound numerical Hartree–Fock values presented by Fraga, Karwowski, and Saxena (FKS).[31]

$$C_6 = C_6^{\mathrm{FKS}}/S \qquad (13)$$

The third degree of freedom contained in eq 12 was determined from an empirical relation obtained between literature values of Lennard-Jones distances and the present repulsive exponentials B.

The derived van der Waals parameters can be compared to van der Waals parameters in the literature explicitly fit to crystal properties. The UFF hydrogen radius and well depth of 2.886 Å and 0.044 kcal/mol are nearly the same the Lennard-Jones radius and well depth of 2.9267 Å and 0.0335 kcal/mol fit to polyethylene.[32] The UFF carbon radius and well depth of 3.851 Å and 0.105 kcal/mol are nearly the same as the Lennard-Jones radius and well depth of 3.805 Å and 0.069 kcal/mol fit to graphite.[32]

When included, electrostatic interactions are calculated by

$$E_{\mathrm{el}} = 332.0637\frac{Q_{\mathrm{i}}Q_{\mathrm{j}}}{\epsilon R_{\mathrm{ij}}} \qquad (14)$$

Q_{i} and Q_{j} are charges in electron units, R_{ij} is the distance in angstroms, and ϵ is the dielectric constant. Partial charges are obtained using the recently published *QEq* charge equilibration scheme.[33] As the resulting charges are dependent upon environment, and hence subject to polarization, the correct dielectric constant is 1 for UFF without a distance cutoff.

Previous UFF Results. In the previous papers of the series, we applied the force field to the structures and energetics of organic molecules[34] and to the structures of main group molecules.[26] UFF correctly predicted the structures of unstrained and uncongested hydrocarbons, silanes, alkenes, saturated amines, saturated ethers and phosphines, aromatic systems, and simple unconjugated multiple-bond-containing compounds such as nitriles, ketones, and imines well. Bond angles are usually correct to within 3°, and bond lengths, to within 0.02 Å. The structures of four- and five-membered rings, congested hydrocarbons, and aromatic ethers were only fairly well described with distance errors of up to 0.033 Å and angle errors of up to 10°. The Si–Si bond lengths of disilanes were poorly reproduced with errors of up to 0.1 Å obtained. UFF predicted the structures of secondary halides reasonably well but was only fair at reproducing the C–X bond lengths of tertiary halides (errors up to 0.08 Å). UFF also could not reproduce the carbon–halide bond lengths in vinyl and aromatic halides, with overestimations as large as 0.1 Å. Geometries of N-, O-, and S-heteroaromatics were also not well described by UFF. This force field was also not adequate to predict the structures of conjugated multiple-bond-containing molecules such as oximes and nitro compounds. Here calculated bond length errors were as large as 0.08 Å, and bond angle errors were as large as 5°.

The magnitudes of errors for main group compounds were somewhat larger than those for organic compounds, though X–C bond distances were well reproduced. Bond distance errors for X–Y polar covalent bonds were generally less than 0.05 Å. Comparable bond length errors were observed for hypervalent X–O and X–N bonds (errors on the order of 0.05 Å) and dative bonds (errors as large as 0.04 Å). The errors in bond lengths for bonds involving centers with multiple electronegative substituents bound to an electropositive center were larger, with errors approaching 0.1 Å.

III. Calculations

Minimizations were carried out on a IRIS 4D20 using a Newton–Raphson minimization scheme with a norm of the gradient convergence criteria of 1×10^{-10} (kcal/mol)/Å and were verified as minima by the absence of negative eigenvalues in the force constant matrix. The structures of most of the compounds were minimized by starting with the X-ray structure coordinates obtained from the Cambridge database.[35]

Two additional atom types for cyclopentadienyl pseudoatoms are included with this work to permit studies of high-valent cyclopentadienyl complexes (Cp) and low-valent cyclopentadienyl complexes with significant back-bonding (Cp_B). As before,[36] the radius for Cp of 0.551 Å was obtained from bis(η^5-cyclopentadienyl)dichlorozirconium(IV).[37] The radius for Cp_B of 0.340 Å was obtained from ferrocene.[38] The pseudoatom to ring carbon distance of 1.1733 Å (k = 700 (kcal/mol)/Å^2) was chosen to attain reasonable cyclopentadienyl ring carbon–carbon distances. The Cp–C_R–C_R and C_R–Cp–C_R angle force constants were set to zero. The Cp–C_R–X θ_0's were set to 180° with a force constant of 100 (kcal/mol)/rd^2. The C_R–Cp–X θ_0's were set to 90° with a force constant of 100 (kcal/mol)/rd^2. An alternative formulation of Cp parametrization has appeared.[15]

IV. Structural Results

Before we discuss the structural results for metal-containing complexes, we must provide a working definition of acceptable

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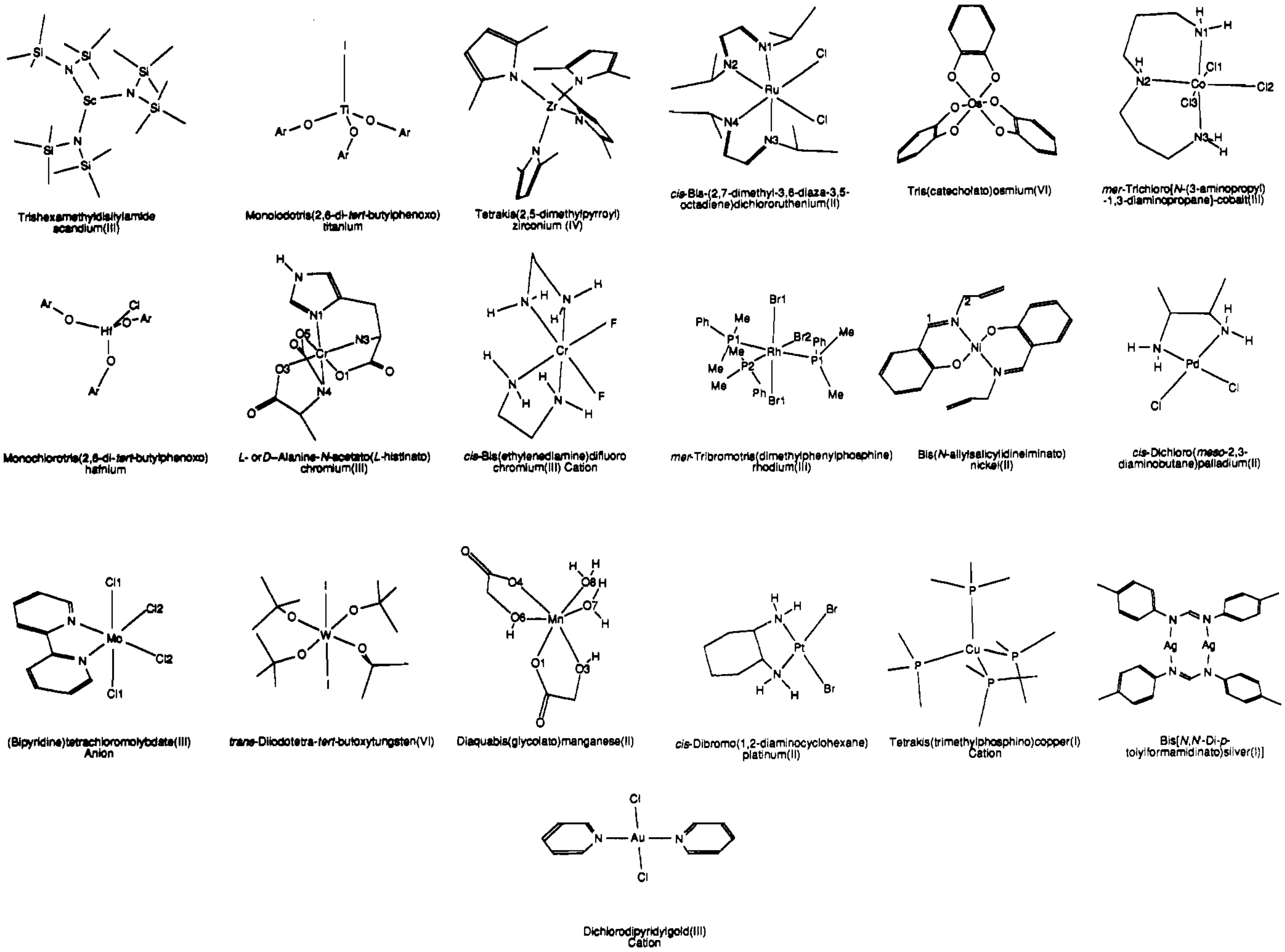

