Interaction of Dihydrogen with Gold (I) Hydride: Prospects for Matrix-Isolation Studies

Craig A. Bayse*

Department of Chemistry, Michigan Technological University, 1400 Townsend Dr., Houghton, Michigan 49931

Received: October 19, 2000; In Final Form: March 19, 2001

Most discussions have described the AuH_3 molecule as a T-shaped complex. A recent study showed that a nonclassical $Au(\eta^2\text{-}H_2)H$ complex was more stable than the classical AuH_3 "aurane" complex by roughly 30 kcal/mol. The present study shows that the nonclassical isomer is only loosely bound ($\Delta E_{dis} = 13.44$ kcal/mol) vs AuH and dihydrogen, and that the dimerization of AuH_3 units to a Au_2H_6 "diaurane" molecule is exothermic by roughly 20 kcal/mol. Additional data is provided which may prove useful for matrix-isolation experiments.

1. Introduction

An attempt to synthesize the classical AuH_3 "aurane" complex was made by Wiberg and Neumaier in the mid 1960s.[1] They used several common agents to reduce $AuCl_3$ to AuH_3; however, they only obtained gold metal and hydrogen gas. Similarly, gold and alkanes were produced from the decomposition of C_{2v} AuR_3 (R = alkyl) complexes.[2] There was some evidence that complexes of the reducing agents were formed at 150 K (i.e., $Au(AlH_4)_3$), but the systems were not stable enough to isolate. Although previous discussions have described AuH_3 as a T-shaped C_{2v} molecule, a recent study has suggested a dihydrogen complex $Au(\eta^2\text{-}H_2)H$ is more likely.[3] Present day matrix isolation studies may be able to produce AuH_3 complexes because interactions of dihydrogen with CuCl,[4] Pd[5] and alkali metal halides[6] have been observed using these methods. Theoretical studies of on each of these complexes shows that the dihydrogen is strongly bound to CuCl (−20 kcal/mol (CPF))[4] and Pd (−17.5 kcal/mol (DFT/B3LYP)),[5] but weakly bound to alkali metal ions (−1.5−2.1 kcal/mol (MP2)).[6]

The orbitally ranked symmetry analysis model (ORSAM) was introduced for the prediction of geometries of molecular systems (specifically of transition metal polyhydride complexes) through consideration of the electron count of the system and the number and type of ligands.[3] According to this model, d^8 ML_3 systems such as AuH_3 can have one of two "high-symmetry" C_{2v} geometries: a T-shaped structure (C_{2v}) and a Y-shaped structure (C_{2v}'). When $L = H^-$, the angle between the equatorial hydride ligands in the C_{2v}' geometry can become so small that the system should be considered a nonclassical $M(\eta^2\text{-}H_2)H$ complex. This case effectively reduces the metal to d^{10} and results in a linear ML_2 system for purposes of ORSAM analysis.

The two C_{2v} geometries result from pseudo Jahn−Teller distortions from D_{3h}. Analogous distortions have been discussed in the Extended Hückel model for the decomposition of trialkylgold(III) complexes[7] where the C_{2v}' geometry lies at the entrance of the exit channel for decomposition. However, previous discussions of AuH_3 systems[8] have only considered distortions along the b_2 coordinate (C_{2v}), probably because analogous halide and alkyl systems are expected to be T-shaped.[7,9] The ORSAM study demonstrated that systems of AuH_3 stoichiometry have a global minimum at the C_{2v}' $Au(\eta^2\text{-}H_2)H$ geometry roughly 30 kcal/mol lower in energy (MP2) than the classical T-shaped C_{2v} AuH_3 complex. Unfortunately, no experimental data is available for either of these species.

Many recent reviews have shown the successes in applications of theoretical methods to transition metal polyhydrides.[10] In this study, theoretical data is provided which may assist experimentalists who wish to search for AuH_3 isomers. The relative energies of the classical and nonclassical isomers are presented as well as the dissociation energies to H_2 and AuH. Theoretical frequencies are included for comparison to experiment. In addition, since AuX_3 (X = halide) complexes are usually found as dimers or polymers,[11] similar oligomers may occur for AuH_3 as suggested by Schwerdtfeger et al.[8] We examine the formation of the dimer Au_2H_6 dubbed here as 'diaurane' in accordance with Wiberg and Neumeier's nomenclature and in loose analogy to diborane.

