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DFT-Supported Threshold Ionization Study of Chromium Biphenyl Complexes: Unveiling the Mechanisms of Substituent Influence on Redox Properties of Sandwich Compounds

Sergey Yu. Ketkov*^[a], Sheng-Yuan Tzeng^[b], Pei-Ying Wu^[b], Gennady V. Markin^[a], and Wen-Bih Tzeng*^[b]

This paper is dedicated to Professor Gleb Abakumov on the occasion of his 80th birthday

Abstract: High-resolution mass-analyzed threshold ionization (MATI) spectra of $(\eta^6-Ph_2)_2Cr$ and $(\eta^6-Ph_2)(\eta^6-PhMe)Cr$ demonstrate that the Ph groups work as electron donors decreasing the ionization energy of the gas-phase bisarene complexes. In contrast to electrochemical data, a close similarity of the Ph and Me group effects on the oxidation of free sandwich molecules has been revealed. However, DFT calculations testify for the opposite shifts of the electron density caused by the Me and Ph substituents in the neutral complexes, the latter behaving as an electron accepting fragment. On contrary, in the bisarene cations the Ph group becomes a stronger donor than methyl. This change provides the similar substituent effects observed with the MATI experiment. On the other hand, the well-documented opposite influence of the Me and Ph fragments on the redox potential of the $(\eta^6-\text{Arene})_2 \text{Cr}^{+/0}$ couple in solution appears to be a result of solvation effects but not intramolecular interactions as shown for the first time in this work.

Introduction

Next year chemists will celebrate a centenary of chromium biphenyl compounds. Synthesized firstly in 1918 by F. Hein,^[1] they have been being considered for a long time as metal phenyl σ -complexes. Only after the synthesis of $(\eta^6-C_6H_6)_2Cr$ (1) by E.O. Fischer and W. Hafner in 1955^[2] and successful employment of the Fischer method to prepare^[3] $(\eta^6-Ph_2)_2Cr$ (2) the idea of ferrocene-like sandwich structures of the "Hein's polyaromatic chromium compounds" has been accepted.^[4] Since then, metal arene complexes, similar to metallocenes, have played key roles in various fields of fundamental and applied chemistry. During last decades considerable interest has been focused on these compounds because of their relevance for studies of metalligand bonding,^[5] organic synthesis,^[6] electrochemistry,^[7] catalysis,^[8] metal-containing polymers,^[9] biomedicine^[10] and nanoelectronics.^[11] The redox properties of sandwich complexes appeared to be of crucial importance for their chemical and biochemical reactivities.^[12] The one-electron oxidation of neutral

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bis(η^{6} -arene)chromium in solution leads to the formation of a stable sandwich cation. For the complex bearing a phenyl group in each ring, the $2^{+/0}$ electrode potential $E_{1/2}$ was found to be nearly solvent independent so this couple was recommended by IUPAC as a reference redox system for non-aqueous solutions.^[7,13] However, despite of numerous studies of the solution-phase oxidation of neutral **2**, to the best of our knowledge, so far there have been no works on the ionization of this key sandwich molecule in the gas phase.

New intriguing insights into the electronic structures of sandwich compounds can be provided by the zero kinetic energy (ZEKE) and mass-analysed threshold ionization (MATI) techniques based on laser excitation of jet-cooled molecules to high Rydberg levels (ZEKE states).^[14] Extremely accurate ionization energies *I* of **1**, alkylated bisarene systems and metallocenes have recently been measured with these methods.^[15] The data obtained form a basis for analysis of fine substituent effects in free sandwich molecules.

Here we exploit high resolution MATI spectroscopy supported by DFT calculations to determine the ionization energy of 2 and to reveal the intrinsic influence of the phenyl substituents on the electronic structure bis(η⁶of arene)chromium. In contrast to the electrochemical studies of $(\eta^6$ -Arene)₂Cr in solution describing the Ph group as an electron withdrawing substituent,^[16] our gas-phase experiments demonstrate that the ring phenylation results in a decrease in the / value of 1. MATI spectra of 2 and $(\eta^6-Ph_2)(\eta^6-PhMe)Cr$ (3) reveal a close similarity in the Ph and Me substituent influence on the ionization energy of $bis(\eta^6$ -arene)chromium. DFT calculations of gas-phase 2 and 3 confirm this similarity. On contrary, in the solution phase, the different solvation energies lead to the opposite ionization energy changes for the complexes bearing Ph and Me groups. The experimentally observed anodic shift of the $(\eta^{6}\mbox{-}Arene)_{2}\mbox{Cr}^{\mbox{+}\prime 0}$ half-wave potential on phenylation of the rings^[16] appears to be, therefore, a result of solvation effects rather than that of the intramolecular substituent influence.

Results and Discussion

The photoionization mass spectrum of 2 (Figure 1a) reveals a clearly defined molecular ion peak at m/z 360 and a weak $(Ph_2)Cr^+$ daughter ion signal at m/z 206. On going to the 3 mass spectrum (Figure 1b) the relative intensity of the $(Ph_2)Cr^+$ peak increases substantially. This change arises from the difference in the dissociation energies of sandwich as will be shown below.

