Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds. 3. STO-3G Basis Sets for First- and Second-Row Transition Metals

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STO-3G minimal basis sets for first- and second-row transition metals have been formulated and applied to the calculation of equilibrium geometries for a variety of inorganic systems, metal carbonyls, and organometallic compounds. While the overall level of agreement with experiment is not as good as that previously noted for main-group compounds, most trends and many subtle features in geometries are reproduced.

INTRODUCTION

Over the past two decades *ab initio* molecular orbital theory has been applied to many diverse areas of chemistry. Literally thousands of *ab initio* calculations have been performed on molecules comprising hydrogen and first-row elements. Far fewer calculations have been reported for molecules containing second-row atoms, and fewer still for compounds incorporating heavier elements. In this latter class, the most numerous are computations which involve transition metals.

Among the first basis sets developed for transition metals were minimal Slater-type representations due to Clementi and Davis.[1] Here, exponents were chosen to yield the lowest energy for the ground state of the free atom. In 1968, Gladney and Veillard[2] described a small contracted basis set of Gaussian-type orbitals with which they calculated the electronic structure of NiF_6^{4-}. In the same year, Basch and Ginsberg[3] constructed a contracted Gaussian basis set for Tc and performed an *ab initio* calculation on TcH_9^{2-}. Other Slater or Gaussian minimal basis set calculations include those on permanganate and chromate,[4] $Ni(CO)_4$,[5] $(C_6H_6)_2Cr$, and $C_6H_6Cr(CO)_3$,[6] a multiconfigurational calculation on VH,[7] a study of the binding of O_2 to Co(acacen),[8] and of the electronic structure of dirhodium tetracarboxylate compounds.[9] The most recent minimal basis sets developed for the first- and second-row transition metals are those due to Huzinaga and his co-workers.[10] The metal basis sets utilized in most calculations also incorporate a set of unoccupied (in the ground-state atom) but low-lying p-type orbitals ($4p$ for first-row metals, $5p$ for second-row metals). This extension above a purely minimal representation is necessary to describe the bonding in molecules.

Steady improvements in the efficiency of algorithms for *ab initio* calculations, combined with enormous gains in speed of available computers, have encouraged more elaborate calculations. Indeed, most of the recent *ab initio* calculations of transition metal compounds have been performed using larger-than-minimal basis sets. The smallest of these involve splitting only the d functions on the metal; all other metal orbitals and all ligand orbitals are described by minimal representations. Hillier and Saunders[11] were among the first to use such split-d basis sets in their calculations of the electronic structure of $Ni(CO)_4$ and $Cr(CO)_6$. Coutière, Demuynck, and Veillard[12] used a split-d basis set to calculate the ionization potentials of ferrocene. These authors found that ionization potentials calculated as the difference in energy between the neutral molecule and the ion were in moderate agreement with experiment, while those obtained using Koopman's theorem were in poor accord with the data. A split-d basis set was used in calculations on $Mn(CO)_5X$: X = H, CH_3, Cl, CN.[13] Connor et al.[14] calculated permanganate, vanadate, and chromate. These investigations showed that the supplementary $4p$ orbitals on the

metal tend to compensate for the inadequacies of the minimal basis set, and furthermore that when the valence d-orbital is split, the participation of the $4p$ functions is greatly diminished. Other calculations employing split-d basis sets include those on $Ni(CN)_4^{2-}$ and $CpNiNO$,[15] as well as investigations of the coordination of O_2 to peroxotitaniumporphyrin[16] and cobalt–imine complexes.[17] In some cases, the valence orbitals on the ligands were also split. For example, Basch[18] has calculated the electronic structure of the Ag^+–ethylene complex using a split-d basis set in which the valence p orbitals on carbon were also split. In the case of permanganate, splitting of the oxygen $2p$ orbitals, in addition to the manganese d orbitals, caused a marked decrease in the population of the manganese $4p$ orbitals.[19] This is consistent with an analysis of the photoelectron spectrum of the compound, which suggests that the $4p$ orbitals on manganese are not significantly involved in the bonding to the oxygen ligands.[14]

