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Clamshell Structure of Sc(biphenyl) from High Resolution Photoelectron Spectroscopy

Bradford R. Sohnlein, Jason F. Fuller, and Dong-Sheng Yang*
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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Biphenyl, $C_{12}H_{10}$, has a planar structure in the crystalline state[1] and is twisted in the gas phase.[2] The dihedral angle of the two phenyl rings is determined by competition between π-conjugation and steric repulsions; the former favors a coplanar configuration, while the latter prefers a nonplanar form.[3−5] Transition metal−biphenyl complexes have been studied for many years in condensed-phase organometallic chemistry, because they are good models for conducting organometallic polymers.[6−12] Like metal−benzene complexes, each π-ring of biphenyl was suspected to have 6-fold binding, and metal interaction with two π-rings formed dinuclear complexes.[6−9] In these dinuclear complexes, two metal atoms generally resided on opposite sides of the biphenyl plane to minimize steric repulsions, although structures with two metal atoms on the same side have been identified as well.[6,9] On the other hand, metal−biphenyl complexes may form different structures in the gas phase, because of the twisted configuration of the ligand and lack of stabilizing solvent and counterion molecules. Structural determination, however, has not been reported for metal complexes with biphenyl or other polyphenyls in the gas phase.[13]

We report here the clamshell structure of $Sc(C_{12}H_{10})$ determined by pulsed field ionization−zero electron kinetic energy (ZEKE) photoelectron spectroscopy, in combination with density functional theory (DFT) calculations. This work presents the first electronic−vibrational spectroscopy of a metal−polyphenyl species and shows a new binding mode of biphenyl.

$Sc(C_{12}H_{10})$ was prepared by the reaction of scandium atoms and biphenyl vapor in a supersonic molecular beam source. Scandium atoms were generated by laser vaporization of a scandium rod with the second-harmonic 532 nm output of a Nd:YAG laser. At room temperature, $C_{12}H_{10}$ vapor was introduced through a stainless steel capillary to a small reaction chamber. This reaction chamber was located a few centimeters downstream from the vaporization region, where gaseous metal atoms entrained in a helium/argon mixture reacted with biphenyl vapor. Masses of reaction products were determined by laser photoionization time-of-flight mass spectrometry. ZEKE spectra were recorded by measuring the ZEKE electron signal as a function of photoexcitation laser wavelength. These ZEKE electrons were obtained by pulsed field ionization of photoexcited high-lying Rydberg states. Further details about the ZEKE apparatus and experimental procedures have been described in a previous publication.[14]

A representative ZEKE spectrum of Sc−biphenyl is shown in Figure 1a. Peaks from single vibrational-mode excitations are labeled in the figure, while others can be easily assigned to transitions involving two or more vibrational modes. The strongest transition occurs at 39114 (5) cm^{-1} [4.8495 (6) eV] and is the origin (0−0) of the electronic transition between the ground vibrational levels of the neutral and ionized molecules. The energy of the 0−0 peak corresponds to the first ionization energy of the neutral species. Above the band origin, the spectrum exhibits peaks spaced in 284, 336, 378, and 568 cm^{-1} intervals. These peaks measure excitations of four vibrational modes in the ion complex. An additional peak (*h*) is observed at 13 cm^{-1} below the band origin. The intensity of this peak depends on the condition of the molecular beam and is attributed to a hot transition from an excited vibrational level of the neutral state. The transition intensity of a sharp line (*Ta*) at 39060 cm^{-1} has a strong power-dependence and corresponds to a resonant two-photon ionization of Ta atom, an impurity of the Sc rod.

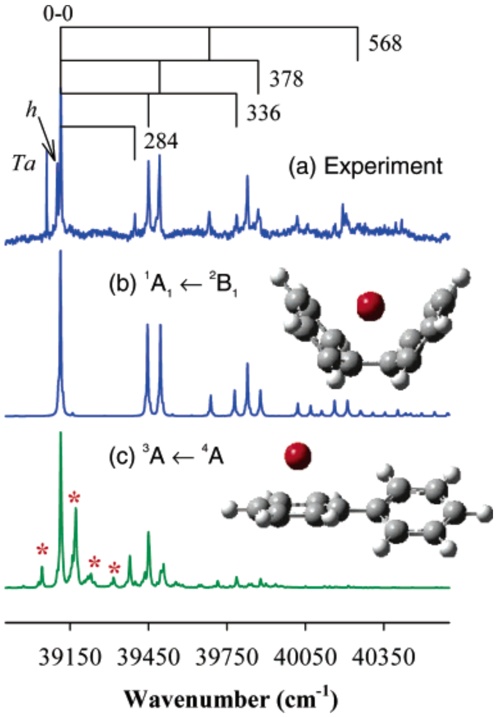

Figure 1. The ZEKE spectrum (a) and simulations (100 K) of the clamshell (b) and half-sandwich (c) isomers of $Sc(C_{12}H_{10})$. Sc atom is red, C atoms are gray, and H atoms are white.