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The photoionization efficiency (PIE) curve and MATI spectrum of **2** are given in Figure 2a,b. The MATI signal reveals one strong peak providing the *I* value of 5.308(2) eV which is 0.158 eV lower than that of unsubstituted **1**. Taking into account the positive shift of reduction potential $E_{1/2}$ on going from the $1^{+/0}$ to $2^{+/0}$ couple^[16] and linear correlations between the *I* and $E_{1/2}$ values,^[17] such a result seems to be rather surprising. One would expect a lower ionization energy for **1** which is oxidized in solution easier than phenylated complex **2**. Such a prediction perfectly works for alkyl substituents in $(\eta^6$ -Arene)₂Cr. Both *I* and $E_{1/2}$ decrease on going from **1** to the alkylated complexes.^[16, 17]



Figure 1. Photoionization mass spectra of 2 (a) and 3 (b) measured at the laser wavenumber of 43500 $\rm cm^{-1}.$

The ionization energy of jet-cooled **2** is close to the $(\eta^6 - \eta^6)$ PhMe)₂Cr (4) / value (5.2999-5.3077 eV).^[15g,h] However, in contrast to the 4 MATI spectrum showing two intense narrow origins (full width at half maximum, FWHM, 20-40 cm⁻¹), which correspond to different rotational isomers, the spectrum of 2 reveals only one rather broad peak (FWHM 190 cm⁻¹). To rationalize this difference we optimized geometries and calculated energies of the 2 stable isomers. In addition to the analogues of 4, which can be obtained by the ligand rotation around the Cr-ring axis, there are also low-energy 2 isomers formed by the substituent rotation around the C-C bond. This results in 8 stable rotamers of complex 2 (Figure 3) with the biphenyl dihedral angles of 30° - 35°. In addition, there are 8 enantiomers energetically equivalent to their counterparts (Figure S1, see Supporting Information). The calculated / values lie within a 100 cm⁻¹ range (Figure 3) so the corresponding MATI signals overlap forming the broad peak observed (Figure 2b). On going from 2 to 3 the number of rotational isomers decreases (Figure 3) and their calculated I value range becomes smaller (ca. 50 cm⁻¹). Accordingly, the experimental MATI spectrum of 3 reveals a narrower peak (FWHM 110 cm⁻¹) providing I = 5.303(2)eV (Figure 2c). The origins corresponding to each 3 isomer as well as the MATI vibronic structure are still unresolved in the spectrum measured at m/z = 298 (the **3**⁺ parent ion).

Surprisingly, a better resolution was achieved when recording the MATI signal at m/z = 206 (Figure 2d). The corresponding fragment ions, $(\eta^6-Ph_2)Cr^*$, are produced by ionization of the $(\eta^6-Ph_2)Cr^0$ neutrals populating the high Rydberg level manifold. These neutral species are formed as a result of the **3**^{*} photodissociation (* denotes the ZEKE-state species):

 $(\eta^{6}-Ph_{2})(\eta^{6}-PhMe)Cr^{*} \rightarrow (\eta^{6}-Ph_{2})Cr^{*} + PhMe, \Delta E_{1}$ (1)



Figure 2. The PIE curve of 2 (a) and MATI spectra of 2 (b) and 3 (c, d). The 3 MATI signals were measured at m/z=298 (c) and m/z=206 (d).

Such a mechanism provides the MATI spectrum measured on the fragment mass to coincide with that of the parent molecule. It might look quite unusual that absorption of an additional UV photon leads to dissociation of a ZEKE-state molecule instead of ionization since the electron detachment requires much less energy. However, the high Rydberg states probed by the pulsed-field ionization (the principal quantum numbers n > 200 which correspond to the Bohr orbit radii r > 2 μ m)^[18] are decoupled from the ionic core^[19] so the Rydberg electron is not perturbed by the ion-core internal dynamics. Accordingly, the core behavior of a ZEKE-state neutral corresponds to that of the free cation. That is why the core dissociation of 3* occurs with no significant influence on the Rydberg electron which follows the $(\eta^6-Ph_2)Cr^+$ daughter ion forming the $(\eta^6-Ph_2)Cr^*$ ZEKE-state neutral. The **3**^{*} dissociation energy ΔE_1 (eq. 1) corresponds, therefore, to the $(\eta^6-Ph_2)Cr^+$ -(η^6 -PhMe) bond cleavage (ΔE_2 , eq. 2). Despite numerous observations of fragment ion MATI signals for weak van der Waals complexes,^[20, 21] compound **3** provides, to the best of our knowledge, the first example of an organometallic MATI spectrum measured on the daughter ion mass. Interestingly, no $(\eta^6$ -PhMe)Cr⁺ ion signals are observed in the **3** photoionization mass spectrum which is indicative of the stronger (η^6 -Ph₂)— $Cr(\eta^{6}-PhMe)^{+}$ bond or/and less stable ($\eta^{6}-PhMe)Cr^{*}$ ZEKE states.

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Figure 3. Stable neutral **2** (top) and **3** (bottom) rotational isomers and their calculated B3PW91/6-311++G(d,p) relative energies $E_{\text{rel.}}$ (cm⁻¹) and ionization potentials *I* (cm⁻¹). The isomer notations correspond to the angles between the C_{ring}-C_{substituent} bonds in the ligands (0°, 60°, 120° or 180°).

To provide a more detailed insight into the **3**^{*} decomposition pathways we calculated the **3**⁺ dissociation energies ΔE_2 and ΔE_3 corresponding, respectively, to (eq. 2) and (eq. 3) at two levels of theory. The high- and low-spin organometallic fragments formed were taken into consideration. For comparison the ΔE values were also computed for **1**⁺. The ground-state electronic configuration of **1**⁺ is ...(e_2)⁴(a_1)¹ (² A_1) doublet^[22] (the C_{6v} point group notations are used for **1**⁺ and the (η^6 -PhH)Cr⁺ fragment). On the other hand, the ground state of the (η^6 -PhH)Cr⁺ ion corresponds to the ...(e_2)²(a_1)¹(e_1)² (⁶ A_1) sextet,^[22] the doublet energy being 0.96 eV higher.^[22d] Accordingly, the lower-energy dissociation process in **1**⁺ is accompanied by the change of the system multiplicity.