Still larger basis sets have been developed for the study of transition metal compounds. The most widely employed are those of Roos, Veillard, and Vinot[20] and of Wachters.[21] The two basis sets proposed by Roos et al.[20] consist of (a) $12s$-, $6p$-, and $4d$-type Gaussians and (b) $9s$-, $5p$-, and $3d$-type Gaussians. Many contractions of these basis sets have been used (with or without supplementation and reoptimization) in calculations on a variety of transition metal compounds.[22] Three different contractions of the Wachters basis set (from $14s$, $9p$, and $5d$ primitives to $8s$, $4p$, and $2d$ orbitals) have also been widely employed.[23] In most cases, these were augmented with two additional p-type orbitals, and frequently with two additional d functions, and were then reoptimized. A variety of other calculations with large basis sets have also been performed.[24]

In none of the aforementioned studies was a full geometry optimization undertaken. Efforts in this direction, however, have been made in recent years. Zielger and Rauk[25] optimized the carbon–metal distances in M–ethylene systems; M = Cu^+, Ag^+, Au^+, using a split-valence basis set on the metal, and found good agreement with the crystal structure data. These same investigators performed partial geometry optimizations on $Ni(CO)_3$—L; L = CO, N_2, CS, PF_3, CH_3CN using a split-valence basis set with a triple-split d shell on Ni, and triple-split valence on H, C, N, O, F, S, and P, and with a set of d orbitals further supplementing the sulfur and phosphorus basis sets.[26] The calculated M—L bond distances for L = CO

and PF_3 were found to be in excellent accord with experimental values. Kitaura, Sakaki, and Morokuma[27] optimized the Ni—C and C—C bond lengths in $Ni(PH_3)_2C_2H_4$ and $Ni(PH_3)_2C_2H_2$ using a modified version of the Roos basis set for Ni and the split-valence 4-31G basis set for the ligands. The reported bond lengths are in good agreement both with experiment, and for the ethylene complex, with the results of a previous *ab initio* calculation where a slightly smaller basis set was used for the ligands.[28] A nearly complete geometry optimization (C—H bond lengths were fixed) on $Ni(C_4H_4)$ was performed recently by Pitzer, Goddard, and Schaefer.[29] Their basis set was formed by augmenting the Wachters representation for Ni with an additional set of diffuse d functions and then reoptimizing. The calculated Ni–ring distance compares well with that from the crystal structure of $Cl_2Ni(C_4Me_4)$. Using a large multiply split-valence basis set, Lüthi et al.[30] obtained a ring–Fe distance in ferrocene some 0.24 Å longer than the experimental value.

Calculations which utilize effective core potentials (pseudopotentials) have received considerable attention in recent years. As inner-shell electrons are not explicitly considered, calculations on heavy elements with large and flexible valence basis sets are possible. Examples of transition-metal-containing species which have been considered to date include Ni_2, NiCO, Cu_2, Au_2^+, Au_2, $HgCl_2$, AuCl, and PtH.[31] Topiol, Moskowitz, and Melius[32] have recently tabulated pseudopotentials for the first-row transition metals.

While a great amount of effort has been expended in this area, it clearly can be seen that consistency in the choice of basis sets used in *ab initio* studies of transition metal compounds is certainly lacking. The prevailing belief, that adequate descriptions of the bonding in these compounds cannot be achieved through the use of minimal basis sets, stems from only a relatively few comparisons. Moreover, no critical evaluation of the utility of minimal basis sets for geometry optimization has yet been presented in the literature.

The STO-3G minimal basis set has been widely and successfully used for over a decade for calculations on molecules containing first- and second-row elements.[33] It has recently been extended to include third-[34] and fourth-row[35] main-group elements. Early indications suggest that here too it is moderately successful as a tool for the description of geometry. Here, we describe the development of STO-3G basis sets for first- and sec-

ond-row transition metals, and seek to assess critically their performance as a means for the calculation of equilibrium geometry.