Electronic structure calculations were performed with Gaussian 03 using the hybrid B3LYP functional and 6-311+G(d,p) basis set.[15] The B3LYP method has been used to complement spectroscopic studies of transition metal−benzene complexes.[16−21] Our DFT calculations on $Sc(C_{12}H_{10})$ predict two isomers: a C_{2v} clamshell structure with Sc binding to both phenyl rings (Figure 1b) and a C_1 half-sandwich structure with Sc binding to only one ring (Figure 1c). For the clamshell structure, the ground electronic state is a doublet ($^2B_1$), with a $3d^3$ valence electron configuration. One can imagine the formation of the complex as occurring by a mechanism in which the two phenyl rings first rotate to become coplanar, and then bend toward the Sc atom as it approaches, forming a structure of C_{2v} symmetry. The structure is clamped in place when the Sc atom coordinates to both phenyl rings. This structure has a twelve-fold binding mode, with the shortest distance (2.16 Å) between Sc

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Table 1. Measured (ZEKE) and Calculated (B3LYP) Ionization Energies (IE, eV) and Vibrational Frequencies (cm^{-1}) of the Clamshell Structure of Sc(biphenyl)[a]

	description	ZEKE	B3LYP
IE	$^1A_1 \leftarrow {}^2B_1$	4.8495(6)	4.864
ν_{17}^+	$Sc^+-C_{12}H_{10}$ stretch	336	333
ν_{16}^+	out-of-plane ring deformation	378	382
ν_{15}^+	out-of-plane ring deformation	568	575
ν_{32}^+/ν_{32}	ring rock	142/155	150/158

[a] ν^+ and ν represent vibrational modes in the $^1A_1$ ion state and $^2B_1$ neutral state, respectively.

and the two carbon atoms of the junction bond. Distances between Sc and other carbon atoms are in the 2.44−2.57 Å range. For the half-sandwich structure, the ground electronic state is a quartet (^4A), with a valence electron configuration of $3d^24s^1$. The two rings in this structure remain twisted, although the dihedral angle is reduced (by ~11°) from the free ligand to the complex. Sc−C distances, 2.44 ± 0.01 Å, are virtually the same as that in the ground state of Sc(benzene).[16] The energy difference between these two structures is 3.9 kcal mol^{-1}, with the clamshell structure lower in energy. Ionization of the clamshell structure removes a Sc $3d_\pi$ electron from the highest occupied orbital of the $^2B_1$ state and yields a $^1A_1$ ion state, whereas ionization of the half-sandwich structure removes a Sc 4s electron of the ^4A state and gives a ^3A ion state. Ionization energies are predicted to be 4.86 eV for the clamshell structure and 5.05 eV for the half-sandwich structure. Since the calculated energy differences between the two isomers and between their ionization energies are well within computational errors, theory alone is not sufficient to determine the preferred structure of this complex.

The spectral simulations of the clamshell and half-sandwich structures (Figure 1b,c) are obtained by calculating multidimensional Franck−Condon factors using the equilibrium geometries and vibrational force fields from the DFT calculations. In these simulations, vibrational frequencies are not scaled, but the ionization energy is shifted to the experimental value for easy comparison. The $^1A_1 \leftarrow {}^2B_1$ simulation of the clamshell structure matches well with the experimental spectrum, although it misses the weak peak at 284 cm^{-1}. In contrast, the $^3A \leftarrow {}^4A$ simulation of the half-sandwich structure severely underestimates the intensities of all major peaks observed in the experiment and exhibits at least four false transitions (marked by asterisks) that do not exist in the measured spectrum. This comparison shows clearly that the observed spectrum originates from the $^1A_1 \leftarrow {}^2B_1$ transition of the clamshell structure.

Table 1 lists the experimental and theoretical ionization energies and vibrational frequencies for the clamshell structure. The 336 cm^{-1} progression is assigned to excitations of a symmetric Sc^+−biphenyl stretch, characterized largely by the Sc^+ displacement (ν_{17}^+). The 378 and 568 cm^{-1} intervals are excitations of two symmetric out-of-plane ring deformations (ν_{16}^+ and ν_{15}^+). Peak *h* at 13 cm^{-1} below the band origin is due to a sequence transition between the first vibrational levels of a nonsymmetric ring rocking mode in the neutral (ν_{32}) and ion (ν_{32}^+) states. This peak is partially overlapped with the band origin in the simulation. The 284 cm^{-1} interval does not correspond to any of the symmetric vibrations in the ion, but is about twice the predicted frequency of ν_{32}^+. Thus, it may be assigned to the first overtone of this rocking mode. The assignment of the 284 cm^{-1} and sequence peaks yields the ν_{32}^+ and ν_{32} frequencies of 142 and 155 cm^{-1}, in good agreement with the calculated values of 150 and 158 cm^{-1}, respectively.

This work demonstrates that ZEKE spectroscopy, combined with DFT, is a powerful approach for determining electronic states and molecular structures of metal−polyphenyl complexes. The formation of the clamshell structure is astounding; it requires both rotation and bending of the phenyl rings. The energy cost for the ring motion is, however, overcome by the stabilization of the metal−π interaction.

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Supporting Information Available: The full list of authors for ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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