 $(\eta^{6}\text{-Ph}_{2})(\eta^{6}\text{-PhMe})\text{Cr}^{*} \rightarrow (\eta^{6}\text{-Ph}_{2})\text{Cr}^{*} + \text{PhMe}, \Delta E_{2} \qquad (2)$

$$(\eta^{6}-Ph_{2})(\eta^{6}-PhMe)Cr^{+} \rightarrow (\eta^{6}-PhMe)Cr^{+} + Ph_{2}, \Delta E_{3}$$
 (3)

The computed ΔE values depend strongly on the functional and basis set used. Those calculated at the B3PW91/6-311++G(d,p) and BPW91/DGDZVP levels of theory are given in Table 1. The computation employing the B3PW91 hybrid functional and extended 6-311++G(d,p) basis set underestimates the (η^6 -PhH)—Cr(η^6 -PhH)⁺ dissociation energy (the experimental value^[23] is 242±15 kJ mol⁻¹). The lower BPW91/DGDZVP level of theory appears to provide a much

better agreement with the experiment (Table 1) which is obviously a consequence of compensated errors. Despite this discrepancy, both DFT calculations reveal similar trends for the 3⁺ dissociation. For the processes leading to the fragment ions in the sextet states, the PhMe detachment requires slightly (4-6 kJ mol⁻¹) lower energy than the (η^6-Ph_2) —Cr $(\eta^6-PhMe)^+$ bond cleavage. However, on going to the reactions proceeding on the doublet potential energy surface (PES) the $(\Delta E_3 - \Delta E_2)$ difference increases dramatically, to 18-33 kJ mol⁻¹ (Table 1) providing the PhMe removal to become much more favourable. The wavenumber of the additional photon absorbed by the dissociating 3* ZEKE species lie in the 42500-43000 cm⁻¹ range of the MATI signal (Figure 2c) which corresponds to the energy of 508 - 514 kJ mol⁻¹. These values exceed substantially the energy required for the 3^+ dissociation on the doublet PES (Table 1). Our DFT calculations confirm, therefore, that photodissociation of the 3* ZEKE species results in the preferable formation of the $(\eta^6-Ph_2)Cr^*$ fragments producing the $(\eta^6-Ph_2)Cr^+$ ions observed in the **3** photoionization mass spectrum (Figure 1b).

Table 1. Calculated 3⁺ gas-phase dissociation energies (kJ mol⁻¹), ΔE_2 and ΔE_3 (eqs. 2 and 3, respectively), corresponding to the (η^6 -Ph₂)Cr⁺ and (η^6 -PhMe)Cr⁺ fragment ions in the sextet and doublet electronic states. For comparison the computed energies of the 1⁺ dissociation to (η^6 -PhH)Cr⁺ and PhH are presented.

| lon | Level of theory | Fragment ion state | ΔE_2 | ΔE_3 |
|-----|--------------------------|--------------------|--------------|--------------|
| 3⁺ | B3PW91/6- 311++G(d,p) | Sextet | 153.7 | 157.3 |
| 1+ | B3PW91/6- 311++G(d,p) | Sextet | 154.5 | 154.5 |
| 3⁺ | B3PW91/6- 311++G(d,p) | Doublet | 327.9 | 360.8 |
| 1⁺ | B3PW91/6- 311++G(d,p) | Doublet | 355.0 | 355.0 |
| 3⁺ | BPW91/ DGDZVP | Sextet | 263.2 | 268.9 |
| 1+ | BPW91/ DGDZVP | Sextet | 265.4 | 265.4 |
| 3⁺ | BPW91/ DGDZVP | Doublet | 367.4 | 385.4 |
| 1⁺ | BPW91/ DGDZVP | Doublet | 379.0 | 379.0 |

Apparently, the **3**^{*} isomers contribute differently to the production of the (η^6 -Ph₂)Cr⁺ fragments, the larger number of ions arising from the species with lower ΔE_1 (or ΔE_2) values. As a result, the MATI signal based on the fragment ions (Figure 1d) differs from that recorded on the parent ion (Figure 1c) by smaller contribution from the more stable **3**^{*} isomers. This leads to the narrower MATI 0₀⁰ peak observed (FWHM 60 cm⁻¹) and to the appearance of two resolved vibronic components separated by 180 and 280 cm⁻¹ from the origin. Since the **3** MATI spectrum

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measured on the daughter ion mass corresponds to that of the parent molecule, the vibronic features observed arise from the excitation of the 3⁺ ionic vibrational levels. The relative energies of the 3* ZEKE-state isomers coincide with those of the 3⁺ ions. The highest calculated $E_{rel.}$ value belongs to the **3_0**⁺ and 3_60_1⁺ species (Table S1, see Supporting Information). The contribution from these rotamers dominates, therefore, in the detected MATI signal (Figure 1d). The calculated ionization energies of 3_0 and 3_60_1 are lower than that of the most stable 3_60_2 isomer (Figure 2). Accordingly, the experimental I value decreases from 5.303 (2) to 5.298(1) eV on going from the parent-ion to the daughter-ion spectrum. The vibronic components separated by 180 and 280 cm⁻¹ from the 0₀⁰ peak can be assigned to the 3_0^+ and $3_60_1^+$ skeletal vibrations v_1 (calculated frequencies 185 and 201 cm⁻¹, respectively) and v_2 (calculated frequencies 283 and 274 cm⁻¹, respectively). The corresponding atomic displacements are shown in Figure S2 (See Supporting Information). Similar vibrational modes are active in the MATI spectrum of 4.^[15g,h]

Both MATI experiments and DFT calculations demonstrate that the effect of two Ph groups on the ionization potential of 1 resembles that of two Me substituents (Table 2). Comparison with the *I* values^[15k] of monosubstituted complexes $(\eta^6-Ph_2)(\eta^6-Ph_$ PhH)Cr(5) and $(\eta^6$ -PhMe) $(\eta^6$ -PhH)Cr(6) makes it possible to estimate the I changes caused by the mutual influence of the Ph and Me groups. The 2 ionization energy predicted on the basis of the doubled difference between the / values of 1 and 5 (1432 cm⁻¹) is 42658 cm⁻¹, or 5.289 eV. This energy can be considered as that corresponding to the "pure" effect of two Ph groups. The experimental ionization energy of 2 is somewhat higher (5.308 eV, Table 2), the difference arising from the Ph-Ph interaction. In contrast to the methyl substituents in 4^[15k,] the mutual influence of two phenyl groups in 2 can't be studied in details because of the broad and structureless MATI peak (Figure 2b). The narrower MATI signal of 3 (Figure 2d) corresponds to the Me-Ph effect of 0.64 kJ mol⁻¹ which is very close to that in **4** (Figure 4).