METHODS

All atomic and molecular calculations have been performed using the Gaussian 83 senes of computer program.[36]

STO-3G minimal basis sets for first- and second-row transition metals have been constructed in a manner analogous to previous developments.[33–35] Basis sets for the elements Sc–Zn comprise 18 atomic orbitals,

$1s$

$2s$, $2p_x$, $2p_y$, $2p_z$

$3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{3zz\text{-}rr}$, $3d_{xx\text{-}yy}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$

$4s$, $4p_x$, $4p_y$, $4p_z$

those for Y–Cd 27 atomic orbitals,

$1s$

$2s$, $2p_x$, $2p_y$, $2p_z$

$3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{3zz\text{-}rr}$, $3d_{xx\text{-}yy}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$

$4s$, $4p_x$, $4p_y$, $4p_z$, $4d_{3zz\text{-}rr}$, $4d_{xx\text{-}yy}$, $4d_{xy}$, $4d_{xz}$, $4d_{yz}$

$5s$, $5p_x$, $5p_y$, $5p_z$.

Each Slater-type atomic orbital ϕ_{nl} is replaced by a linear combination of N Gaussians,

$$\phi_{nl}\ (\zeta = 1,\mathbf{r}) = \sum_{k=1}^{N} d_{nl,k} g_l(\alpha_{n,k},\mathbf{r})$$

where the subscripts n and l define the specific atomic orbitals (e.g., ϕ_{1s}) and g_l are normalized Gaussian functions. The Gaussian exponents α and linear expansion coefficients d have been chosen as least-squares fits to Slater orbitals with exponent $\zeta = 1$.

Two features of the Gaussian expansions need to be noted. The first is that Slater $2s$, $3s$, $4s$, and $5s$ functions are written in terms of $1s$ Gaussians; also, $3p$, $4p$, and $5p$ functions are expressed as sums of $2p$ Gaussians, and $4d$ functions in terms of $3d$ Gaussians. Use of Gaussians of lowest possible n quantum number (g_{1s}, g_{2p}, and g_{3d}) greatly

Table I. Optimum atom exponents for STO-3G basis sets.

Atom	ζ_{1s}	$\zeta_{2s}=\zeta_{2p}$	$\zeta_{3s}=\zeta_{3p}$	ζ_{3d}	$\zeta_{4s}=\zeta_{4p}$	ζ_{4d}	$\zeta_{5s}=\zeta_{5p}$
Sc	20.56	8.22	3.21	2.33	1.16		
Ti	21.54	8.70	3.44	2.68	1.21		
V	22.53	9.18	3.67	2.70	1.25		
Cr	23.52	9.66	3.89	3.23	1.29		
Mn	24.50	10.13	4.11	3.49	1.32		
Fe	25.49	10.61	4.33	3.71	1.36		
Co	26.47	11.09	4.55	3.94	1.40		
Ni	27.46	11.56	4.76	4.16	1.43		
Cu	28.44	12.04	4.98	4.38	1.46		
Zn	29.43	12.52	5.19	4.61	1.50		
Y	38.29	16.72	7.97	7.97	3.29	3.46	1.24
Zr	39.27	17.19	8.21	8.21	3.48	3.00	1.29
Nb	40.26	17.66	8.51	8.51	3.67	2.92	1.35
Mo	41.24	18.12	8.82	8.82	3.87	2.99	1.40
Tc	42.22	18.59	9.14	9.14	4.05	3.12	1.45
Ru	43.21	19.05	9.45	9.45	4.24	3.26	1.49
Rh	44.19	19.51	9.77	9.77	4.41	3.42	1.53
Pd	45.17	19.97	10.09	10.09	4.59	3.58	1.57
Ag	46.15	20.43	10.41	10.41	4.76	3.74	1.60
Cd	47.14	20.88	10.74	10.74	4.93	3.96	1.63

Table II. Optimum valence-shell scale factors for molecules containing first-row transition metals. STO-3G basis sets.