2. Theoretical Section

Calculations were performed in four basis sets based upon the Dunning triple-ζ basis for hydrogen[12] and the Ermler-Christiansen gold basis[13] with relativistic effective core potentials (RECPs) using the GAMESS−UK suite of programs.[14]

Basis set I:Au: Ermler−Christiansen RECP (5s6p4d)/[4s4p4d]
H: Dunning (5s1p)/[3s1p] H: p($\zeta = 1.0$)
Basis set II: Basis I + Au: f ($\zeta = 1.1$) (5s6p4d1f)/[4s4p4d1f]
Basis set III: Basis I + Au: d($\zeta = 0.03$), f ($\zeta = 1.2, 0.4$) (5s6p5d2f)/[4s4p5d2f]; H: p ($\zeta = 1.1, 0.33$) (5s2p)/[3s2p]
Basis set IV: Basis III + Au: p($\zeta = 0.016$), d($\zeta = 0.01$), f($\zeta = 0.1$) (5s7p6d3f)/[4s5p6d3f];
H: s($\zeta = 0.25$), d($\zeta = 1.0$) (6s2p1d)/[4s2p1d]

The metal basis sets include the (n+1)s and p orbitals in accordance with studies by Couty and Hall.[15] Cartesian functions were used, thus each d and f function adds an s and p orbital, respectively, to the basis set (i.e., BSII (contracted) for Au could be written as [8s5p4d1f]).

Geometry optimizations of H_2, AuH, AuH_3 and $Au(\eta^2\text{-}H_2)H$ were performed in BSI−BSIII at the HF, MP2, MP3, and CCSD(T) levels. Fletcher−Powell optimization algorithms[16] were used to find the geometries in BSII and BSIII and with the MP3 and CCSD(T) methods. Zero-point energies (ZPE), thermal corrections and entropic corrections were calculated at the MP2 level at 150 K in BSI using the Gaussian 98 package[17] and applied to all calculations at higher levels of theory. Basis

10.1021/jp003853m CCC: $20.00

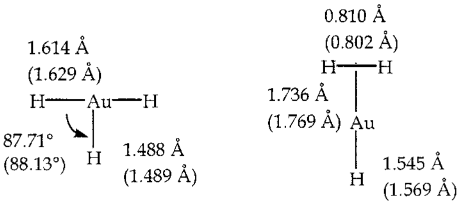


Figure 1. Structural parameters for the C_{2v} and C_{2v}' isomers of AuH_3 at the MP2/BSIII (CCSD(T)/BSIII) levels.

TABLE 1: Relative Energies between T-shaped (C_{2v}) and Y-shaped (C_{2v}') Geometries

method	$\Delta E(C_{2v}'-C_{2v})$ (kcal/mol)	$\Delta E(C_{2v'}-C_{2v})$ (kcal/mol)	$\Delta E(C_{2v'}-C_{2v})$ (kcal/mol)
	BSI	BSII	BSIII
HF//HF	−36.47	−34.28	−34.61
MP2//MP2	−25.37	−25.70	−30.88
MP3//MP2	−31.53	−26.72	
CCSD(T)//MP2	−31.18	−26.09	
MP3//MP3	−25.76	−27.08	−30.14
CCSD(T)//CCSD(T)	−26.30	−26.30	−29.92

set superposition error (BSSE) calculations[18] were performed in BSI−BSIII on the MP2//MP2 and CCSD(T)//CCSD(T) geometries. Optimizations of the Au_2H_6 isomers were performed in Basis I and II at the MP2 level and corrected for ZPE.

Calculations on analogous gold trichlorides were performed at the MP2 level in BSI on gold. The chlorine centers were represented by a triple-ζ Stevens, Basch, and Krauss basis with a Wadt-Hay effective core potential.[19] A d polarization function was added to chlorine ($\zeta = 0.619$).

3. Results and Discussion

Ground State of AuH_3. The relative energies of the two isomers are listed in Table 1. Selected geometric parameters are shown in Figure 1 with additional geometric data listed in the Supporting Information (Table S1). At all levels of theory, the nonclassical C_{2v}' isomer is shown to be the global minimum with relative energies ranging from 25 to 30 kcal/mol. The geometries for both systems are consistent for all basis sets and levels of theory although the addition of the f-type polarization function in BSII leads to a slight contraction of the Au−H_{eq} bond length in the C_{2v} systems which does not appear in the larger BSIII calculations.