The dimethylated complex 4 reveals actually two types of the Me-Me interaction.^[15k] The Type 1 effect shown by the 60°, 120° and 180° rotamers arises from the changes in the electronic structure of complex 1 on introduction of one electron-donating Me group. These changes prevent the second Me substituent to shift the electron density and to decrease *I*. The contribution of the Type 1 effect to the experimental / change is 0.62 kJ mol⁻¹ (Figure 4). The Type 1 Me-Me influence is present in any 4 rotamer. In the 0° rotamer of 4 with the cis-conformation of the substituents, an additional effect (Type 2 Me-Me influence) appears due to the direct interaction between the closely located Me groups.^[15]] This effect contributes 0.76 kJ mol⁻¹ to the I change (Figure 4). As a result of these effects two origins are observed in the 4 MATI spectrum.^[15g,I] In contrast to 4, the 3 MATI spectrum measured at the daughter ion mass (Figure 2d) reveals only one origin. Accordingly, the DFT calculations predict no high-energy shift of the 3_0 rotamer / value as compared to other 3 rotational isomers (Figure 3). The Type 2 Me-Ph influence in **3_0** appears to be, therefore, different from the Me-Me interaction in 4_0. Nevertheless, the experimentally observed ionization energy decrease on introduction of two Me (complex 4), two Ph (compound 2) or Me and Ph (complex 3) groups is quite similar (Table 2).



Figure 4. The expected (in absence of the mutual substituent influence) and experimentally observed ionization energies of $(\eta^6\text{-PhR})(\eta^6\text{-PhR})Cr$ (R,R' = Me, Ph). For complex **2** (R,R' = Ph), the range of the observed *I* values corresponds to the broad MATI peak (Figure 2b). For compound **3** (R= Ph, R' = Me), the experimental ionization energy is determined on the basis of the MATI spectrum measured at the $(\eta^6\text{-PhR})Cr^+$ fragment ion mass (Figure 2d). The data for **4** (R,R' = Me) were taken from our previous study.^[15k]

Table 2. Experimental and calculated gas-phase ionization energies *I* (eV) of complexes 1-4^[a] and substituent-induced shifts ΔI (eV) together with computed ionization free energy changes $\Delta \Delta G_{ion}$ (kJ mol⁻¹) in gas and DMSO solution.

| Complex | l _{exp} ^{gas} /l _{calc} ^{gas} | $\Delta I_{ m exp}^{ m gas}/\Delta I_{ m calc}^{ m gas}$ | $\Delta\Delta G_{ion}^{gas}/\Delta\Delta G_{ion}^{DMSO}$ |
|----------------|---|--|--|
| 1 ⁰ | 5.4661(6) ^[b] /5.420 | 0/0 | 0/0 |
| 2 ⁰ | 5.308(2)/5.220 | -0.159/-0.200 | -14.1/8.3 |
| 30 | 5.303(1)/5.232 | -0.156/-0.188 | -13.9/1.8 |
| 4 ⁰ | 5.2999(6) ^[c] /5.231 | -0.167/-0.189 | -14.7/-6.2 |

[a] The calculated I and ΔI values are given for the **2_120_2**, **3_120_2** and **4_120** isomers of complexes **2-4**, respectively. [b] Ref.15a,b. [c] Ref.15e,g .

The MATI spectra demonstrate that the Ph fragment in chromium bisarene complexes works as a typical electron donor decreasing the I value. However, the calculated changes in MO energies and electron density distribution are indicative of the electron withdrawing Ph effect in the neutral sandwich molecule. The HOMO energy decreases and the substituent AIM^[24] charge changes from positive to negative on going from **1**⁰ to **2**⁰ (Table 3). The opposite trends caused by the introduction of two donor Me groups are clearly seen when comparing the corresponding parameters in 1^{0} and 4^{0} (Table 3). As compared to the H atom in 1° the Ph substituent in 3° withdraws 0.048 e while the Me fragment donates only 0.009 e which shows a stronger Ph influence on the electron density shift. On contrary, in the ionic bisarene species the Ph fragment acts as an electron donor. The E_{HOMO} and substituent charge increase when one goes from 1⁺ to 2⁺ (Table 3). Comparison of the ligand charge distributions in the mixed 3⁺ system demonstrates that the Ph group in the bisarene ion is a stronger electron donor than the Me substituent.

The combination of the substituent effects in the neutral and ionic bisarene species provides practically equal ΔI values for 2, 3 and 4 (Table 2).

ZEKE spectroscopy revealed an *I* decrease by 0.308 eV on phenylation of $(\eta^6-Ph_2)Sc.^{[15m]}$ However, the metal-ligand interaction in this molecule is quite different from that in $(\eta^6-Ph_2)_2Cr$ because of the $(\eta^6-Ph_2)Sc$ clamshell structure so the Ph substituent effects in these systems are incomparable. The similarity in the Ph and Me fragment influence on the *I* value of **1** has recently been observed when studying MATI spectra of monosubstituted bisarene complexes.^[15k] It was not possible, however, to compare the MATI and electrochemical data because of too small changes in the experimental $E_{1/2}$ values caused by a single Ph group. The gas-phase *I* decrease on going from **1** to **2** (Table 2) contradicts the electrochemical data as mentioned above. To explain this discrepancy we calculated solvation free energies ΔG_{solv} of the neutral and ionic bisarene complexes in DMSO and MeCN at 298 K.