Atom	Molecule[a]	ζ_{3d}	$\zeta_{4s} = \zeta_{4p}$
Sc	Sc(OH)$_3$[b]	1.06	1.53
	ScF$_3$	1.16	1.71
Ti	Ti(C$_5$H$_5$)Cl$_3$[c]	1.69	1.63
	TiCl$_4$	1.84	1.72
	Ti(CH$_3$)$_4$[d]	2.22	1.70
V	VF$_5$	2.21	2.05
	V(C$_5$H$_5$)(CO)$_4$[e]	2.61	1.38
	VOCl$_3$	2.74	1.68
Cr	Cr(CO)$_6$[f]	2.99	2.05
	CrO$_4^{2-}$	3.03	1.60
	Cr(C$_6$H$_6$)$_2$	3.08	1.63
Mn	Mn(CO)$_5$H	3.43	1.56
	MnO$_4^{-}$[g]	3.47	1.75
Fe	Fe(C$_5$H$_5$)$_2$	3.75	1.68
	Fe(CO)$_5$	3.78	1.39
Co	Co(CO)$_4$SiH$_3$	4.08	1.51
	Co(C$_3$H$_5$)(CO)$_3$	4.10	1.55
Ni	Ni(CN)$_4^{2-}$[h]	4.29	1.59
	Ni(CO)$_4$	4.33	1.49
	Ni(C$_5$H$_5$)NO	4.38	1.65
Cu	Cu(CN)$_4^{3-}$[b]	4.53	1.39
	Cu(C$_5$H$_5$)PH$_3$[i]	4.59	1.64
Zn	Zn(CN)$_4^{2-}$[j]	4.79	1.61
	Zn(CH$_3$)$_2$	4.85	1.88
	ZnCl$_2$[k]	5.01	1.93

[a] Unless otherwise noted, experimental data from ref. 38.

[b] A. F. Wells, *Structural Inorganic Chemistry*, Oxford Claredon Press, Oxford, 1975.

[c] P. Ganis and G. Allegra, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, [8] *33*, 304 (1962).

[d] Ti–C bond length assumed equal to the average of bond lengths in (C$_6$H$_5$CH$_2$)$_4$Ti; I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccala, *J. Am. Chem. Soc.*, **93**, 3787 (1971). HCTi and HCH bond angles assumed tetrahedral and CH bond lengths assumed 1.09 Å.

[e] J. B. Wilford, A. Whitla, and H. M. Powell, *J. Organomet. Chem.*, **8**, 495 (1967).

[f] L. E. Sutton, *Sp. Publ. Chem. Soc.*, **1958**, 11.

[g] G.J. Palenik, *Inorg. Chem.*, **6**, 503 (1967).

[h] E. Miltolt and K. J. Watson, *Acta Chem. Scand.*, **23**, 14 (1969).

[i] Cu–ring and Cu–P distances assumed equal to those in C$_5$H$_5$CuPϕ_3; F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, **92**, 2353 (1970); PH$_3$ group assumed to have local C$_{3v}$ symmetry with r(PH) = 1.415 Å and $\angle$(HPCu) = 114.3°.

[j] A. Sequelra and R. Chidambaram, *Acta Crystallogr.*, **20**, 910 (1966).

[k] B. Brehler, *Naturwissenschaften*, **46**, 554 (1959).

simplifies calculation of integrals. A second feature is that expansions of Slater functions of given n quantum number often share Gaussian exponents. For the first-row transition metals, ϕ_{2s} and ϕ_{2p} utilize a single set of exponents, α_{2k}, ϕ_{3s}, ϕ_{3p}, and ϕ_{3d}, a set α_{3k}, ϕ_{4s}, and ϕ_{4p}, and exponents α_{4k}.

Exponents α_{4k} are utilized by ϕ_{4s}, ϕ_{4p}, and ϕ_{4d} for second-row metals, and ϕ_{5s} and ϕ_{5p} share a common set α_{5k}. While these exponent constraints somewhat limit the flexibility of the atomic representations, they also lead to significant gains in the efficiency of two-electron integral evaluation.[37]

Table III. Optimum valence-shell scale factors for molecules containing second-row transition metals. STO-3G basis sets.