Figure 1. Structural formulas and numbering of atoms for a set of coordination compounds.

error. Comparison with alternative theoretical methodologies will be used to assess the terms "good", "fair", and "poor". For small organic molecules (H_mABH_n), average absolute errors have been reported[39] for an *ab initio* Hartree–Fock wave function with the 6-31G* basis of 0.030 Å for AB single bonds, 0.018 Å for AB multiple bonds, 0.014 Å for AH bonds, and 1.5° for bond angles (smaller basis sets gave correspondingly larger errors and inclusion of electron correlation decreased the error). For metal-containing compounds calculations with an *ab initio* Hartree–Fock wave function and the STO-3G basis gave errors as large as 0.2 Å, though errors of 0.08 Å are more typical. For carbonyl complexes, errors of ±0.2 Å are typical. Little systematic study has been done, but improvement in the basis is reported to lower the error to 0.02 Å.[40] Errors of less than 0.02 Å in bond distances and bond angle errors of less than 2° will still be considered in "good agreement with experiment", as defined for organic compounds. It seems reasonable, however, that larger errors might be acceptable in defining "fair" and "poor" for metal complexes. Bond distance errors of less than 0.08 Å and bond angle errors of less than 5° will be described as being in "fair agreement with experiment"; structures with larger errors will be considered to be in "poor agreement with experiment".

The ability of UFF to correctly reproduce experimental geometries of a variety of metal complexes was investigated. The complexes chosen for study are representative of different rows of the periodic table, diverse compound classes (coordination complexes, compounds with metal–ligand multiple bonds, and organometallic compounds), different oxidation states, and a variety of combinations of atomic associations in general. As discussed below for each individual compound, most of the metric results are in good agreement with experiment, although the force field should be categorized as giving structures in only fair agreement with experiment (bond distance errors of less than 0.08 Å and bond angle errors of less than 5°). The largest errors in UFF geometries are observed for high-valent transition metals participating in metal–ligand π bonding and in complexes with a high degree of electrostatic bonding rather than covalent bonding. Smaller errors, partially compensated for by half-integral bond orders, are seen for compounds with a *trans* influence and organometallic complexes back-bonded with phosphines and carbonyls.

The structural formulas and the numbering of atoms are given in Figures 1–3. Selected structural parameters calculated with UFF, along with the experimental values, are collected in Tables IV–VII.

A. Coordination Complexes. Selected structural parameters for several coordination complexes are collected in Table IV. The structural formulas and the numbering of atoms are given in Figure 1.

Tris[bis(trimethylsilyl)amido]scandium(III).[41] X-ray studies have shown that the molecule is pyramidal with three planar silylamido groups. The calculated N–Sc–N bond angles are only 0.7° smaller than experiment. The calculated silicon–carbon bonds are overestimated by 0.01–0.02 Å. The Sc–N amide bond distances are well described if a bond order of $1^1/_2$ is used; the bonds are only short by 0.014 Å on average.

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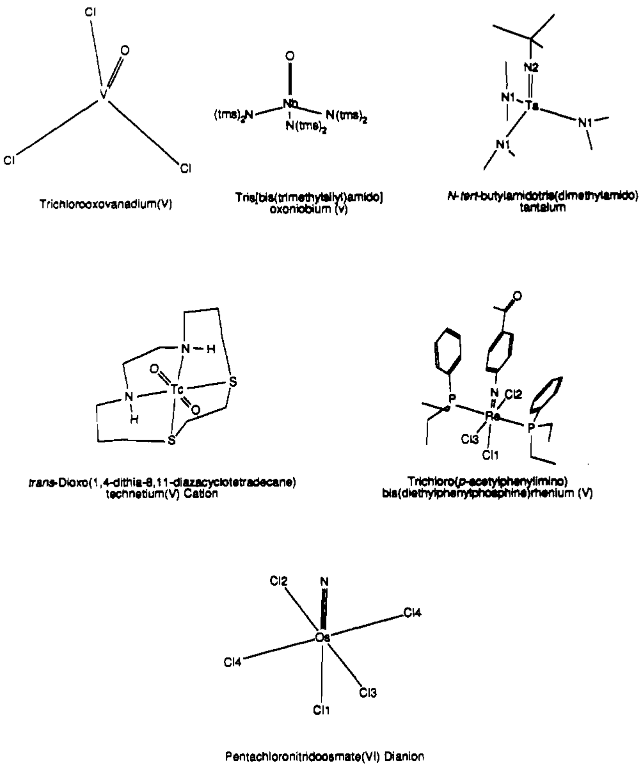


Trichlorooxovanadium(V)

Tris[bis(trimethylsilyl)amido] oxoniobium (v)

N-*tert*-butylamidotris(dimethylamido) tantalum

trans-Dioxo(1,4-dithia-8,11-diazacyclotetradecane) technetium(V) Cation

Trichloro(*p*-acetylphenylimino) bis(diethylphenylphosphine)rhenium (V)