The ΔG_{solv}^{DMSO} value changes by -24.3 and -0.4 kJ mol⁻¹ on going from $\mathbf{1}^0$ to $\mathbf{2}^0$ and $\mathbf{4}^0$, respectively (Table 3). For the $\mathbf{1}^+$ and $\mathbf{2}^+$ ionic species the ΔG_{solv}^{DMSO} difference is substantially smaller than that for the neutrals (-1.6 kJ mol⁻¹). The same trend is observed for MeCN solution (Table S3, see Supporting Information). The large ΔG_{solv} values of neutral complex 2 appear to be the main reason for the change of the ionization free energy shift $\Delta\Delta G_{ion}$ sign on going from the gas to solution phase (Table 2). The DFT calculations predict a solution-phase ΔG_{solv} increase on phenylation of **1** and a decrease on methylation. The changes of the ionization free energy on going from 1 to 2 and 4, $\Delta\Delta G_{ion}$, are estimated to be -14.1 and -14.7 kJ mol⁻¹, respectively, for the gas phase and 8.3 and -6.2 kJ mol⁻¹, respectively, for DMSO solution. The latter $\Delta\Delta G_{ion}$ values correspond to the shifts of the 1^{+/0} reduction potential being equal to 0.085 and -0.065 V, respectively. These calculated shifts correlate very well with the experimental half-wave potential changes $\Delta E_{1/2}$ on going from 1 to 2 (0.101 V) and 4 (-0.064 V) in DMSO.[16]

Table 3. α -HOMO orbital energies E_{HOMO} (eV), substituent AIM^[19] charges q_{R} (a.u.) and solvation free energies $\Delta G_{\text{solv}} \stackrel{\text{DMSO}}{\sim}$ (kJ mol⁻¹) for complex 1 and its disubstituted derivatives 2-4^[a] in the neutral/ionic form.

| Complex | E _{HOMO} | q _R | ΔG_{solv}^{DMSO} |
|---|-------------------|---|--------------------------|
| 1 ⁰ /1 ⁺ | -4.37/-10.47 | 0.0327/0.1281 | -31.8/-218.6 |
| 2 ⁰ / 2 ⁺ | -4.49/-9.57 | -0.0104/0.1383 | -56.1/-220.2 |
| 3 ⁰ / 3 ⁺ | -4.38/-9.75 | -0.0154 ^[b] ;0.0419 ^[c] / 0.1422 ^[b] ;0.1360 ^[c] | -44.4/-214.8 |
| 4 ⁰ / 4 ⁺ | -4.26/-10.13 | 0.0387/0.1384 | -32.2/-209.8 |

[a] The 2-4 isomers correspond to those in Table 1. [b] R=Ph. [c] R=Me.

Conclusions

In conclusion, this work demonstrates that DFT-supported MATI spectroscopy provides new insights into the concept of substituent effects in bisarene complexes. The / values of complexes 2 (5.308(2) eV) and 3 (5.303(2) eV) have been determined for the first time. A surprisingly well-resolved MATI spectrum arising mainly from the 3_0 and 3_60_1 isomers (I = 5.298(1) eV) have been obtained on the mass of the $(\eta^6-Ph_2)Cr^+$ daughter ion. The high-resolution MATI spectra of bis(benzene)chromium phenylated derivatives show that the Ph groups decrease the ionization energy of the free sandwich molecule similar to the donor Me substituents. DFT calculations show, however, that the Ph effect on the electron density distribution studied separately for the neutral and ionic species differs strongly from that of the Me fragments. A comparatively large solvation free energy of neutral 2 appears to be responsible for the solution-phase ΔG_{ion} value increase on introduction of two Ph group into the 1 molecule. The positive shift of the 1^{+/0} half-wave potential on phenylation of the rings is, therefore, a result of solvation effects but not from intramolecular interactions. Such a conclusion can be applicable to other types of sandwich complexes. For instance, solvation effects can contribute to the anomalous behavior of reduction potentials of the zirconocene complexes bearing the SiMe₃ substituents in the rings.^[25] Similar to 1 ferrocene also demonstrates a decrease in the gas-phase ionization energy but a positive shift of a redox potential in solution on phenylation of the rings.^[26] A poor resolution of traditional photoelectron spectra of ferrocenes^[26a] made, however, unavailable a detailed quantitative investigation of the substituent influence. The DFT-supported MATI spectroscopy provides a powerful tool for such studies as demonstrated in this work.

Experimental Section and Computational Methods

Chemicals

All operations with the air-sensitive chromium complexes were carried out under inert atmosphere or in vacuum. Bis(η^6 -biphenyl)chromium (2) was synthesized by reduction of CrCl₃ with the Al powder in the presence of AlCl₃ and biphenyl (the Fischer–Hafner method).^[3] To prepare (η^6 -biphenyl)(η^6 -toluene)chromium (3) the biphenyl-toluene 1:1 mixture was used in the Fisher-Hafner synthesis. As a result a mixture of symmetric (2, 4) and asymmetric (3) bisarene complexes was obtained. More volatile complex 4 was mainly removed by a 2-hour heating of the sample at 100 °C in vacuum. The residue represented a mixture of 2 and 3 as indicated by mass spectrometry. The target species were selected in the photoionization mass spectra (Figure 1) to measure the MATI signals.

Instrumentation

The threshold ionization experiments were carried out with the setup described elsewhere.^[27] The organometallics were heated to 190-210 °C and the sample vapour was seeded into 1.5 bar of helium, expanded into the vacuum through a pulsed valve. The supersonic jet was collimated by a skimmer to form a molecular beam. Tuneable laser pulses in the 230-238 nm region were generated by the frequency doubling of the dye laser output (Lambda-Physik, Scanmate UV with the BBO-I crystal) pumped by a Nd:YAG laser (Quanta-Ray PRO-190-10). The wavelengths of the dye

laser were calibrated with a laser wavemeter (Coherent, WaveMaster). A pulsed electric field of ~1 V/cm applied about 20 ns after the laser shot removed the prompt ions. A second pulse of electric field (+200 V/cm) was applied about 10.6 µs later to ionize the high-n Rydberg neutrals. The newly formed threshold ions were detected by a microchannel plate detector after their separation in the TOF mass spectrometer.