Atom	Molecule[a]	ζ_{4d}	$\zeta_{5s} = \zeta_{5p}$
Zr	ZrF_4	4.46	2.16
Nb	NbF_5	2.89	2.29
Mo	MoF_6	2.92	2.40
Ru	$Ru(C_5H_5)_2$	3.21	1.92
	RuO_4	3.30	2.13
Pd	$Pd(CN)_4^{2-}$ [b]	3.55	1.83
	$Pd(CO)_4$ [c]	3.61	1.68
Ag	AgF	3.86	1.91
	$AgCl$	3.87	1.89
Cd	$Cd(CH_3)_2$	3.95	2.09

[a] Unless otherwise noted experimental data for diatomic molecules are from ref. 39, for polyatomic molecules from ref. 38.

[b] S.Jérôme-Lerutte, *Acta Crystallogr. Sect. B*, **27**, 1624 (1971).

[c] Geometry estimated on the basis of analogies between known carbonyls of other first- and second-row metals: T_d symmetry, $r(PdC)$ = 1.86, $r(CO)$ = 1.16.

All Gaussian expansions utilized in this work have been published previously for $N = 2$–6.[33-35]

Least-squares fits to Slater orbitals of arbitrary exponent may be obtained by scaling

$$\phi(\zeta,\mathbf{r}) = \zeta^{3/2}\phi(\zeta = 1,\mathbf{r}).$$

For first-row metals, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p}$, and $\zeta_{4s} = \zeta_{4p}$; for the second row, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$, $\zeta_{4s} = \zeta_{4p}$, and $\zeta_{5s} = \zeta_{5p}$. Optimum scale factors for atoms (subject to the above constraints) have been obtained by optimization of the UHF ground-state energy. The STO-3G expansion (i.e., $N = 3$) has been employed. The results are presented in Table I. Note that the optimizations here were carried out using basis sets which lack the (unoccupied) valence p functions (i.e., $4p$ for Sc–Zn, $5p$ for Y–Cd). Had these been included, the entire valence sp shell would have contracted in order to utilize the unoccupied p functions to augment the description of the underlying orbitals. Such a contraction also occurs and is unavoidable for the valence $4d$ functions on the second-row metals, in particular, for those elements to the left which incorporate relatively few d electrons. Here contraction improves the description of inner-shell $3d$ orbitals. With the exception of these leftmost elements (Y, Zr, and Nb), a near-linear relationship exists between optimum ζ_{3d} for first-row metals and ζ_{4d} for second-row metals. In addition, opti-

mum atomic scale factors ζ_{4s} ($=\zeta_{4p}$) for first-row metals correlate with ζ_{5s} ($= \zeta_{5p}$) values for the analogous second-row elements. These relationships will be employed below to arrive at scale factors suitable for use in molecules.

Table II lists optimum valence-shell ($\zeta_{3d},\zeta_{4s} = \zeta_{4p}$) scale factors for representative molecules containing first-row transition metals; the corresponding values ($\zeta_{4d},\zeta_{5s} = \zeta_{5p}$) for a few compounds incorporating second-row metals are found in Table III. The data for first-row metals were used in conjunction with best-atom exponents (Table I) to arrive at a set of standard scale factors suitable for use in molecular calculations. These are given in Table IV. Standard scale factors for second-row metals could have been arrived at in an analogous manner (i.e., by use of the data in Table III). Such a procedure would, however, lead to unrealistically high ζ values (at least for the metals to the left of the row) due to collapse of valence d and sp functions into the inner shell. The data in Table III support such a contention (e.g., ζ_{4d} and $\zeta_{5s} = \zeta_{5p}$ for ZrF_4). With this in mind, it was decided that a better approach would be to fix the standard scale factors for second-row metals in relation to those for the analogous first-row elements, by reference to the fit for atoms (excluding Y, Zr, and Nb). The values so derived are also presented in Table IV. These scale factors

Table IV. Standard valence-shell scale factors for molecules.