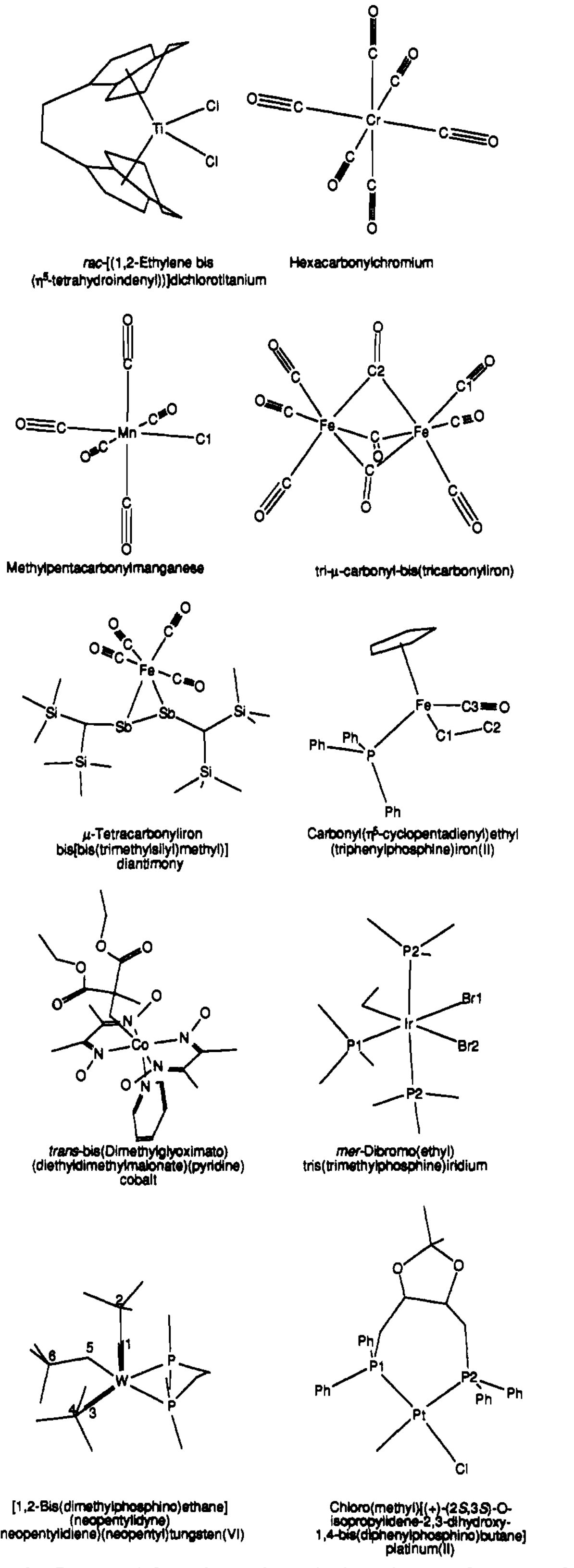
Pentachloronitridoosmate(VI) Dianion

Figure 2. Structural formulas and numbering of atoms for a set of molecules with metal–ligand multiple bonds.

Iodotris(2,6-di-*tert*-butylphenoxo)titanium.[42] The structure of this complex has been analyzed crystallographically, and the titanium was shown to occupy a distorted tetrahedral environment, with short Ti–O distances and large Ti–O–C angles. The distortion is underestimated by UFF: the calculated O–Ti–O bond angles are too small by 6°. The calculated Ti–O distances are 0.08 Å longer than experiment using a Ti–O bond order of 1 and an O_3_z atom type. The Ti–O–C bond angles (157.5° experimentally) are underestimated by 5.5°. The Ti–O bond length and Ti–O–C angle errors are consistent with Ti–O π bonding not being considered in the force field calculation. The calculated Ti–I bond distance is 0.162 Å long, which is consistent with Ti–I π bonding not being considered in the force field and a lack of a multiple electronegative substituent effect in the force field.[26]

Tetrakis(2,5-dimethylpyrroyl)zirconium(IV).[43] X-ray diffraction studies indicate that the ZrN_4 core is tetrahedral. The Zr–N amide bond distances are well described if a bond order of $1^1/_2$ is used (the bonds are only 0.007 Å long on average).

Chlorotris(2,6-di-*tert*-butylphenoxo)hafnium.[44] X-ray diffraction studies of this compound show it has a slightly distorted tetrahedral geometry, with large (155.8°) Hf–O–C angles. The calculated Hf–O distance is 0.145 Å longer than experiment if an O_3_z atom type is used and a Hf–O bond order of 1 is used. The Hf–O–C bond angles, on average, are 1.7° smaller than experiment. As with the titanium alkoxide above, the errors in the calculated Hf–O–C angle and Hf–O bond distance are consistent with Hf–O π bonding not being considered by a universal force field. The calculated Hf–Cl bond distance is 0.197 Å long, which is consistent with Hf–Cl π bonding not being considered in the force field and a lack of a multiple electronegative substituent effect in the force field.[26]



rac-[(1,2-Ethylene bis (η^5-tetrahydroindenyl))]dichlorotitanium

Hexacarbonylchromium

Methylpentacarbonylmanganese

tri-μ-carbonyl-bis(tricarbonyliron)

μ-Tetracarbonyliron bis[bis(trimethylsilyl)methyl)] diantimony

Carbonyl(η^5-cyclopentadienyl)ethyl (triphenylphosphine)iron(II)

trans-bis(Dimethylglyoximato) (diethyldimethylmalonate)(pyridine) cobalt

mer-Dibromo(ethyl) tris(trimethylphosphine)iridium

[1,2-Bis(dimethylphosphino)ethane] (neopentylidyne) (neopentylidiene)(neopentyl)tungsten(VI)

Chloro(methyl)[(+)-(2*S*,3*S*)-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] platinum(II)

Figure 3. Structural formulas and numbering of atoms for a set of organometallic molecules.