Gas-phase calculations

The optimized geometries, vibrational frequencies and free Gibbs energies of gas-phase complexes 1 - 4 in the neutral singlet and cationic doublet ground states were calculated using the Gaussian 09 program $\mathsf{package}^{[28]}$ with the B3PW91 hybrid functional $^{[29]}$ and the triple- ζ 6-311++G(d,p) basis set including both polarization and diffuse functions.^[30] This level of theory provided an excellent agreement with the experimental MATI data for monosubstituted bisarene complexes.[15k] Representative B3PW91/6-311++G(d,p) optimized structures are given in Figure S1, and the relative energies of the gas-phase 2 and 3 isomers are provided in Table S1 and Table S2, respectively (see Supporting Information), together with the ionization potentials. These parameters were calculated using the sums of the electronic energy E_{el} and zero point vibrational energy (ZPVE). The atomic charges were calculated within the frames of the Bader's atoms-in-molecule theory $^{\left[24\right] }$ on the basis of the wavefunctions of optimized molecules with use of the AIMALL code.[31] The B3PW91/6-311++G(d,p) calculations appear to underestimate the 1+ dissociation energy as mentioned above so to estimate the ΔE_2 and ΔE_3 values (eqs. 2, 3) we carried out also calculations of the 1+, 3+, $(\eta^6$ -PhH)Cr⁺, $(\eta^6$ -Ph₂)Cr⁺, $(\eta^6$ -PhMe)Cr⁺, PhH, PhMe and Ph₂ species at the BPW91/DGDZVP level of theory using the generalized gradient approximations (GGA) functional^[32] and the double- ζ basis set^[33] with polarization functions. This combination of the functional and basis set is closer to that used $\ensuremath{\mathsf{previously}}^{\ensuremath{\mathsf{[22d]}}}$ for 1+ and provides a better agreement with the experimental 1+ dissociation energy.^[23] However, the improved results obtained at the lower level of theory are indicative of compensated errors rather than of the better model.^[34] Both levels of theory reveal, nevertheless, similar trends for the 3⁺ dissociation energies (Table 1).

Solution-phase calculations

Solution-phase parameters of complexes 1 - 4 (Table S3, see Supporting Information) were computed at the B3PW91/6-311++G(d,p) level of theory using the SMD continuum model^[35] which is considered to be one of the best approaches to computational analysis of salvation effects. $\ensuremath{^{[36]}}$ The geometries of the 1, 2_120_2, 3_120_2 and 4_120 neutrals and ions were optimized in the DMSO and MeCN self-consistent reaction fields. The continuum solvent models define^[37] the solvation free energy as

(4)

$$\Delta G_{\rm solv} = E^{\rm soln} + G_{\rm nes} - E^{\rm gas}$$

where E^{soln} and E^{gas} correspond to the electronic energies of the solute in solution and gas phase, respectively, and G_{nes} denotes the sum of nonelectrostatic contributions. The differences in the thermal corrections to the energy in the two phases are implicitly incorporated into the (E^{soln} + G_{nes}) term via the parameterisation providing the best agreement with the experimental solvation free energies. Then the free energy G^{soln} solution is given by eq. 5 since the solvation free energy represents the difference between G^{soln} and G^{gas}

$$G^{\text{soln}} = E^{\text{soln}} + G_{\text{nes}} + \Delta G_{\text{corr}}^{\text{gas}}$$
 (5)

Accordingly, we used the thermal corrections to energy calculated in the gas phase, ΔG_{corr}^{gas} , to estimate the changes in ionization free energies, $\Delta\Delta G_{ion}$, on going from 1 to its substituted derivatives both in the gas phase and in solution (Table S4, see Supporting Information). An alternative approach^[38] suggests to use the solution-phase vibrational frequencies to calculate the solute's free energy. However, the 1 - 4 optimized geometries in solution appeared to be similar to those in the gas phase. In that case, the vibrational contributions to a solute's free energy are insensitive to the phase where the frequencies are computed.^[38] The changes in $1^{*/0}$ reduction potentials ΔE_{red} caused by the introduction of substituents into the 1 molecule were calculated from the solution-phase $\Delta\Delta G_{ion}$ values (Table S4, see Supporting Information) using eq. 6

(6)

(7)

$$\Delta E_{\rm red} = \Delta \Delta G_{\rm ion}$$

reduction processes

/ F

where **F** is the Faraday's constant. The ΔE_{red} quantity refers to the

 $(\eta^6\text{-}Arene)_2Cr^+ + e^- \rightarrow (\eta^6\text{-}Arene)_2Cr^0$

while the $\Delta\Delta G_{ion}$ values describe the reverse oxidation reactions so the signs in the left-hand and right-hand sides of eq. 6 are the same.