First-Row Metal			Second-Row Metal		
Atom	ζ_{3d}	$\zeta_{4s} = \zeta_{4p}$	Atom	ζ_{4d}	$\zeta_{5s} = \zeta_{5p}$
Sc	1.10	1.60	Y	1.40	1.80
Ti	1.90	1.70	Zr	1.95	1.90
V	2.55	1.70	Nb	2.40	1.90
Cr	3.05	1.75	Mo	2.70	1.95
Mn	3.45	1.65	Tc	3.00	1.85
Fe	3.75	1.55	Ru	3.20	1.75
Co	4.10	1.55	Rh	3.45	1.75
Ni	4.35	1.60	Pd	3.60	1.80
Cu	4.60	1.60	Ag	3.75	1.80
Zn	4.90	1.90	Cd	3.95	2.10

and those for the first transition series are used in all calculations which follow. Total atomic energies corresponding to STO-3G basis sets with standard scale factors are presented in Table V.

As expected, STO-3G orbital energies for transition metal atoms deviate significantly from near Hartree–Fock values.[40] For first-row metals, valence 4s orbital energies differ, in the mean, by 12% from Hartree–Fock values; a much larger average deviation of 63% is found for valence 3d orbital energies. Similar behavior has been noted previously by Tatewaki, Sakai, and Huzinaga[10b] for single-zeta metal basis sets.

PERFORMANCE OF STO-3G BASIS SETS

STO-3G basis sets have been used widely to calculate equilibrium geometries; literally hun-

Table V. Total atomic energies for first- and second-row transition metals. Standard scale factors.

Atom	E(hartrees)	Atom	E(hartrees)
Sc	-752.04754	Y	-2396.17158
Ti	-839.74311	Zr	-3500.27755
V	-933.13948	Nb	-3712.58292
Cr	-1032.36935	Mo	-3932.56707
Mn	-1137.61678	Tc	-4159.80286
Fe	-1248.69957	Ru	-4394.44955
Co	-1366.04460	Rh	-4636.45041
Ni	-1489.72716	Pd	-4886.08162
Cu	-1619.87789	Ag	-5143.26109
Zn	-1756.70047	Cd	-5408.24867

dreds of comparisons with experimental structures have been made. Because the model is computationally simple, it is broadly applicable, and complete structure optimizations on molecules with five to ten heavy (nonhydrogen) atoms have become commonplace. While the vast majority of calculations performed to data have been for systems comprising first- and/or second-row atoms, STO-3G structures which have been obtained for molecules containing third- and fourth-row main-group elements appear to be of comparable quality. Our attention here focuses on the performance of STO-3G in the calculation of equilibrium structures for molecules containing first- and second-row transition metals.

A. Transition Metal Inorganic Compounds

STO-3G equilibrium structures for a number of inorganic compounds incorporating a first- or second-row transition metal are compared with experimental geometries in Table VI. Highly polar molecules (e.g., CuF and AgF) and molecules with formal multiple bonds (e.g., $VOCl_3$) are poorly described. This parallels behavior previously noted for the analogous main-group systems. Bonds of lesser polarity (e.g., to chlorine instead of fluorine) are better described, although errors in distances are seldom less than 0.03 Å and often approach 0.1 Å. The calculations depict unequal axial and equatorial bond distances in VF_5, but essentially identical lengths in the corresponding niobium compound; recent experimental data for VF_5 concur; the reported bond lengths in NbF_5 repre-

Table VI. Calculated and experimental equilibrium geometries for transition metal inorganic compounds.

Molecule	Point Group	Geometrical Parameter	STO-3G	Expt.[a]
ScF_3	D_{3h}	r(ScF)	1.852	1.91
$TiCl_4$	T_d	r(TiCl)	2.167	2.170
VF_5	D_{3h}	$r(VF_{ax})$	1.648	1.734[b]
		$r(VF_{eq})$	1.616	1.708
$VOCl_3$	C_{3v}	r(VO)	1.465	1.570
		r(VCl)	2.108	2.142
		<(ClVCl)	110.1	111.3
CuF	$C_{\infty v}$	r(CuF)	1.595	1.745
CuCl	$C_{\infty v}$	r(CuCl)	2.071	2.051
$ZrCl_4$	T_d	r(ZrCl)	2.408	2.32
NbF_5	D_{3h}	$r(NbF_{ax})$	1.848	1.88[c]
		$r(NbF_{eq})$	1.847	
AgF	$C_{\infty v}$	r(AgF)	1.767	1.983
AgCl	$C_{\infty v}$	r(AgCl)	2.165	2.281

[a] Except where otherwise noted experimental data for diatomic molecules are from ref. 39, for polyatomic molecules from ref. 38.

