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Communications

Utility of the Semiempirical INDO/1 Method for the Calculation of the Geometries of Second-Row Transition-Metal Species

In recent years the use of second-row transition metals and their compounds in catalysis and advanced materials has spurred interest (e.g. Y in high-temperature superconductors,[1] Tc radiopharmaceuticals,[2] Mo[3] and Ru[4] oxidation catalysts, Rh[5] hydroformylation catalysts, and the Pd[6] catalyst in the Wacker process). However, the application of quantum chemical methods to transition-metal compounds in general, and the second- and third-row transition metals in particular, has been fraught with difficulties.[7,8] Second-row transition-metal complexes have received less attention due to the greater number of electrons and orbitals.[7,8] It is our aim to show that a semiempirical method such as the INDO/1 method,[9-11] while not specifically parametrized for geometries, can yield important results. As with any method, caution must be exercised not to apply the method to problems that are beyond the level of theory employed, or the model invoked.

Designing a successful semiempirical theory is a reasonably complex endeavor. To date much of our research has been focused on the calculation of optical properties. The efficiency of the INDO model has extended its use to the calculation of molecular geometries,[12] and its successes in this area are remarkable in view of the little attention paid to this property in the parametrization of the basic theory.[13] Previous studies on second-row transition-metal complexes using an INDO-type model have proven fruitful,[14,15] although they have not been applied to the variety of compounds considered here. These methods are somewhat different from the present model, as discussed in detail elsewhere.[11] The basis set chosen for these studies is single-ζ for the 5s and 5p AOs and double-ζ for the 4d. The radial extents of these orbitals are chosen to match overlaps of multiple-ζ functions between the given metal and nitrogen, to within 5%, from a separation of 1–3 Å. The values of β used for this study are given in Table I.

The results of geometry optimizations on model systems are given in Table II. The results are quite good. The average percent error for all species is 4.4% ($N = 48$) or 10 pm (measured by $[\sum(R_{\mathrm{INDO}} - R_e)^2/N]^{1/2}$. N is the number of distinct M–X bonds; e.g., in a trigonal-bipyramidal structure $N = 2$ ($\mathrm{M{-}X_{ax}}$ and $\mathrm{M{-}X_{eq}}$). The average error for each individual transition metal ranges from 2.6% for Ru (3 pm, $N = 4$) and Nb (5 pm, $N = 7$) to 9.7% (22 pm, $N = 4$) for Ag. There is average error of 3.3% for ions ($N = 15$) and 3.7% for metal–oxo diatomics.

There is a 3.3% (10 pm) average error for coordinatively saturated molecules, i.e. coordination number ≥4 about the central metal. For coordinatively saturated molecules errors in the experimentally determined bond lengths are unknown in many cases. For the cases where experimental errors are known, they are relatively small for bonds to larger atoms but significant for smaller atoms. In MoO_2Cl_2 the uncertainty is ±10 and ±3 pm for the Mo–O and Mo–Cl bonds, respectively.[17] Thus, calculated errors may range between 1.8% and 12.4% for the Mo–O bond.

A comparison of INDO/1 and ab initio calculations for experimentally characterized systems is of interest. The average errors for the INDO/1 and ab initio results are 6.5% (10 pm)

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Table I. β Bonding Parameters (eV)[a]

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
$\beta_s = \beta_p$	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0	−1.0
β_d	−14.14	−17.03	−19.81	−21.83	−23.55	−26.29	−27.17	−27.59	−27.94

[a] See refs 9 and 10.