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- F. Hein, Ber. Dtsch. Chem. Ges. 1919, 52, 192. [1]
- E. O. Fischer, W. Z. Hafner, Naturforsch. 1955, 10b, 665. [2]
- E. O. Fischer, D. Seus, Chem. Ber. 1956, 89, 1809. [3]
- a) H. Zeiss, M. Tsutsui, J. Am. Chem. Soc. 1957, 79, 3062; b) H. [4] Werner, Angew. Chem. Int. Ed. 2012, 51, 6052; Angew. Chem. 2012, 124, 6156.
- a) D. Seyferth, Organometallics 2002, 21, 2800; b) Ch. Elschebroich in [5] Organometallics, Wiley-VCH, Weinheim, 2006, pp 528-549; c) C. O. Ulloa, M. Ponce-Vargas, R. De Mattos Piccoli, G. F. Caramori, G. Frenking, A. Muñoz-Castro, RSC Advances 2015, 5, 7803.
- E. P. Kündig, A. Pape, Top. Organomet. Chem. 2004, 7, 71. [6]
- a) P. De Vreese, K. Haerens, E. Matthijs, K. Binnemans, Electrochimica [7] Acta 2012, 76, 242; b) G. Gritzner, In Handbook of Reference Electrodes, (Eds.: G. Inzelt, A. Lewandowski, F. Scholz), Springer, Berlin, 2013, pp 25-31; c) J. Jörissen, B. Speiser in Organic Electrochemistry, Fifth Edition: Revised and Expanded, (Eds.: O. Hammerich, B. Speiser), CRC Press, Boca Raton, 2015, pp.263-330.
- a) D. Astruc in Organometallic chemistry and catalysis, Springer, Berlin, [8] 2007, pp 251-288; b) M. P. Boone, D. W. Stephan, J. Am. Chem. Soc. 2013, 135, 8508; c) P. Kumar, R. K. Gupta, D. S. Pandey, Chem. Soc. Rev. 2014, 43, 707-733; d) M. Bochman in Organometallics and Catalysis: An Introduction, Oxford University Press, Oxford, 2015, pp. 432.
- a) H. Braunschweig, A. Damme, S. Demeshko, K. Dück, T. Kramer, I. [9] Krummenacher, F. Meyer, K. Radacki, S. Stellwag-Konertz, G. R. Whittell, J. Am. Chem. Soc. 2015, 137, 1492; b) H. Xiang, J. Yang, J. G. Hou, Q. Zhu, J. Am. Chem. Soc. 2006, 128, 2310.
- a) R. Carter, A. Westhorpe, M. J. Romero, A. Habtemariam, C. R. [10] Gallevo, Y. Bark, N. Menezes, P. J. Sadler, R. A. Sharma, Scientific Reports 2016, 6, 20596; b) A. L. Noffke, A. Habtemariam, A. M. Pizarro, P. J. Sadler, Chem. Commun. 2012, 48, 5219; c) B. Albada, N. Metzler-Nolte, Chem. Rev. 2016, 116, 11797.
- P. Plachida, D. R. Evans, R. Solanki in Nanoelectronic Device [11] Applications Handbook, (Eds.: J. E. Morris, K. Iniewski), CRC Press, Boca Raton, 2013, pp 409-420.
- [12] a) D. R. van Staveren, N. Metzler-Nolte, Chem. Rev. 2004, 104, 5931; b) G. T. Yee, J. S. Miller in Magnetism: Molecules to Materials, Vol. 5,

(Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2005**, pp 223-260; d) M. Meilikhov, K. Yusenko, A. Torrisi, B. Jee, C. Mellot-Draznieks, A. Pöppl, R. A. Fischer, *Angew. Chem. Int. Ed.* **2010**, *49*, 6212; *Angew. Chem.* **2010**, *122*, 6348; e) P. Neumann, H. Dib, A. -M. Caminade, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2015**, *54*, 311; P. Neumann, H. Dib, A. -M. Caminade, E. Hey-Hawkins, *Angew. Chem.* **2015**, *127*, 316.

- [13] G. Gritzner, J. Kuta, Pure Appl.Chem. 1984, 56, 461.
- [14] a) E. W. Schlag in ZEKE Spectroscopy, Cambridge University Press, Cambridge, **1998**, pp 1-287; b) D.-S. Yang, Coord. Chem. Rev. **2001**, 214, 187.
- a) S. Y. Ketkov, H. L. Selzle, E. W. Schlag, Mol. Phys. 2004, 102, [15] 1749–1757; b) K. W. Choi, S. K. Kim, D.-S. Ahn, S. Lee, J. Phys. Chem. A 2004, 108, 11292; c) S. Y. Ketkov, H. L. Selzle, E. W. Schlag, Organometallics 2006, 25, 1712; d) B. R. Sohnlein, D.-S. Yang, J. Chem. Phys. 2006, 124, 134305; e) S. Yu. Ketkov, H. L. Selzle, F. G. N. Cloke, Angew. Chem. Int. Ed. 2007, 46, 7072; S. Yu. Ketkov, H. L. Selzle, F. G. N. Cloke, Angew. Chem. 2007, 119, 7202 f) B. R. Sohnlein, Y. Lei, D.-S. Yang, J. Chem. Phys. 2007, 127, 114302/1; g) J. S. Lee, S. Kumari, D.-S. Yang, J. Phys. Chem. A 2010, 114, 11277; h) S. Ketkov, H. Selzle, F. G. Cloke, G. Markin, Y. Schevelev, G. Domrachev, E. Schlag, J. Phys. Chem. A 2010, 114, 11298-11303; i) D.-S. Yang, J. Phys. Chem. Lett. 2011, 2, 25; j) S. Kumari, D.-S. Yang, J. Phys. Chem. A 2013, 117, 13336; k) S. Y. Ketkov, G. V. Markin, S. Y. Tzeng, W. B. Tzeng, Chem. Eur. J. 2016, 22, 4690; I) S. Y. Ketkov, H. L. Selzle, Angew. Chem. Int. Ed. 2012, 51, 11527; S. Y. Ketkov, H. L. Selzle, Angew. Chem. Int. Ed. 2012, 124, 11695; m) B. R. Sohnlein, J. F. Fuller, D.-S. Yang, J. Am. Chem. Soc. 2006, 128, 10692.
- [16] a) T. T.-T. Li, C. H. Brubaker, *J. Organomet. Chem.* **1981**, *216*, 223; b)
 L. P. Yur'eva, S. M. Peregudova, L. N. Nekrasov, A. P. Korotkov, N. N.
 Zaitseva, N. V. Zakurin, A. Yu. Vasil'kov, *J. Organomet. Chem.* **1981**, *219*, 43; c)
 L. P. Yur'eva, L. N. Nekrasov, S. M. Peregudova, *Russ. Chem. Rev.* **1993**, *62*, 121.
- [17] a) L. P. Yur'eva, S. M. Peregudova, D. N. Kravtsov, A. Yu. Vasil'kov, L. N. Nekrasov, N. L. Asfandiarov, M. M. Timoshenko, Yu. V. Chizhov, J. Organomet. Chem. **1987**, 336, 371; b) Y. Fu, L. Liu, H.-Z. Yu, Y.-M. Wang, Q.-X. Guo, J. Am. Chem. Soc. **2005**, 127, 7227.
- [18] a) R. Lindner, H.-J. Dietrich, K. Müller-Dethlefs, *Chem. Phys. Lett.* **1994**, 228, 417. b) W. A. Chupka, *J. Chem. Phys.* **1993**, *98*, 4520. c) T.F. Gallagher, *Rydberg Atoms*, Canbridge University Press, New York, 2005, 495 pp.
- [19] a) R. Signorell, F. Merkt in *The Role of Rydberg States in Spectroscopy* and Photochemistry, (Ed.: C. Sándorfy), Kluwer Academic Publishing, NewYork, **2002**, pp.479-504; b) P. Hobza, K. Müller-Dethlefs in *Noncovalent Interactions. Theory and Experiment*; RSC Publishing, Cambridge, **2010**, pp.34-39.
- [20] a) D. M. Chapman, K. Müller-Dethlefs, J. B. Peel, *J. Chem. Phys.* **1999**, *111*, 1955. b) S. R. Haines, C. E. H. Dessent, K. Müller-Dethlefs, *J. Chem. Phys.* **1999**, *111*, 1947. c) S. R. Haines, W. D. Geppert, D. M. Chapman, M. J. Watkins, C. E. H. Dessent, M. C. R. Cockett, K. Müller-Dethlefs, *J. Chem. Phys.* **1998**, *109*, 9244. d) J. E. Braun, T. Mehnert, H. J. Neusser, *Int. J. Mass Spectrom.* **2000**, *203*, 1.
- [21] a) J. E. Braun, H. J. Neusser, P. Harter, M. Stockl, J. Phys. Chem. A 2000, 104, 2013. b) S. Chervenkov, P. Q. Wang, J. E. Braun, H. J. Neusser, J. Chem. Phys. 2004, 121, 7169. c) S. Georgiev, T. Chakraborty, H. J. Neusser, J. Phys. Chem. A 2004, 108, 3304. d) S. Georgiev, H. J. Neusser, Chem. Phys. Lett. 2004, 389, 24. e) H. J. Neusser, K. Siglow, Chem. Rev. 2000, 100, 3921.
- [22] a) F. Meyer, F. A. Khan, P. B. Armentrout, J. Am. Chem. Soc. 1995, 117, 9740. b) Y. Li, J. E. McGrady, T. Baer, J. Am. Chem. Soc. 2002,