(L- or D-Alanine-*N*-acetato)(L-histidinato)chromium(III).[45] X-ray analysis of this classical coordination complex shows the environment around Cr is distorted octahedral. UFF can only partially reproduce the distortion, with bond angle errors of up to 8°. The H-bonding network observed in the experimental structure likely contributes to the distortion from octahedral

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Table IV. Calculated and Experimental Structures of Selected Metal Complexes

	bond (Å)/angle (deg)			bond (Å)/angle (deg)	
	UFF	exptl		UFF	exptl
Tris[bis(trimethylsilyl)amido]scandium(III)					
Si–C(range)	1.858–1.871	1.87–1.89[a]	N–Sc–N	114.3	115.5
Sc–N	2.035	2.049			
Iodotris(2,6-di-*tert*-butylphenoxo)titanium					
Ti–I	2.796	2.634[b]	O–Ti–O(av)	106.5	112.7
Ti–O(av)	1.878	1.798	Ti–O–C(av)	152.0	157.5
I–Ti–O(av)	112.3	106.0			
Tetrakis(2,5-dimethylpyrroyl)zirconium(IV)					
Zr–N(av)	2.086	2.079[c]	N–Zr–N(av)	109.5	109.5
Chlorotris(2,6-di-*tert*-butylphenoxo)hafnium					
Hf–Cl1	2.562	2.365[d]	Hf–O–C(av)	154.1	155.8
Hf–O(av)	2.072	1.927			
(L- or D-(alanine-*N*-acetato)(L-histidinato)chromium(III)					
Cr–O(av)	1.908	1.955[e]	O1–Cr–N3	88.0	80.1
Cr–N1	2.153	2.036	O3–Cr–O5	89.9	93.5
Cr–N3	2.140	2.062	O3–Cr–N4	89.0	81.6
Cr–N4	2.136	2.078	O5–Cr–N4	89.1	83.9
O1–Cr–N1	89.8	89.5	N1–Cr–N3	88.9	87.2
cis-Bis(ethylenediamine)difluorochromium(III) Cation					
Cr–F	1.855	1.883[f]	F–Cr–F	89.7	93.5
Cr–N(av)	2.148	2.087	N–Cr–N	84.7	82.9
N–C(av)	1.437	1.488			
(Bipyridine)tetrachloromolybdate(III) Anion					
Mo–Cl1(av)	2.387	2.431[g]	Cl–Mo–Cl	180.0	172.2
Mo–Cl2(av)	2.392	2.436	Cl2–Mo–Cl2	88.8	94.6
Mo–N(av)	2.274	2.163	N–Mo–N	76.2	75.1
trans-Diiodotetra-*tetra*-butoxytungsten(VI)					
W–I	2.754	2.829[h]	I–W–I	179.5	180.0
W–O	1.890	1.840	O–W–O	90.0	90.0
O–C	1.277	1.448	W–O–C	149.4	160.5
Diaquabis(glycolato)manganese(II)					
Mn–O1	2.095	2.180[i]	Mn–O8	2.119	2.173
Mn–O4	2.097	2.147	O1–Mn–O3	86.4	74.4
Mn–O3	2.099	2.165	O1–Mn–O8	178.1	168.9
Mn–O6	2.101	2.225	O7–Mn–O8	90.1	87.2
Mn–O7	2.122	2.124			
cis-Bis(2,7-dimethyl-3,6-diaza-3,5-octadiene)dichlororuthenium(II)					
Ru–Cl(av)	2.416	2.422[j]	Ru–N4	2.013	2.048
Ru–N1	2.019	2.054	Cl–Ru–Cl	91.1	92.0
Ru–N2	2.015	2.000	N1–Ru–N2	82.5	78.4
Ru–N3	2.034	2.051	N3–Ru–N4	82.6	77.5
mer-Trichloro[*N*-(3-aminopropyl)-1,3-diaminopropane]cobalt(III)					
Co–Cl1	2.231	2.243[l]	Co–N3	1.965	1.976
Co–Cl2	2.231	2.309	Cl1–Co–Cl3	176.9	177.4
Co–Cl3	2.238	2.277	Cl1–Co–Cl2	88.7	91.2
Co–N1	1.968	1.967	N1–Co–N2	90.4	93.1
Co–N2	2.020	2.009	N2–Co–N3	96.2	96.8
Tribromotris(dimethylphenylphosphine)rhodium(III)					
Rh–P1(av)	2.332	2.392[m]	P2–Rh–Br2	177.2	174.1
Rh–P2	2.234	2.296	P1–Rh–P1	174.2	166.8
Rh–Br1(av)	2.464	2.498	Br1–Rh–Br1	175.4	177.6
Rh–Br2	2.465	2.568			
Bis(*N*-allylsalicylidineaminato)nickel(II)					
Ni–O	1.805	1.844[n]	N–Ni–O(intra)	90.9	93.0
Ni–N	1.842	1.905	N–Ni–O(inter)	89.1	87.1
O–C	1.322	1.311	N–Ni–N	180.0	180.0
N–C1	1.346	1.323	O–Ni–O	180.0	180.0
N–C2	1.463	1.505			
cis-Dichloro(*meso*-2,3-diaminobutane)palladium(II)					
Pd–Cl(av)	2.314	2.317[o]	Cl–Pd–Cl	89.8	95.3
Pd–N(av)	2.008	2.029	N–Pd–N	88.1	83.6
N–C(av)	1.466	1.506			
cis-Dibromo(1,2-diaminocyclohexane)platinum(II)					
Pt–Br(av)	2.519	2.434[p]	Br–Pt–Br	89.9	95.61
Pt–N(av)	2.040	2.06	N–Pt–N	87.4	83.5
Tetrakis(trimethylphosphine)copper(II) Cation					
Cu–P(av)	2.231	2.261[q]	P–Cu–P(av)	109.5	109.5

Table IV (Continued)

	bond (Å)/angle (deg)			bond (Å)/angle (deg)	
	UFF	exptl		UFF	exptl
		Bis[(*N,N'*-di-*p*-tolylformamidinato)silver(I)]			
Ag–Ag	2.842	2.705[r]	N–Ag–N(av)	168.1	168.8
Ag–N(av)	2.072	2.105	N–C–N(av)	123.5	124.9
N–C(av)	1.376	1.300			
		Dichloropyridylgold(III) Cation			
Au–Cl(av)	2.263	2.274[s]	Cl–Au–N(av)	90.0	90.0
Au–N(av)	1.947	1.971			

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Table V. Experimental and Calculated Structures for Tris(ethylenediamine)cobalt(III)

	exptl[a]	exptl σ	UFF	calc[b]	calc[c]	calc[d]	calc[e]
Co–N, Å	1.969	0.022	1.940	2.018	1.98	1.973	1.965
C–N, Å	1.489	0.038	1.460	1.475	1.48		1.49
C–C, Å	1.500	0.035	1.520	1.541	1.52		1.52
N–Co–N(intraring), deg	85.37	1.3	88.85	86.6	86.5		88.0
N–Co–N(trans), deg	174.72	1.3	178.22				

[a] Obtained from a set of 28 X-ray structures from the Cambridge Structural Database[35] with $R < 0.1$. The standard deviations, σ, are reported as discussed previously: Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, P.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1989**, S1. [b] Niketic, S. R.; Rasumssen, K. *Acta Chem. Scand.* **1978**, *A32*, 391. [c] Brubaker, G. R.; Johnson, D. W. *Coord. Chem. Rev.* **1984**, *53*, 1. [d] Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2496. [e] Yoshikawa, Y. *J. Comput. Chem.* **1990**, *11*, 326.

symmetry. This H-bonding effect is not included in the force field. Fair agreement between UFF and experiment is observed for the Cr–ligand distances: the calculated Cr–O bond distances, on average, are 0.047 Å short; the histidine Cr–N distance is 0.117 Å long using a bond order of $^1/_2$ (the distance would be 0.047 Å short using a bond order of 1); and the calculated amino Cr–N distances are 0.078 and 0.058 Å long.

