Zero Kinetic Energy Spectroscopy: Mass-Analyzed Threshold Ionization Spectra of Chromium Sandwich Complexes with Alkylbenzenes, $(\eta^6-\text{RPh})_2\text{Cr}$ $(R = \text{Me}, \text{Et}, i-\text{Pr}, t-\text{Bu})^{\dagger}$

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For over 25 years zero kinetic energy (ZEKE) spectroscopy has yielded a rich foundation of high-resolution results of molecular ions. This was based on the discovery in the late 60's of long-lived ion states throughout the ionization continuum of molecular ions. Here, an example is chosen from another fundamental system pioneered at this university. The mass-analyzed threshold ionization (MATI) spectra of jet-cooled chromium bisarene complexes (η^6 -RPh)₂Cr (R = Me (1), Et (2), *i*-Pr (3), and *t*-Bu (4)) have been measured and interpreted on the basis of DFT calculations. The MATI spectra of complexes 1 and 2 appear to reveal features arising from ionizations of the isomers formed by the rotation of one arene ring relative to the other. The 1 and 2 MATI spectra show two intense peaks corresponding to the 0_0^0 ionizations with inverse intensity ratios. As indicated by the DFT calculations, the intensity ratio change on going from 1 to 2 results from different isomers contributing to each MATI peak. The ionization energies corresponding to the 0_0^0 peaks are 42746 \pm 5 and 42809 \pm 5 cm⁻¹ for compound 1 and 42379 \pm 5 and 42463 \pm 5 cm⁻¹ for complex 2. The 1 and 2 spectra show also the weaker features representing transitions to the vibrationally excited cationic levels, the signals of individual rotamers being detected and assigned on the basis of calculated vibrational frequencies. The MATI spectra of compounds 3 and 4 reveal only one strong peak because of close ionization potentials of the isomers contributing to the MATI signal. The **3** and **4** ionization energies are 42104 ± 5 and 41917 \pm 5 cm⁻¹, respectively. The precise values of ionization energies obtained from the MATI spectra reveal a nonlinear dependence of the IE on the number of Me groups in the alkyl substituents of $(\eta^6-\text{RPh})_2$ Cr. This can be explained by an increase in the molecular zero point energies on methylation of the substituents.

Introduction

Zero kinetic energy (ZEKE) spectroscopy¹ is based on the discovery of a very large number of unexpected long-lived high Rydberg states close to the ionization continuum, each one due to a molecular ionic state with its own Rydberg series. Very slight fields were found to perturb the original high Rydberg states and convert them to quantum numbers with an extremely long lifetime. This has been discovered now also for Rydberg states above n = 1000 in the stellar atmosphere of the Milky Way in Cassiopeia² and in the laboratory by Held et al.³ by applying very small external fields. The resolution obtained is enormous and is due to the separation of ZEKE states from the nonzero normal states. The separation is provided either by delayed pulses or by steric diffusion of the hot states away from the ZEKE states. ZEKE and the related mass-analyzed threshold ionization (MATI) spectroscopy appeared to be efficient techniques for studying complicated organometallic systems, such as bis(η^6 -benzene)chromium. Over 50 years have passed since the discovery⁴ of this "18-electron" sandwich compound. (η^6 - $C_6H_6)_2Cr$ and its numerous derivatives have played an outstanding role in both theoretical and experimental organometallic chemistry.^{5–9} Together with metallocenes,⁸ the $(\eta^{6}\text{-arene})_2$ Cr complexes represent unique model systems for investigating the nature of the chemical bond in metal π -complexes. It has been recently shown^{6–18} that laser photoionization techniques can be successfully employed for investigations of spectroscopic properties of bisbenzene complexes. Unprecedented resolution achieved in the methods of resonance enhanced multiphoton ionization,^{9–12} ZEKE,^{14,17} and MATI^{10,11,13,16,19} spectroscopy provides new precise information concerning ionization energies (IEs), excited-state properties, and vibrational frequencies of free sandwich neutrals and cations.

An appearance of substituents in the benzene rings strongly changes the reactivity of sandwich systems, the properties of substituted molecules being dependent not only on the substituent nature but also on the conformational behavior. Detection and high-resolution spectroscopic investigation of individual bisarene rotational isomers would provide unique information on the substituent role in the formation of the electronic structures of sandwich systems. Here, we report the results of a MATI spectroscopic study of the chromium bisarene complexes in which each ligand bears an alkyl group, the substituent containing 1-4 carbon atoms. Such systems are of special interest since the fragments of different size can lead to changes in the rotational behavior of the arene ligands in a sandwich

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molecule. A part of this work concerning $bis(\eta^6$ -toluene)chromium has been briefly reported recently.¹⁹

Experimental and Computational Details

Syntheses. Complexes (η^6 -arene)₂Cr (arene = MePh (1), EtPh (2), *i*-PrPh (3), and *t*-BuPh (4)) were prepared by co-condensation of chromium atoms with a corresponding organic ligand at liquid-nitrogen temperature^{20,21} and purified by recrystallization from light petroleum, repeated vacuum sublimation, or both. This method provides individual bisarene compounds.²¹ The purity of the organometallics obtained was checked with ¹H and ¹³C NMR as well as with mass spectrometry. Since bisarene systems are air- and moisture-sensitive, all operations with these compounds were carried out in argon or in vacuum.