124, 4487. c) C. W. Bauschlicher, H. Partridge, S. R. Langhoff, *J. Phys. Chem.* **1992**, *96*, 3273. d) R. Sahnoun, C. Mijoule, *J. Phys. Chem. A* **2001**, *105*, 6176.

- [23] Y. Li, T. Baer, J. Phys. Chem. A 2002, 106, 9820.
- [24] The atomic charges were calculated with use of the Bader's atom-inmolecule (AIM) theory: a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford UK, **1990**; b) F. Cortes-Guzman, R. F. W. Bader, *Coord. Chem. Rev.* **2005**, *249*, 633.
- [25] C. E. Zachmanoglou, A. Docrat, B. M. Bridgewater, G. Parkin, G. Brandow, J. E. Bercaw, C. N. Jardine, M. Lyall, J. C. Green, J. B. Keister, J. Am. Chem. Soc. 2002, 124, 9525.
- [26] a) D. L. Lichtenberger, H.-J. Fan, N. E. Gruhn, J. Organomet. Chem.
 2003, 666, 75-85; b) M. Yang, C. Batchelor-McAuley, L. M. Gonçalves,
 C. F. Lima, V. Vyskoĉil, K. Tschulik, R. G. Compton, *Electroanalysis*2016, 28, 197.
- [27] Y. Xu, S. Y. Tzeng, V. Shivatare, K. Takahashi, B. Zhang, W. B. Tzeng, J. Chem. Phys. 2015, 142, 124314.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, [28] J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09. Revision A.02. Gaussian, Inc., Wallingford CT. 2009.
- [29] a) D. Becke, J. Chem. Phys. 1992, 98, 5648; b) P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 1996, 54, 16533.
- [30] a) D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639. b) R.
 Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, 72, 650; c) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R.
 Schleyer, *J. Comp. Chem.* **1983**, *4*, 294.
- [31] AIMAII (Version 13.05.06), T. A. Keith, T. K. Gristmill, Software, Overland Park KS, USA, 2013, http://aim.tkgristmill.com.
- [32] a) A. D. Becke, *Phys. Rev. A* 1988, *38*, 3098. b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B*, 1992, *46*, 6671. c) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B*, 1996, *54*, 16533.
- [33] a) N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* **1992**, *70*, 560. b) C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D.
 Dobbs, D. A. Dixon, *J. Phys. Chem.* **1992**, *96*, 6630.
- [34] W. Koch, M. C. Holthausen, A Chemist's Guide to Density Functional Theory, Wiley-VCH, Heidelberg, 2001, 313 pp.
- [35] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378.
- [36] J. Ho, M. L. Coote, C. J. Cramer, D. G. Truhlar in Organic Electrochemistry, Fifth Edition: Revised and Expanded, (Eds.: O. Hammerich, B. Speiser), CRC Press, Boca Raton, 2015, pp. 229-259.
- [37] J. Ho, A. Klamt, M. L. Coote, J. Phys. Chem. A 2010, 114, 13442.
- [38] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D.G. Truhlar, J. Phys. Chem. B 2011, 115, 14556.



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FULL PAPER

Precise ionization potentials: Highresolution MATI spectra reveal a similar decrease in the $(\eta^6$ -Arene)₂Cr gas-phase ionization energy (IE) by the Ph and Me substituents. DFT provides, however, quite different mechanisms of the substituent influence. On the other hand, the positive shift of the solution-phase redox potential on going from $(\eta^6$ -PhH)₂Cr^{+/0} to $(\eta^6$ -Ph₂)₂Cr^{+/0} appears to be a result of solvation effects but not intramolecular interactions.



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DFT-Supported Threshold Ionization Study of Chromium Biphenyl Complexes: Unveiling the Mechanisms of Substituent Influence on Redox Properties of Sandwich Compounds