***cis*-Bis(ethylenediamine)difluorochromium(III) Cation.**[46] Structural studies of this cation show that the two fluorine atoms are in *cis* positions. The calculated Cr–F bond distances are 0.028 Å short. The calculated Cr–N amino bond distances are only in fair agreement with experiment; similar errors are observed for the related (L- or D-alanine-*N*-acetato)(L-histidinato)chromium(III) complex (see above). The calculated C–N bond distances are on average 0.016 Å long. The F–Cr–F angle is 3.8° small, and the N–Cr–N angle is 1.8° large.

(Bipyridine)tetrachloromolybdate(III) Anion.[47] The structure has been analyzed crystallographically, and the Mo atom is shown to be surrounded by four Cl ions and a bipyridine ligand in a distorted octahedral arrangement. The bipyridine occupies two *cis*-equatorial sites, and the Cl ions are found in axial and equatorial positions. The UFF geometry is in fair agreement with experiment. The calculated Mo–Cl distances are 0.044 and 0.064 Å short. The calculated Mo–N distances are 0.111 Å long if a bond order of $^1/_2$ is used (and 0.064 Å short if a bond order of 1 is used). The calculated Cl–Mo–Cl *trans* angle is 7.8° too large. The Cl–Mo–Cl *cis* angle is 5.8° too small. The N–Mo–N angle is 1.1° too large.

***trans*-Diiodotetra-*tert*-butoxytungsten(VI).**[48] Structural studies of this complex show the molecule has C_{4h} symmetry: all angles around the tungsten are rigorously 90 or 180°; the W–I distances are equal, and the four W–O distances are equal. The angles at W are accurately described by UFF. The calculated W–O distances are overestimated by 0.05 Å. The W–I distances are underestimated by 0.075 Å. The calculated W–O–C bond angle is 11.1° too small. The errors in calculated W–O–C angle and W–O bond distance are consistent with W–O π bonding not being considered by a universal force field.

Diaquabis(glycolato)manganese(II).[49] X-ray studies have shown that the Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from each glycolate ligand and two water O atoms in *cis* positions. The bonding in this high-spin d^5 compound is likely to be electrostatic rather than covalent. It is thus is not expected to be well described by UFF, which assumes discrete covalent bonds. Indeed, the predicted glycolate Mn–O bond distances range from 0.05 to 0.124 Å short. The water Mn–O distances are 0.002 Å short and 0.054 Å short.

***cis*-Bis(2,7-dimethyl-3,6-diaza-3,5-octadiene)dichlororuthenium(II).**[50] With the exception of the Ru–N distances, the coordination environment calculated by UFF is in good agreement with the experimental X-ray structure. The calculated Ru–Cl distances are 0.006 Å short, on average. The calculated Cl–Ru–Cl angle is 0.9° too small, and the N–Ru–N angles are 4.1 and 5.1° too large. The Ru–N distances range from being 0.034 Å too short to being 0.015 Å too long (using a bond order of 1$^1/_2$). Since ruthenium is a low-spin d^6 ion in this complex, a bond order of 1$^1/_2$ is appropriate due to back-bonding involving the C–N π^* orbitals.[25]

Tris(catecholato)osmium(VI).[51] The molecular structure of this compound has been determined by X-ray crystallography. The coordination geometry is slightly distorted octahedral. Fair agreement with experiment is obtained with a universal force field. The Os–O distances are on average 0.032 Å too short, and the C–O distances are 0.068 Å too long on average.

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Table VI. Calculated and Experimental Structures of Selected Metal Complexes with Metal–Ligand Multiple Bonds

	bond (Å)/angle (deg)			bond (Å)/angle (deg)	
	UFF	exptl		UFF	exptl
Trichlorooxovanadium(V)					
V–Cl	2.339	2.142[a]	Cl–V–Cl	109.5	111.3
O–V	1.647	1.570			
Tris[bis(trimethylsilyl)amido]oxoniobium(V)					
Nb–O	1.699	1.699[b]	O–Nb–N(av)	104.5	101.88
Nb–N(av)	2.025	2.020	N–Nb–N(av)	114.0	115.87
Si–N(av)	1.811	1.760			
(*tert*-Butylimido)tris(dimethylamido))tantalum					
Ta–N1	2.079	1.99[c]	N2–C	1.411	1.42
Ta–N2	1.837	1.77	N1–Ta–N2	109.1	108.0
N1–C	1.455	1.50	N1–Ta–N1	110.3	110.9
Tetrachloro(sulfido)tungsten(VI)					
W–S	2.016	2.086[d]	Cl–W–Cl(*cis*)	90.0	86.5
W–Cl	2.379	2.277	Cl–W–Cl(*trans*)	180.0	151.6
S–W–Cl	90.0	104.2			
trans-Dioxo(1,4-dithia-8,11-diazacyclotetradecane)technetium(V) Cation					
Tc–O(av)	1.664	1.748[e]	O–Tc–O	179.1	176.6
Tc–S(av)	2.503	2.395	N–Tc–N	85.7	82.9
Tc–N(av)	2.136	2.150	S–Tc–S	85.3	84.1
Trichloro[(*p*-acetylphenyl)imido]bis(diethylphenylphosphine)rhenium(V)					
Re–N	1.693	1.690[f]	N–Re–P(av)	89.6	96.1
Re–Cl1	2.330	2.410	N–Re–Cl2	89.6	93.2
Re–Cl2	2.330	2.399	P–Re–Cl1	90.5	83.9
Re–Cl3	2.330	2.433	Cl2–Re–Cl1	90.4	86.8
Re–P(av)	2.449	2.459	Re–N–PHNC	180.0	175.8
Pentachloronitridoosmate(VI) Dianion					
Os–N	1.660	1.614[g]	Os–Cl(2,3,4,5)	2.277	2.362
Os–Cl1	2.277	2.605			

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***mer*-Trichloro[*N*-(3-aminopropyl)-1,3-diaminopropane]cobalt(III).**[52] The structure has been analyzed crystallographically and shows that the triamine chelate is bonded with the primary amino groups *trans*. Overall, the experimental structure is well reproduced by UFF. The calculated Co–N distances are in very good agreement with experiment (errors within 0.011 Å). The calculated axial Co–Cl distances are 0.012 and 0.039 Å too short. The calculated equatorial Co–Cl bond (*trans* to nitrogen) is 0.078 Å too short. The bond angles at Co are well reproduced by the force field.