The bonding of dihydrogen to a transition metal occurs primarily through the donation of electron density from the σ bonding orbital of H_2 to an empty orbital on the metal center ($M \leftarrow \sigma$). The resulting electron-transfer reduces the dihydrogen bond strength and increases the H−H bond length. A secondary bonding effect can occur through back-donation from a filled metal d_π orbital into the σ^* of H_2 ($M \rightarrow \sigma^*$). If this interaction is strong enough, the dihydrogen unit is cleaved through oxidative addition, effectively oxidizing the metal from M(N) to M(N + 2). In the present case of AuH_3, conditions are not favorable for oxidative addition. The preference of Au(I) versus Au(III) may seem unusual, but the relative energies of the gold system are smaller than those for the comparable AgH_3 system (56 kcal/mol[3]) where the occurrence of a Ag(III) T-shaped C_{2v} complex would be unexpected. Regardless of the oxidation state of the metal, both of these isomers are expected to use 6p orbitals in their bonding. Mulliken population analyses at the HF level in BSI at the MP2/BSI geometry show that the 6p orbital is significantly populated in both geometries: 0.66e in C_{2v} (p_x) and 0.30e in C_{2v}' (p_z). The lower population in the nonclassical C_{2v}' case is consistent with donation of electron density from the H_2 σ orbital to an empty metal orbital.[3] These values are significantly larger than the population of the $6p_z$ orbital in AuH (0.09e) where p orbitals are not essential to bonding. Furthermore, analysis of the MO coefficients indicates that the M−H_2 interaction occurs mostly through the primary $M \leftarrow \sigma$ interaction as very little σ^* character appears in the d_π MO.

TABLE 2: Theoretical and Experimental H−H Stretching Frequencies for AuH_3, $Au(\eta^2\text{-}H_2)H$, $Cu(\eta^2\text{-}H_2)Cl$, PdH_2, and $Pd(\eta^2\text{-}H_2)$

	AuH_3	PdH_2[a]	$Au(\eta^2\text{-}H_2)H$	$Cu(\eta^2-H_2)Cl$[b]	$Pd(\eta^2-H_2)$[a]
ν M(H_2) (cm^{-1})	2160[d]	2199[b,c]	3830[d]	3517[d] (3222)[e]	2935[b,c] (2971)[e]
ν M(HD) (cm^{-1})	1794[d]		3336[d]	3055[d] (2900)[e]	(2334)[e]
ν M(D_2) (cm^{-1})	1534[d]		2719[d]	2489[d] (2395)[e]	(2169)[e]

[a] Data from ref 5. [b] Data from ref 4. [c] Theoretical frequencies at the DFT/B3LYP level. [d] Theoretical frequencies at the MP2 level. [e] Experimental infrared frequencies.

In the nonclassical Y-shaped complex, the H−H distance of the coordinated dihydrogen is only slightly longer than in free hydrogen and the resulting donation of electron density into the metal σ orbital increases the axial Au−H distance slightly vs free AuH. By comparison, the dihydrogen distance in Cu(η^2-H_2)Cl (0.807 (MP2) and 0.794 Å(CPF))[4] is similar to that in the nonclassical gold complex, but the M−H_2 bond distance is shorter (1.572 (MP2) and 1.611 Å (CPF))[4] in accordance with the smaller copper atom. The H−H bond length in Pd(η^2-H_2) is stretched by 0.05 Å over Au(η^2-H_2)H.[5] The classical aurane complex is essentially the nonadiabatic doubly excited state of the Y-shaped complex where a pair of electrons are excited from the a_1 $M \leftarrow \sigma$ orbital into the b_2 metal p−H_2 bonding orbital. The geometric parameters for aurane are similar to those found previously except for a slightly shorter equatorial Au−H bond length (1.641 Å[8] vs 1.629 Å) in the present work due to an improved basis set.