Table II. INDO/1 Geometry Optimization Results

		R_e(calc)			% error	
species[a]	bond	INDO/1	ab initio[b]	R_e(exptl)[c]	INDO/1	ab initio
YO ($^2\Sigma^+$)	Y–O	174		179	−2.8	
YF ($^1\Sigma^+$)	Y–F	189		193	−2.1	
YCl ($^1\Sigma^+$)	Y–Cl	239		240	−0.4	
YH ($^1\Sigma^+$)	Y–H	173	193 (NR)/194(R)	192	−9.9	+0.5/1.0
YH($^3\Delta$)	Y–H	178	201 (NR)		−9.4	
YF$^+$ ($^2\Sigma^+$)	Y–F	187		191 ($^2\Delta$)	−2.0	
ZrO ($^1\Sigma^+$)	Zr–O	166		171	−2.9	
$ZrCl_4$[d] ($^1A_1$)	Zr–Cl	234	244 (STO3G)	232 ± 1	+0.9	+5.2
$ZrCl_4$[d] ($^1A_1$)	Zr–Cl	X	240 (NR)/238 (R)	232 ± 1	X	+3.4/+2.6
$ZrCl_6^{2-}$ ($^1A_{1g}$)	Zr–Cl	249		245	+1.6	
$ZrMe_4$[d] ($^1A_1$)	Zr–C	204	237 (STO3G)	227[e]	−10.1	+4.4
ZrF_7^{3-}[f] (^1A)	Zr–F	212		210	+0.9	
ZrO ($^3\Delta$)	Zr–O	167		178	+6.2	
NbF_7^{2-}[g] ($^1A_1$)	Zr–F	198		197	+0.5	
NbO ($^3\Sigma^+$)	Nb–O	162		168	−3.6	
NbF_5[h] ($^1A_1'$)	Nb–F_{ax}	186	185 (STO3G)	188	−1.1	−1.6
	Nb–F_{eq}	184	185 (STO3G)	188	−2.1	−1.6
$Nb(O_2)_4^{3-}$[i]	Nb–O_{ax}	207		201[j]	+3.0	
	Nb–O_{eq}	209		204[j]	+2.5	
NbN ($^3\Delta$)	Nb–N	160		169	+5.3	
MoH_6 ($^1A_{1g}$)	Mo–H	174	187 (NR)/185 (R)		−7.0/−5.9	
Mo ($^5\pi$)	Mo–O	161	171 (NR)[k]		−5.8	
Mo ($^7\pi$)	Mo–O	192	206 (NR)[k]		−6.8	
MoF_6 ($^1A_{1g}$)	Mo–F	182		183	−0.5	
MoO_2Cl_2[l]	Mo–O	162		175 ± 10	+7.4	
	Mo–Cl	237		228 ± 3	+3.9	
$Mo(O_2)_4^{2-}$[i]	Mo–O_{ax}	197		200[j]	−1.5	
	Mo–O_{eq}	192		197[j]	−2.5	
RuO ($^5\Delta$)	Ru–O	171	174 (NR)[m]		−2.3	
RuO$^+$ ($^4\Delta$)	Ru–O	178	175 (NR)[n]		+1.7	
$RuCp_2$[p] ($^1A_1'$)	Ru–C	224	215 (STO3G)	221	+1.4	−2.7
RuO_4[d] ($^1A_1$)	Ru–O	170.5		170.4	+0.06	
$RhCl_6^{3-}$ ($^1A_{1g}$)	Rh–Cl	253		250	+1.2	
$Rh(NH_3)_5Cl^{2+}$	Rh–Cl	243		240	+1.3	
	Rh–N	214		223[q]	−4.0	
	Rh–N_{trans}	217		223[q]	−2.7	
RhC ($^2\Sigma^+$)	Rh–C	166		161	+3.1	
Rh_2form_4 (D_{4h})	Rh–Rh	257		239[r]	+7.5	
	Rh–O	207		204[r]	−1.5	
PdH ($^2\Sigma^+$)	Pd–H	168		153	+9.8	
PdO ($^1\Sigma^+$)	Pd–O	185	186 (SDCI+Q)[k]		−0.5	
PdO ($^3\pi$)	Pd–O	189	185 (SDCI+Q)[k]		+2.2	
$PdCl_4^{2-}$[s]	Pd–Cl	255		230	+10.9	
PdF_6^{2-} ($^1A_{1g}$)	Pd–F	208		189	+10.1	
AgCl ($^1\Sigma^+$)	Ag–Cl	261	178 (STO3G)	228	+14.5	−21.9
	Ag–Cl	X	242 (NR)/233 (R)	X		+6.1/+2.2
AgF ($^1\Sigma^+$)	Ag–F	221	177 (STO3G)	198	+11.6	−10.6
AgO ($^2\pi$)	Ag–O	209	212 (SCF+CI+Q)[k]	200	+4.5	+6.0
AgH ($^1\Sigma^+$)	Ag–H	175	161–174 (NR)	162	+8.0	−0.6 to 7.4
	Ag–H	X	168–180 (R)	X		+3.7 to 11.1