Tris(ethylenediamine)cobalt(III) Trication.[53] The molecular structure of this complex has been determined by X-ray crystallography in a number of crystal environments. In addition, a number of molecular mechanics force fields have been developed to reproduce structures of this class of complex (Co–N_6). Because of the special place this molecule holds in transition metal force field literature, we have collected (in Table V) experimental structural data, averaged over 28 structural determinations, the results from UFF, and literature results using four separate force fields developed specifically for Co–N compounds. All of the force fields do a reasonable job of reproducing the average experimental structure. For the universal force field the calculated Co–N distance is 0.03 Å shorter than the average experimental distance. The calculated C–N distance is also 0.03 Å shorter than the average experimental distance. The calculated C–C distance is 0.02 Å longer than the average experimental distance. The intra-ring N–Co–N bond angle is 3.5° larger than the average experimental angle. The *trans* N–Co–N bond angle is also 3.5° larger than the average experimental angle.

***mer*-Tribromotris(dimethylphenylphosphine)rhodium(III).**[27] Structural studies of this complex show the ligands are bound to the Rh atom in an octahedral arrangement. Repulsion between the PMe_2Ph groups (P2–Rh–P2 = 166.8°), a strong *trans* influence acting on the two phosphines (P2) *trans* to each other, and a smaller *trans* influence acting on the bromine (Br2) *trans* to P1 are also evident. The calculated Rh–P1 bond distances are on average 0.060 Å shorter than experiment (bond order $1^{1}/_{2}$). The Rh–P2 bond distance is 0.062 Å short (bond order 2). The Rh–Br1 distances on average are 0.034 Å short. The Rh–Br2 distance is 0.103 Å short—the effect of the *trans* phosphine is not included in the force field. The P1–Rh–P1 angular distortion observed experimentally is reproduced in the calculation, but the angle is underestimated by 7.4°.

Bis(*N*-allylsalicylidineaminato)nickel(II).[54] X-ray studies have shown that this Schiff base complex is nearly planar. The immediate coordination environment at Ni is calculated by UFF to be nearly planar, but significant distortions from planarity are observed in the next nearest neighbors. The calculated Ni–O bond is 0.039 Å short, and the Ni–N bond is 0.063 Å short. The computed C–O distance in the chelate ring is 0.011 Å long; the N–C imine distance is 0.023 Å long; and the N–C amine distance is 0.042 Å short. The intrachelate N–Ni–O bond angle is 2.1° small, and the interchelate angle is 2° too large. The C, N, and O atoms of the salicylideneaminato ligands are described with resonating atom types and internal bond orders of $1^{1}/_{2}$. The bonds to Ni use bond order 1.

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(53) The average experimental structural data for tris(ethylenediamine)cobalt(III) were obtained from a set of 28 X-ray structures for the Cambridge Structural Database[25] with $R < 0.1$: BESFAG, BIRSUO, COCRCL, COCREN, COENCH, COENCL, COENSI, COENTC, COENTD10, COTENC, ENCCUC10, ENCOCD, ENCOCT, ENCOCT01, ENCOIH, ENCOPB, ENCOPB01, ENCOPC, ENCOPN, ENCOSN, ENICON, GAPHUA, CELJIQ, GINLUK, GINMAR, SAYKUY, TENCON, ZZZAZY10.

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Table VII. Calculated and Experimental Structures of Selected Organometallic Complexes

	bond (Å)/angle (deg)			bond (Å)/angle (deg)	
	UFF	exptl		UFF	exptl
rac-[1,2-Ethylenebis(η^5-tetrahydroindenyl)]dichlorotitanium					
Ti–C(av)	2.461	2.414[a]	Ti–Cl(av)	2.364	2.348
Hexacarbonylchromium					
Cr–C(av)	1.838	1.918[b]	C–O(av)	1.128	1.141
Methylpentacarbonylmanganese					
Mn–C1	2.131	2.185[c]	Mn–C(O)	1.869	1.860
Tris(μ-carbonyl)bis(tricarbonyliron)					
Fe–Fe	2.592	2.523[d]	Cl–O(av)	1.128	1.126
Fe–Cl(av)	1.839	1.836	C2–O(av)	1.220	1.160
(μ-Tetracarbonyliron)bis[bis(trimethylsilyl)methyl]diantimony					
Sb–Sb	2.858	2.774[e]	Fe–Sb–C(av)	101.4	107.5
Sb–Fe(av)	2.751	2.715	Sb–Fe–Sb	62.6	61.5
Fe–CO(av)	1.836	1.801	C–Sb–Sb–C	158.8	153.0
Carbonyl(η^5-cyclopentadienyl)ethyl(triphenylphosphine)iron(II)					
Fe–C1	2.064	2.065[f]	Fe–P	2.246	2.186
Fe–C_{Cp}(av)	2.213	2.115	C3–O	1.128	1.163
Fe–C3	1.815	1.719			
trans-Bis(dimethylglyoxaimato)(diethyl dimethylmalonate)(pyridine)cobalt					
Co–N_{eq}(av)	1.930	1.887[g]	Co–C	2.070	2.047
Co–N(Pyr)	1.956	2.075	N_{eq}–Co–N_{eq}(av)	84.1	81.1
[1,2-Bis(dimethylphosphino)ethane](neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI)					
W–C1	1.814	1.785[h]	W–C5–C6	123.6	124.5
W–C3	1.969	1.942	P–W–P	81.6	75.5
W–C5	2.208	2.258	C1–W–C3	100.6	108.7
W–C1–C2	175.1	175.3	C1–W–C5	88.4	108.8
W–C3–C4	133.5	150.4			
mer-Dibromo(ethyl)tris(trimethylphosphine)iridium					
Ir–Br1	2.560	2.584[i]	Ir–C	2.172	2.123
Ir–Br2	2.540	2.636	C–C	1.521	1.501
Ir–P1	2.277	2.263	Ir–C–C	114.4	121.3
Ir–P2	2.368	2.344			
Chloro(methyl)[(+)-(2*S*,3*S*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]platinum(II)					
Pt–C	2.132	2.17[j]	Cl–Pt–C	87.2	82.0
Pt–Cl	2.365	2.323	P1–Pt–P2	95.0	98.7
Pt–P1	2.226	2.233	P2–Pt–C	174.8	168.4
Pt–P2	2.317	2.322	P1–Pt–Cl	175.8	173.6

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***cis*-Dichloro(*meso*-2,3-diaminobutane)palladium(II).**[55] Structural studies of this complex show square planar coordination. Two chlorine atoms are in *cis* positions, and the diamino ligand occupies two *cis* positions. The calculated results are in good to fair agreement with the experimental structure. The calculated Pd–Cl distances are only 0.003 Å too small. The Pd–N distances are 0.021 Å too small. The N–C distances 0.040 Å too short. The small experimental angular distortion away from strict square planarity is underestimated by approximately 5° with the UFF force field.