[b] K. Hagen, M. M. Gilbert, L. Hedberg, and K. Hedberg, reported at the Ninth Austin Symposium on Molecular Structure, Austin, Texas, March 1982.

[c] Axial and equatorial bond lengths assumed equal.

sent the weighted mean of axial and equatorial distances.

B. Metal Carbonyl Complexes

Calculated STO-3G level equilibrium geometries for a selection of transition metal carbonyls and carbonyl hydrides are compared with experimental structures in Table VII. Only systems comprising first-row metals have been sampled. The theory does not perform well; calculated bond lengths to carbon are usually but not always given as too small [by as much as 0.24 Å in $Ni(CO)_4$]. The theoretical structure for iron pentacarbonyl is disturbing, but not atypical. Experimentally, both axial and equatorial bonds to carbon are essentially identical; on the other hand, the calculations show axial linkages 0.24 Å longer than the measured distances, and show the equatorial bond to

be 0.2 Å shorter. It should be noted that the STO-3G basis set does not reproduce accurately the known (coordinate) bond distances in borane–carbonyl complexes.[41] The STO-3G BC bond length in BH_3CO is 0.09 Å greater than the experimental value; that in BF_3CO is 0.05 Å less than the measured length.

C. Transition Metal Organometallics

Table VIII compares STO-3G and experimental equilibrium structures for a number of simple organometallics. Only mononuclear systems have been considered, and only those described in terms of singlet electronic ground states. Compounds incorporating both first- and second-row metals are represented.

The simple theory describes certain aspects of

Table VII. Calculated and experimental equilibrium geometries for transition metal carbonyls and carbonyl hydrides.

Molecule	Point Group	Geometrical Parameter	STO-3G	Expt.[a]
$Cr(CO)_6$	O_h	$r(CrC)$	1.789	1.92 b
		$r(CO)$	1.167	1.16
$HMn(CO)_5$	C_{4v}	$r(MnC_{ax})$	1.732	1.823
		$r(MnC_{eq})$	1.723	1.823
		$r(MnH)$	1.624	1.50
		$r(C_{ax}O_{ax})$	1.162	1.139
		$r(C_{eq}O_{eq})$	1.163	1.139
		$<(C_{eq}MnH)$	72.7	83.6
		$<(MnC_{eq}O_{eq})$	170.9	--
$Fe(CO)_5$	D_{3h}	$r(FeC_{ax})$	2.016	1.824
		$r(FeC_{eq})$	1.643	1.824
		$r(C_{ax}O_{ax})$	1.147	1.145
		$r(C_{eq}O_{eq})$	1.171	1.145
$Ni(CO)_4$	T_d	$r(NiC)$	1.583	1.836[c]
		$r(CO)$	1.162	1.142

[a] Unless otherwise noted experimental data are from ref. 38.
[b] See footnote f of Table II for reference to experimental structure.
[c] L. Heoberg, T. Lijima, and K. Heoberg, *J. Chem. Phys.*, **70**, 3224 (1979).

Table VIII. Calculated and experimental equilibrium geometries for transition metal organometallics.