[a] The symmetry of the lowest energy electronic state, as determined by the INDO/1 method, for a particular multiplicity is given in parenthesis. The symmetry of the molecule is given in those cases in which the choice is not obvious. Diatomics are, of course, $C_{\infty v}$, and six-coordinate molecules are octahedral. [b] NR: nonrelativistic, ab initio calculation, extended basis set R: relativistic, ab initio calculation, extended basis set. STO3G: nonrelativistic, ab initio calculation with the minimal basis set STO-3G as reported in ref 16a. NR and R are from the review of Pyykkö.[16b] [c] Bond lengths given for diatomic and polyatomics are from Huber and Herzberg[17a] and Sutton,[17b] respectively, unless otherwise noted. [d] Tetrahedral geometry, T_d. [e] Estimated by Pietro et al.[16a] from $Zr(CH_2C_6H_5)_4$. [f] Pentagonal bipyramid, D_{5h}. [g] Capped octahedron, C_{3v}. [h] Trigonal Bipyramid, D_{3h}. For NbF_5 Pietro and Hehre[16a] cite equivalent experimental Nb–F bond lengths for both the axial and equatorial F. This must be viewed with some caution, sinc NbF_5 exists as a trimer in the gas phase. Also, there is the possibility of fluxional behavior (see: Hargittai, M. *Coord. Chem. Rev.* **1988**, *91*, 35). [i] Dodecahedral, D_{2d}. [j] See ref 18. [k] See ref 19. [l] C_{2v} [m] See 20a. [n] See ref 20b. [p] Eclipsed Conformation, D_{5h}. [q] Experimental error uncertain. [r] See ref 21. [s] Square planar, D_{4h}.

and 5.6% (15 pm; 10 pm excluding the STO-3G calculation of AgCl), respectively.

An investigation of geometrical isomers in coordinatively saturated systems was performed to see if INDO could reproduce experimental results for the geometry of the global minimum.

$ZrCl_4$ was geometry optimized within the constraints of both T_d (tetrahedral) and D_{4h} (square-planar) symmetry. The D_{4h} local minimum is calculated to be 28.3 kcal mol^{-1} higher in energy than the T_d global minimum, in agreement with experimental[17] and theoretical considerations.[22] For d^8 $PdCl_4^{2-}$, the D_{4h} isomer is lower in energy, in agreement with experiment, than singlet and triplet tetrahedral minima by 176 and 6.3 kcal mol^{-1}, respectively.

In our previous study[23] of η^2-tetraperoxides, $M(O_2)_4^{2-}$, small distortions of each MO_2 fragment from a symmetrical, isosceles triangle geometry were observed, i.e. one M–O bond shorter than the other. INDO/1 calculations were able to reproduce this experimentally observed distortion for $Nb(O_2)_4^{3-}$ and $Mo(O_2)_4^{2-}$.[23]

The five-coordinate complex NbF_5 was optimized within the constraints of D_{3h} (trigonal-pyramidal) and C_{4v} (square-pyramidal) symmetry. These minima are calculated to be within $^1/_2$ kcal mol^{-1} of each other. The specific geometry at each minimum is of interest. For the TBP5 and SQP5 geometries the $Nb{-}F_{ax}$ and $Nb{-}F_{basal}$ bonds, respectively, are calculated to be longer than the $Nb{-}F_{eq}$ and $Nb{-}F_{apical}$ bonds, respectively, in keeping with basic electronic structural arguments.[24]

For seven-coordinate structures NbF_7^{2-} and ZrF_7^{3-}, the different polytopes were compared in two distinct ways. First, the M–F bonds were kept fixed ("frozen") and idealized (in terms of bond angles) seven-coordinate structures assumed. Second, these idealized, frozen structures were allowed to relax, for NbF_7^{2-}, by submitting them to a geometry optimization. Three seven-coordinate polytopes[25] were considered: the pentagonal bipyramid (PBP7), capped octahedron (CO7), and capped trigonal prism (CTP7). These structures are calculated to be close in energy, as expected. For the frozen approximation the PBP7 is favored on the basis of smaller nuclear–nuclear repulsions. For the fully optimized NbF_7^{2-} structures the CO7 was calculated to be the global minimum by 3 kcal mol^{-1} versus the PBP7. The CTP7 relaxes to the PBP7. In the PBP7, NbF_7^{2-}, the $Nb{-}F_{ax}$ bonds are shorter than the $Nb{-}F_{eq}$ bonds, in keeping with previous analyses.[25]

In the geometry optimization of $Rh(NH_3)_5Cl^{2+}$, an interesting result is obtained: $R(\text{RH–Cl}) = 243$ pm, $R(\text{Rh–N}) = 214$ pm, and $R(\text{Rh–N}_{trans}) = 217$ pm. Thus, the INDO/1 geometry optimization correctly describes the well-known "trans" influence;[23] i.e., the bond trans to Cl^- is longer than those which are cis.

Although this work does not represent an exhaustive study of the INDO/1 model for the calculation of geometric quantities for second-row transition-metal species, the results allow several conclusions to be drawn. First, INDO/1 does as good a job in predicting geometries as does minimal basis set ab initio calculations on large, coordinatively saturated molecules. Second, the INDO/1 method in the majority of the cases studied here reproduces the energy ordering of geometric isomers.