The MP2//BSI vibrational frequencies have been listed in the Supporting Information (Table S2). Mixed hydride-deuteride complexes have also been calculated for comparison to experiment. In the nonclassical complex Au(η^2-H_2)H, the calculated intensities for all of the IR frequencies do not exceed 50 km/mol and the Raman intensities do not exceed 110 Å^4/amu. The most important absorbances for identifying these gold complexes in the frozen matrix and distinguishing between the aurane and nonclassical isomers are the symmetric H−H stretching modes (Table 2). However, the calculations do not show any significant intensity for this mode in the IR spectrum for this band, probably due to the lack of a large change in dipole moment. The larger calculated Raman intensities suggest that Raman spectroscopy is a more appropriate tool for examining this system. For the C_{2v} complex, the Raman band is shifted to 2160 cm^{-1} versus free dihydrogen (4271 cm^{-1} MP2/BSI) and is close to the equivalent IR band in PdH_2. Monodeuteration in the axial position shifts the band to 1794 cm^{-1} and dideuteration shifts it to 1533 cm^{-1}. This mode in the nonclassical Y-shaped complex is much closer to the value for free hydrogen as expected. These frequencies range from 3830 cm^{-1} for Au(η^2-H_2)H, 3335 cm^{-1} for the monodeuterated complex and 2722 cm^{-1} for the dideuterated complex. Compared to Cu(η^2-H_2)Cl, the H−H stretch in the nonclassical complex is closer to free H_2 regardless of the similar bond distances. However, the symmetric H−H stretching band in Pd(η^2-H_2) is shifted to a lower wavenumber due to a longer H−H distance.

TABLE 3: Dissociation Free Energies of Au(η^2-H_2)H to AuH and H_2 at 150 K

method	basis	ΔE_{dis} (kcal/mol)	ΔG_{dis} (kcal/mol)	BSSE (kcal/mol)
MP2//MP2	I	11.16	5.75[a]	2.64
	II	13.57	8.04[a]	2.10
	III	15.91	10.05[a]	0.95
	IV	16.76	10.90[a,b]	
MP3//MP2	I	9.48	4.07[a]	
	II		4.84[a]	
CCSD(T)//MP2	I	9.35	3.94[a]	
	II		4.84[a]	
MP3//MP3	I	9.55	4.14[a]	
	II	10.52	5.11[a]	
	III	12.74	6.88[c]	
CCSD(T)//MP3	I	9.40	3.99[a]	
	II		4.97[a]	
CCSD(T)//CCSD(T)	I	9.37	3.95[a]	2.92
	II	10.40	4.99[a]	2.84
	III	12.56	6.7[a]	0.76
	IV	13.44	7.58[a,b]	

[a] Includes thermal, entropy ($\Delta S_{dis} = 27.11$ cal/(mol K)), and ZPE corrections from MP2//MP2 optimized geometry in Basis I. [b] Performed from the MP2/BSIII or CCSD(T)/BSIII optimized geometry.

The need for high angular momentum functions in correlated calculations is demonstrated well in the present calculations. The addition of a single set of f-type polarization function to the metal in BSII lowers the energy by 205 kcal/mol at the MP2 level and 185 kcal/mol at the CCSD(T) level. Use of two sets of polarization functions on Au and H in BSIII stabilizes by an additional 50 kcal/mol at the CCSD(T) level. The calculations in BSIV appear to approach the CCSD(T) basis set limit as only an additional 6.2 kcal/mol of stability are added. It may be useful to note the "agreement" between the MP3 and CCSD(T) values. Other agreements between MP3 and coupled-cluster calculations for transition metal systems have been noted in previous studies.[15b,20]

Dissociation Energy of Au(η^2-H_2)H. As the nonclassical C_{2v}' complex is significantly more stable than the classical system, it may be possible to obtain a "AuH_3" complex starting from AuH and H_2. The free energies of dissociation to dihydrogen and AuH are listed in Table 3 and include ZPE corrections. The AuH bond length (CCSD(T)//CCSD(T), BSIII) is consistent with previous theoretical studies[21] and in complete agreement with the experimental value of 1.524 Å.[22] The MP2/BSI and MP3/BSI frequencies for AuH (2316 and 2291 cm^{-1}, respectively) are within 10−15 cm^{-1} of the experimental values.[22] The relative energy of the dissociative process is 13.44 kcal/mol ($\Delta G_{dis} = 7.58$ kcal/mol) at the CCSD(T)/BSIV//CCSD(T)/BSIII level from the C_{2v}' complex and exothermic by about 10 kcal/mol from the C_{2v} geometry. Thus, the ΔE_{dis} is comparable to other transition metals complexes such as Cu(η^2-H_2)Cl [4] and Pd(η^2-H_2).[5] In comparison, the dissociation energy of C_{2v} $AuCl_3$ to Cl_2 and AuCl is endothermic by approximately 30 kcal/mol at the MP2//MP2 level.