***cis*-Dibromo(1,2-diaminocyclohexane)platinum(II).**[56] The structure of this complex has been analyzed crystallographically and shows square planar coordination. Two bromine atoms are in *cis* positions, and the diamino ligand occupies two *cis* positions. The structure calculated by UFF is in good to fair agreement with the experimental result. The Pt–Br distances, on average, are 0.085 Å too long. The Pt–N distances are 0.02 Å too short. The small experimental angular distortion away from strict square planarity is underestimated by approximately 6° with the UFF force field.

Tetrakis(trimethylphosphine)copper(I) Cation.[57] Structural analysis shows the molecule is a nearly perfect tetrahedron. The agreement between the force field and experiment is good. The computed Cu–P distances are underestimated by 0.03 Å on average using a Cu–P bond order of $1^1/_2$, and the tetrahedral nature of the complex is well reproduced.

Bis[(*N*,*N'*-Di-*p*-tolylformamidinato)silver(I)].[58] X-ray studies have shown that the central group $Ag_2(NCN)_2$ is essentially planar. The calculated Ag–Ag distance is underestimated by 0.137 Å. The Ag–N distances are 0.033 Å short on average. The resonating C–N bond orders were set to $1^1/_2$. The C–N distances are 0.076 Å long on average. The N–Ag–N bond angle is only 0.7° small. The N–C–N angles are 1.4° small on average.

Dichlorodipyridylgold(III) Cation.[59] Structural studies of this cation show the gold atom surrounded by two Cl atoms and two pyridine molecules in a square planar arrangement. The structure calculated by UFF is in good agreement with the experimental results. The calculated Au–Cl distance is 0.011 Å short on average, and the Au–N distance is 0.024 Å short.

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B. Coordination Complexes with Metal–Ligand Multiple Bonds. Selected geometric results for several metal–ligand multiple-bond complexes are listed in Table VI. The structural formulas and the numbering of atoms are given in Figure 2.

Trichlorooxovanadium(V).[60] The electron gas diffraction structure of this molecule has been determined. The calculated V–O bond distance is 0.077 Å too long even with a bond order of 3. The V–Cl distances are 0.197 Å too long, which is consistent with V–Cl π bonding not being considered in the force field and a lack of a multiple electronegative substituent effect in the force field.[22] The Cl–V–Cl angle is 1.8° too small.

Tris[bis(trimethylsilyl)amido]oxoniobium(V).[61] X-ray studies have shown that the coordination environment of Nb is a distorted tetrahedron, with planar nitrogen atoms. The calculated O–Nb–N angle is 2.6° too large. The calculated N–Nb–N angle is 1.9° too small. The Nb–O bond distance (bond order 3) is well predicted. The calculated Nb–N amide bond distances are 0.005 Å too long (bond order $1^1/_2$), and the calculated Si–N bond distances are 0.051 Å too long.

(*tert*-Butylimido)tris(dimethylamido)tantalum.[62] The structure has been determined by X-ray crystallography and shown to have a tetrahedral symmetry. The metal–imido unit is linear. The calculated Ta–N imide bond is 0.067 Å long with a Ta–N bond order of 3. The calculated Ta–N amide bonds are 0.099 Å long if a bond order of $1^1/_2$ is used. The amide C–N bond distances are 0.045 Å short, and the imide C–N bond distance is 0.009 Å short. The symmetry of the complex is well described by UFF with angular errors of ±1°.

Tetrachlorosulfidotungsten(VI).[63] The structure of this molecule has been determined by gas-phase electron diffraction. It was found to be square pyramidal of C_{4v} symmetry. The calculated W–S distance is 0.07 Å short (bond order 3, S_2 atom type). The calculated W–Cl distances are 0.102 Å long, which is consistent with W–Cl π bonding not being considered in the force field and a lack of a multiple electronegative substituent effect in the force field.[22] The basal distortion of the square pyramid is not included in the force field since an octahedral atom type (W_6+6) was used. The experimental angular distortions are underestimated by up to 30°.

***trans*-Dioxo(1,4-dithia-8,11-diazacyclotetradecane)technetium(V) Cation.**[64] Structural studies of this cation indicate the coordination around technetium can be approximated by a compressed octahedron. The calculated *trans* Tc–O bonds are 0.082 Å short (bond order 2). This error is not unexpected considering that the strong *trans*-influencing character of oxo ligands is not accounted for in the force field. The calculated Tc–S bonds are 0.108 Å long if a bond order of $^1/_2$ is used (and 0.066 Å short if a bond order of 1 is used). The calculated Tc–N amino bonds are 0.014 Å short if a bond order of $^1/_2$ is used (and 0.162 Å short if a bond order of 1 is used). The angles about Tc are up to 2.8° in error.

Trichloro[(*p*-acetylphenyl)imido]bis(diethylphenylphosphine)rhenium(V).[65] X-ray studies have shown that the molecule is distorted from ideal octahedral configurations by a movement of the ligands *cis* to the arylimido group away from the N atom. The Re–N distance is accurately described by UFF using a bond order of 3. The calculated Re–P distances are 0.01 Å short. The Re–Cl distances are poorly described by UFF, being underestimated by up to 0.1 Å.

Pentachloronitridoosmate(VI) Dianion.[66] Structural studies of this dianion show the coordination about the Os atom is distorted octahedral. The Cl atoms *cis* to the nitrido ligand are bent away from the N atom. The Os–Cl distance *trans* to the N atom is considerably longer than the Os–Cl distances *cis* to the N atom. The calculated Os–N triple-bond distance is 0.046 Å long using a bond order of 3. The computed equatorial Os–Cl distances are underestimated by 0.085 Å. The Os–Cl bond *trans* to the nitrido group is underestimated by 0.328 Å. This axial ligand is only weakly coordinated to the complex—it predominantly just fills the sixth coordination site in the octahedron and is associated through crystal packing forces.

C. Organometallic Complexes. Selected structural results for several organometallic complexes are collected in Table VII. The structural formulas and the numbering of atoms are given in Figure 3.

***rac*-[1,2-Ethylenebis(η^5-tetrahydroindenyl)]dichlorotitanium.**[67] The structure for this *ansa* metallocence is fairly well described by the force field. The calculated Ti to η^5 carbon atom distances are long by 0.047 Å, on average. The Ti–Cl distances are long by 0.016 Å, on average.

Hexacarbonylchromium.[68] This molecule has been studied by neutron diffraction and found to be octahedral. The computed Cr–C bond distance is only 0.08 Å short (bond order 2) even though a chromium atom type for Cr(III) is used for this Cr(0) complex. The computed C–O distance is 0.013 Å small (bond order 3).