It should be emphasized again that no exhaustive or comprehensive investigation has been made of the INDO/1 parameters. That the model works as well as it does with so little effort testifies to the strength of the model. We believe that very useful results can be obtained by this model, but as always, the proper care of interpretation must be exercised.

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Isolation and Characterization of $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$: A Neutral Dihydrogen Complex of Iridium

The nature of metal–hydrogen interactions in iridium polyhydride complexes has been the focus of several recent studies.[1-4] All reported iridium nonclassical, η^2-dihydrogen[2,3] complexes have been cationic while the neutral iridium polyhydride complexes that have been studied appear to be classical hydrides.[1,5] In contrast, we have isolated $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$ (**1**) in which dihydrogen is coordinated to a neutral iridium center. The metal–hydrogen interactions in **1** exhibit dynamic behavior that we have examined both in solution and in the solid state. This dynamic behavior is remarkably different than that which has been observed[2,3] for cationic η^2-hydrogen iridium complexes.

We initially obtained **1** through treatment of THF solutions of $IrCl_3\cdot 3H_2O$ and 2 equiv of $P(i\text{-}Pr)_3$ with 2 equiv of sodium naphthalide under an atmosphere of hydrogen (Scheme I). Filtration of the reaction mixture, followed by removal of the THF solvent, produced an oil from which orange crystals of **1** arose upon standing under an atmosphere of H_2. The crystals were found to contain an equimolar amount of napthalene. The polyhydride complex **1** is stable only in the solid state under an atmosphere of hydrogen and slowly converts to $IrH_2Cl[P(i\text{-}Pr)_3]_2$[6] (**2**), through elimination of H_2 under 1 atm of argon. In solution, **1** was found to establish an equilibrium with **2** through the reversible loss of H_2 (Scheme I).[7] Prompted by these observations, we have discovered that **1** can be prepared more conveniently through the reaction of **2** with H_2 either in solution or the solid state. Thus, a pentane solution of **2** placed under 1 atm of hydrogen and allowed to stand at room temperature gives rise to orange crystals[8] of the less soluble **1** in 70–80% yield.

Scheme I

$$IrCl_3\cdot 3H_2O + 2P(i\text{-}Pr)_3 + 2NaC_{10}H_8 \xrightarrow[\text{THF/25 }^\circ\text{C}]{H_2}$$

$$IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2 \rightleftharpoons IrH_2Cl[P(i\text{-}Pr)_3]_2 + H_2$$

The ^1H NMR spectrum of a sample of **1** in CD_2Cl_2 solution at 22 °C under 1 atm of hydrogen exhibits a broad ($\omega_{1/2} \approx 700$ Hz) singlet at ca. −17 ppm. Reduction of the hydrogen pressure by partial evacuation results in the resonance sharpening and moving up field toward a limiting value of −33.0 ppm, the chemical shift which is observed for the hydride resonance of **2** under an atmosphere of argon at 22 °C. A sample of **1** that was dissolved in CD_2Cl_2, freeze/pump/thaw degassed and allowed to stand under an atmosphere of argon for 12 h was seen to produce a hydride signal identical with that observed for **2** (δ −33.0 ppm, $J_{P-H} = 13$ Hz). Conversely, spectra identical with those of **1** under

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(7) A similar equilibrium has been suggested (Mura, P.; Segre, A.; Sostero, S. *Inorg. Chem.* **1989**, *28*, 2853–2858) as part of the solution behavior of $Ir^{IV}H_2Cl_2[P(i\text{-}Pr)_3]_2$. However, the solution behavior of **1** (see below) does not suggest further equilibria with paramagnetic Ir(IV) species.

(8) ^1H NMR (300 MHz, 20 °C in CD_2Cl_2 under 1 atm H_2): δ 2.36 (m, 6 H), 1.26 (m, 36 H), −17.0 (br s). $^{31}P\{^1H\}$ NMR (122 MHz, 20 °C in CD_2Cl_2 under 1 atm H_2): δ 51 ppm (br s). Anal. Calcd: C, 39.15; H, 8.40; Cl, 6.42. Found: C, 39.94; H, 8.40; Cl, 6.66. IR (KBr in gas cell under H_2): ν_{M-H} 2204 (vw) and 2152 (m) cm^{-1} (deuteride ν_{M-D} 1568 (vw) and 1540 (m) cm^{-1}). As has been the case with previously isolated dihydrogen[2] complexes of iridium, no absorptions assignable to the H–H modes of **1** could be conclusively identified in comparison with the IR spectrum of the HD-substituted complex.

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