BSSE corrections are included in Table 3, but are not included in the listed values of ΔE_{dis} and ΔG_{dis}. BSSE can effectively measure the completeness of a basis set such that the more complete the basis, the lower the BSSE correction. In the present calculations, the BSSE is not significantly changed by the addition of an f-type polarization function in BSII. However, double polarization functions on both Au and H in BSIII give a reduction in BSSE for a corrected ΔG_{dis} of 5.94 kcal/mol at the CCSD(T) level. BSIV is expected to have very little BSSE as it appears close to the basis set limit. However, the large counterpoise correction in the smaller basis sets casts doubt on the general validity of these corrections.

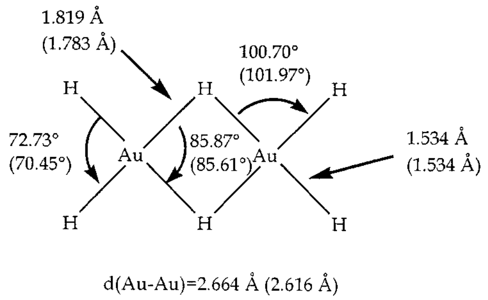
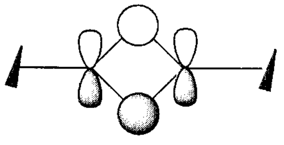


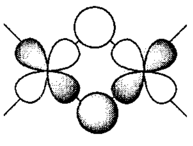
Figure 2. Structural parameters for diaurane at the MP2/BSI (MP2/BSII) level.

Dimerization of AuH_3. Due to the tendency of AuF_3 and $AuCl_3$ to form polymers and dimers, respectively,[8,11] the possibility of dimerization to Au_2H_6 (or diaurane) is also considered. MP2 geometry optimizations of four different D_{2h} isomers gave only the planar dimer shown in Figure 2. The structure is similar to previous calculations of Au_2H_6 at the HF level and the X-ray crystal structure of Au_2Cl_6.[8]

Calculations also show that the dissociation energy of diaurane to two Au(η^2-H_2)H units is endothermic by 20.1 kcal/mol at MP2/BSII. Dissociation to two auranes is endothermic by 72.9 kcal/mol (ΔE_{dis} (HF) = 49.5 kcal/mol).[8] The geometry of diaurane (Figure 2) is fairly consistent between BSI and BSII. The bond distances between the terminal hydrides and the gold centers are unchanged, but the distances between gold and the bridging hydrides decreases by 0.05 Å thus contracting the ring slightly. The change from a nonclassical minimum in the monomer to a classical isomer in the dimer results from the types of metal AOs available for bonding in the molecule. In Au_2H_6, the hydride ligands decompose as $2a_g + b_{1g} + b_{2u} + 2b_{3u}$. Because each metal center is d,[8] each one contributes a 6s, 5d and 6p orbital for bonding with the hydride ligands.[3] Examination of the decomposition of the metal orbitals in D_{2h} symmetry shows that two b_{3u} combinations are required: one 5d and one 6p. The stability imparted through the mixing of these two orbitals explains why **II**, the isomer directly analogous to diborane, is not a minimum. Twisting the terminal hydrides out of the plane prohibits mixing of the p **A** and d **B** combinations.



A



B

The calculated frequencies for diaurane are listed in the Supporting Information (Table S3). The most intense band for diaurane and diaurane-d_6 is the b_{3u} stretching mode which appears at 1100 cm^{-1} and shifts to 784 cm^{-1} in the perdeuterated complex. The analogous band in $(PdH)_2$ appears at 1348 cm^{-1} with a shift to 950 cm^{-1} in $(PdD)_2$.[5] The calculated spectra of the dimers of the mixed hydride-deuteride AuH_3 complexes have also been included for completeness.