Molecule	Point Group	Geometrical Parameter	STO-3G	Expt.[a]
$Ti(CH_3)_4$	T_d	$r(TiC)$	2.096	2.14 b
		$r(CH)$	1.085	--
		$<(HCH)$	107.2	--
$Cr(C_6H_6)_2$	D_{6h}	$r(CrC)$	2.095	2.150
		$r(CC)$	1.426	1.423
		$r(CH)$	1.092	1.090
		$<(\alpha)^c$	178.6	175.3
$Fe(C_5H_5)_2$	D_{5h}	$r(FeC)$	2.144	2.064
		$r(CC)$	1.424	1.440
		$r(CH)$	1.076	1.104
		$<(\alpha)^c$	177.2	176.3

Table VIII   *(continued from previous page)*

Molecule	Point Group	Geometrical Parameter	STO-3G	Expt.
$(C_2H_4)Fe(CO)_4$	C_{2v}	$r(FeC_{ax})$	2.078	1.796
		$r(FeC_{eq})$	1.770	1.836
		$r(FeC)$	1.940	2.117
		$r(C_{ax}O_{ax})$	1.144	1.146
		$r(C_{eq}O_{eq})$	1.160	1.146
		$r(CC)$	1.497	1.46
		$r(CH)$	1.078	--
		$<(C_{ax}FeC_{ax})$	171.8	180.0[d]
		$<(C_{eq}FeC_{eq})$	127.4	105.2
		$<(\beta)^e$	137.6	180.0[d]
		$<(HCH)$	109.1	--
$(C_5H_5)NiNO$	C_{5v}	$r(NiC)$	2.081	2.11
		$r(NiN)$	1.424	1.626
		$r(CC)$	1.420	1.43
		$r(NO)$	1.268	1.165
		$r(CH)$	1.078	1.09[d]
		$<(\alpha)^c$	179.5	--
$Zn(CH_3)_2$	D_{3d}	$r(ZnC)$	1.682	1.929
		$r(CH)$	1.083	1.090[f]
		$<(HCH)$	105.6	107.7
$Zr(CH_3)_4$	T_d	$r(ZrC)$	2.369	2.27[g]
		$r(CH)$	1.087	--
		$<(HCH)$	106.8	--
$Ru(C_5H_5)_2$	D_{5h}	$r(RuC)$	2.146	2.196
		$r(CC)$	1.426	1.439
		$r(CH)$	1.079	1.130
		$<(\alpha)^c$	182.3	--
$Cd(CH_3)_2$	D_{3d}	$r(CdC)$	2.159	2.112
		$r(CH)$	1.082	1.090[f]
		$<(HCH)$	107.4	108.4

[a] Unless otherwise noted experimental data are from ref. 38.

[b] Average of four TiC bond distances in tetrabenzyltitanium; I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Am. Chem. Soc.*, **93**, 3787 (1971).

[c] Angle between the CH bond and the plane of the ring. Values less than 180° indicate bending of CH toward the metal.

[d] Assumed.

[e] Angle between bisector of HCH plane and ethylene CC bond.

[f] Assumed; error in HCH angle following depends on validity of assumption.

[g] Average of four ZrC bond distances in tetrabenzylzirconium; G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *J. Chem. Soc., Chem. Commun.*, 677 (1971).

the bonding in these compounds remarkably well. For example the calculated metal-to-carbon distances in all four arene complexes considered (dibenzene chromium, ferrocene, cyclopentadienyl nickel nitrosyl, and rutheneocene) are within 0.08 Å of their respective experimental values. In addition, the geometries of the benzene and cyclopentadienyl rings incorporated into these compounds appear to be portrayed accurately. The measured metal–carbon bond lengths in tetramethyltitanium and tetramethylzirconium also are reproduced adequately by the STO-3G calculations. While the calculated Zn–C bond length in dimethylzinc is 0.25 Å too short, the experimental Cd—C distance in the analogous second-row compound is reproduced well by the STO-3G calculations. The metal–nitrogen distance in cyclopentadienyl nickel nitrosyl is grossly underestimated (by 0.2 Å). The bonding of ethylene to the iron tetracarbonyl fragment is also poorly represented.

CONCLUSION

STO-3G basis sets for first- and second-row transition metals have now been formulated. While they do not appear to provide as uniform an account of molecular equilibrium geometry as the analogous main-group representations, some aspects of bonding, especially of organometallic compounds, are well described. Much further *systematic* work is required, directed at both improvements in basis set and exploration of the limitations of the single-determinant approximation.

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