Methylpentacarbonylmanganese.[69] The Mn–C distance for the metal–methyl bond is 0.054 Å short by UFF, and the Mn–C distances for the equatorial metal–carbonyl bonds are only 0.009 Å long (bond order 2).

Tris(μ-carbonyl)bis(tricarbonyliron).[70] The structure of this dinuclear complex has been determined by X-ray diffraction. The agreement between the experimental and UFF-predicted structures is good to fair. The terminal carbonyl Fe–C distances are overestimated by 0.003 Å (bond order 2). The bridging carbonyl Fe–C distances are overestimated by 0.044 Å. The terminal carbonyl C–O distances are 0.002 Å long, and the bridging carbonyl C–O distances are 0.06 Å long. The Fe–Fe distance is overestimated by 0.069 Å.

(μ-Tetracarbonyliron)bis[bis(trimethylsilyl)methyl]diantimony.[71] The structure of this molecule was determined by X-ray diffraction. It can be viewed as a distilbene π complex η^2-coordinated to a $Fe(CO)_4$ moiety. The geometry around the Fe atom can be viewed as being trigonal bipyramidal with the distilbene occupying a single equatorial site. Nonetheless the structure of this complex is reasonably well described by UFF using an octahedral Fe. The calculated Fe–C distances are 0.035 Å long (bond order 2). The Fe–Sb distance is 0.036 Å long. The calculated Sb–Sb distance is 0.084 Å long, presumably because of some unaccounted for multiple bonding in the Sb–Sb bond. The Fe–Sb–C angle is 6.1° small. The Sb–Fe–Sb angle is 1.1° large. The C2–Sb–Sb–C1 dihedral angle is 5.8° large.

Carbonyl(η^5cyclopentadienyl)ethyl(triphenylphosphine)iron(II).[72] The structure has been determined by X-ray crystallography. The Fe–C alkyl distance is correctly reproduced by UFF (the Fe3+2 radius was selected from this bond). The Fe to η^5

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carbon atom distances are 0.098 Å long on average. The Fe–C carbonyl distance is 0.096 Å long (bond order 2). The Fe–P distance is 0.06 Å long. The carbonyl C–O distance is 0.035 Å short.

***trans*-Bis(Dimethylglyoximato)(diethyl dimethylmalonate)(pyridine)cobalt.**[73] X-ray studies of this cobaloxime have been carried out. The calculated structural parameters are in fair agreement with the experimental results. The calculated glyoximato Co–N distances are 0.043 Å long on average. The calculated pyridine Co–N distance is 0.119 Å short, consistent with a significant *trans* influence from the alkyl group (if a bond order of $^{1}/_{2}$ is used, the calculated pyridine Co–N distance is 0.047 Å long). The Co–C distance is only 0.023 Å long.

***mer*-Dibromoethyltris(trimethylphosphine)iridium.**[74] The *trans* influence is operating in this complex. The computed Ir–Br1 distance is only underestimated by 0.024 Å, but the Ir–Br2 bond distance (*trans* to an alkyl group) is underestimated by 0.096 Å. The calculated Ir–P1 bond distance (*trans* to Br) is 0.014 Å long (bond order 2), and the Ir–P2 bond distance (*trans* to P) is only 0.024 Å long (bond order $1^{1}/_{2}$). The calculated C–C bond distance of the ethyl group is 0.02 Å long, and the Ir–C–C bond angle is 6.9° smaller than experiment.

[1,2-Bis(dimethylphosphino)ethane](neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI).[75] X-ray studies have shown that the coordination environment of the W is distorted square pyramidal. The experimental distortion of the square pyramid plane away from tungsten is not accounted for in the present force field because an octahedral atom type is used for tungsten (W_6+6). Large angular errors at W result: the UFF C1–W–C3 angle is too small by 8°, and the C1–W–C5 angle is too small by 20°. The experimental M–C single-, double-, and triple-bond distances are well reproduced for this unique complex. This is a remarkable result considering that a single covalent W radius is used in the UFF force field—the bond order correction can correctly account for the change in bond distance as a function of bond order. The W–C single bond is 0.05 Å short, the W–C double bond is 0.027 Å long, and the W–C triple bond is 0.029 Å long. The electronic effect at metal alkylidene centers whereby the M–C–C angle is enlarged as a result of a electronic donation from the α-C–H bond to the metal center is not accounted for in the UFF force field, and hence the W–C6–C7 bond angle is 17° too small. The W–C–C angles for the W–C single and triple bonds are in error by less than 1°.

Chloro(methyl)[(+)-(2*S*,3*S*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]platinum(II).[76] The structure of this complex has been analyzed crystallographically, and the coordination of the platinum has been shown to be essentially square planar. The two Pt–P bond distances are significantly different, consistent with *trans* influence arguments. The Pt–P1 (*trans* to Cl) is 0.007 Å short (bond order 2). The computed Pt–P2 (*trans* to carbon) distance is only 0.005 Å short (bond order $1^{1}/_{2}$). The calculated Pt–C and Pt–Cl distances are only 0.04 Å short and long, respectively.

IV. Conclusions

The universal force field, a general force field developed from first principles, was applied to metallo inorganic complexes. The magnitudes of errors in the structures of metal-containing compounds are somewhat larger than those for organic compounds but comparable to the errors for main group compounds. Experimental M–C bond distances are well reproduced by UFF, as are the M–C double- and triple-bond distances in the (alkylidene)(alkylidyne)tungsten complex. This result gives strong support for the bond order correction scheme employed in UFF. For M–Y polar covalent bonds the bond distance errors are generally less than 0.05 Å. The largest errors are observed for high-valent transition metals participating in metal–ligand π bonding (errors of up to 0.15 Å in M–X distances) and in complexes with a high degree of electrostatic bonding rather than covalent bonding. Smaller errors are seen for compounds subject to a *trans* influence and for organometallic complexes back-bonded to phosphines and carbonyls.

The addition of two covalent radii to give a bond length provides an effective construct for highlighting structural-electronic effects. For example, the well-known concepts of electronegativity and carbonyl back-bonding both arose from discrepancies between "standard" bond distances and observed bond distances. Similarly, this construct can give clues for evolving the next generation of the universal force field. Structural-electronic effects underlined by UFF are transition metal back-bonding to phosphines and carbonyls, the *trans* influence, and high-valent metal–ligand π bonding.

A general and intuitively satisfying way to account for back-bonding in phosphines and carbonyls with multiple M–C or M–P bond orders was presented. We have not developed a systematic way to represent the *trans* influence, but use of half-integer bond orders is remarkably effective for describing the *trans* influence in metal phosphines; a similar approach might be successfully applied to other *trans*-influencing ligands. An accurate description of high-valent metal–ligand π bonding was not given in this work, although using multiple bond orders is clearly a place to begin. Work on the development of the next generation of UFF and its application to catalytic and bioinorganic systems is continuing in these laboratories.

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