4. Conclusions

This study confirms the stability of a nonclassical Au(η^2-H_2)H isomer over a classical AuH_3 isomer. However, the nonclassical system is only bound by approximately 13.44 kcal/mol vs AuH and H_2. Therefore, the species would be expected to have only a transient existence, as suggested by the observations in Neumeier and Wiberg's experiments.[1] However, modern matrix isolation experiments may allow observation of these species through characteristic bands in the Raman spectra. The AuH_3 systems also have an exothermic path to dimerization to the D_{2h} square planar dinuclear molecule which may also be observed. Identification of diaurane in the matrix should be obvious from the shifts vs AuH_3, $Au(\eta^2\text{-}H_2)H$, and AuH.

Acknowledgment. The author thanks Prof. Michael B. Hall at Texas A&M University for a generous donation of computer time.

Supporting Information Available: Geometric parameters for T-shaped and Y-shaped AuH_3 complexes, theoretical (MP2/BSI) frequencies of the two AuH_3 isomers, and theoretical frequencies for diaurane Au_2H_6. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wiberg, E.; Neumaier, H. *Inorg. Nucl. Chem. Lett*. **1965**, *1*, 35.

(2) (a) Gilman, H.; Woods, L. A. *J. Am. Chem. Soc*. **1948**, *70*, 550. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(3) Bayse, C. A.; Hall, M. B. *J. Am. Chem. Soc*. **1999**, *121*, 1348.

(4) Plitt, H. S.; Bär, M. R.; Ahlrichs, R.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 832.

(5) Andrews, L.; Manceron, L.; Alikhani, M. E.; Wang, X. *J. Am. Chem. Soc*. **2000**, *122*, 11 011.

(6) McKee, M. L.; Sweany, R. L. *J. Phys. Chem. A* **2000**, *104*, 962.

(7) (a) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K.; *J. Am. Chem. Soc*. **1976**, *98*, 7255. (b) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 1857.

(8) Schwerdtfeger, P.; Boyd, P. D. W.; Brienne, S.; Burrell, A. K. *Inorg. Chem*. **1992**, *31*, 3411 and references therein.

(9) Puddephatt, R. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1987.

(10) (a) Lin, Z.; Hall, M. B. *Coord. Chem. Rev*. **1994**, *135/136*, 845 (b) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev*. **2000**, *100*, 601.

(11) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier, Amsterdam, 1978.

(12) Dunning, T. H. *J. Chem. Phys*. **1970**, *55*, 716.

(13) Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; Lajohn, L. A.; Christiansen, P. A. *J. Chem. Phys*. **1990**, *93*, 6654.

(14) GAMESS−UK is a package of ab initio programs written by Guest, M. F.; van Lenthe, J. H.; Kendrick, J.; Schoffel, K., Sherwood, P. with contributions from Amos, R. D.; Buenker, R. J.; Dupuis, M.; Handy, N. C.; Hillier, I. H.; Knowles, P. J.; Bonacic-Koutecky, V.; von Neissen, W.; Harrison, R. J.; Rendell, A. P.; Saunders, V. R.; Stone, A. J. The package is derived from the original GAMESS code due to Dupuis, M.; Spangler, D.; Wendoloski, J. Warrington, UK. 1995.

(15) (a) Couty, M.; Hall, M. B. *J. Comput. Chem*. **1996**, *17*, 1359. (b) Couty, M.; Bayse, C. A.; Hall, M. B. *J. Phys. Chem*. **1996**, *100*, 13 976.

(16) (a) Fletcher, R.; Powell, M. J. D. *Comput. J*. **1963**, *6*, 163. (b) Davidon, W.; *Arg. Nat. Lab. Rep.*, ANL-5990. (c) Binkley, J. S. *J. Chem. Phys*. **1976**, *64*, 5142.

(17) Gaussian 98 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(18) Hobza, P.; Zahradnik, R. *Chem. Rev*. **1988**, *88*, 871.

(19) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys*. **1984**, *81*, 6026. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys*. **1985**, *82*, 284.

(20) Bayse, C. A.; Hall, M. B.; Pleune, B.; Poli, R. *Organometallics* **1998**, *17*, 4309.

(21) Collins, C. L.; Dyall, K. G.; Schaefer, H. F. *J. Chem. Phys*. **1995**, *102*, 2024.

(22) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.