Spectroscopic Measurements. The spectroscopic studies were performed with a MATI spectrometer described elsewhere.^{11,15,22-25} In a typical experiment, a sample of a sandwich complex at 120-160 °C seeded in Ar at 1.4 bar was expanded through a heated pulsed nozzle into the vacuum chamber (10^{-5}) Torr). Two skimmers were used to select the center part of the cooled molecular beam. The target molecules were excited by a laser beam at a distance of 170 mm from the nozzle. A tunable dye laser (Quanta Ray PDL-1) pumped by a Nd:YAG laser (Quanta Ray DCR1-A) was employed. The laser pulse wavenumbers were controlled by a Burleigh WA-4500 pulsed wavemeter and were reproducible within 2 cm⁻¹. They were corrected from air to vacuum. The laser resolution was 0.5 cm^{-1} . The frequency-doubled pulse energy was $10-40 \ \mu$ J, as measured with a Ophir-DGX powermeter. The pulse duration was 8 ns. The laser beam was focused by a quartz lens (focal length f = 22 cm).

The frequency-doubled laser was scanned in the region corresponding to the ionization energies of the bisarene complexes, which were determined previously from analysis of Rydberg structures in the gas-phase electronic absorption spectra.²⁶ In the photoionization experiments, the sandwich molecules were ionized by the laser radiation. The ions formed in the ionization chamber were extracted into a reflectron timeof-flight mass spectrometer (RETOF) with a resolution of 2000 $M/\Delta M$ and detected with a multichannel detector. In the MATI experiment, the excited molecules drifted through a series of in-line ion optic plates. To separate the ZEKE-state neutrals from the background ions, the molecular beam was exposed to a spoiling field (0.4 V cm^{-1}) in the laser excitation region. A 75-ns electric pulse providing a zero potential has been applied simultaneously with the laser excitation pulse to stabilize the ZEKE-state molecules formed. The stabilization effect arises from "locking" of long-lived Rydberg states with higher azimuthal quantum numbers.²⁵ An electric pulse of 200 V cm⁻¹, applied between the last set of plates, $30 \,\mu s$ after the laser pulses, ionized the ZEKE neutrals and extracted the ions into the RETOF mass spectrometer.

Computational Studies. To interpret the results of MATI measurements, DFT calculations of the **1–4** molecules have been performed at the BPW91/TZVP level of theory with the Gaussian 03 program package.²⁷ The employment of the generalized gradient approximation functional BPW91^{28,29} in combination with the triple- ζ basis set TZVP^{30,31} has been earlier shown to provide a very good agreement with the experiment for the IE and vibrational frequencies of $(\eta^6-C_6H_6)_2$ Cr, $(\eta^6-C_6D_6)_2$ Cr,³² and compound **1**.¹⁹ The geometries of rotational isomers of the **1–4** neutrals and cations were optimized in this work, and the frequencies of normal vibrations were calculated. For the **1** molecule, the computations were performed also for



Figure 1. One-photon MATI spectrum of $(\eta^6\text{-MePh})_2\text{Cr}$. Band *a* corresponds to the S₀⁻¹ (**1_60**, **1_120**, **1_180**) and B₀⁻¹ (**1_0**) ionizations leading to the vibrationally excited cations.

the transition states forming on rotation of an arene ligand. The substituent conformations in the 2 and 3 complexes are responsible for appearance of the additional isomers differing by the positions of the methyl groups relative to the two benzene rings. These species were also taken into consideration when calculating the ionization energies (IEs). The adiabatic IE values were obtained as differences between the cation and neutral ground electronic state energies at the vibrational zero-point levels. To increase the accuracy of the energy and frequency calculations, the very tight convergence criteria were used in the optimization procedure.

Results and Discussion

The MATI spectrum of complex 1 (Figure 1) appears to differ strongly from those of bis(η^6 -benzene)chromium^{13,16,17} and unsymmetrical (η^6 -*m*-xylene)(η^6 -benzene)chromium (**5**),¹⁶ in which a single strong MATI peak corresponding to the 0_0^0 ionization transition was observed. On going to the spectrum of the 1 molecule, this peak splits into two components. Some of us have earlier shown that the two intense MATI signals in the 1 spectrum arose from the sandwich rotational isomers.¹⁹

 $Bis(\eta^6$ -toluene)chromium represents a simple example of a disubstituted bisarene system showing conformational dynamics. The DFT calculations^{19,33} predict an existence of four stable rotational isomers of complex 1 with eclipsed benzene rings and relative Me orientation dihedral angle φ equal to 0°, 60°, 120° and 180° (Figure 2). These conformations of the neutral complex are labeled here as 1_0, 1_60, 1_120 and 1_180, respectively. The BPW91/TZVP computations¹⁹ predict **1_180** to be the most stable isomer, the rotation barriers being 210-340 cm⁻¹ (Figure 2). According to these calculations, the adiabatic ionization energy of the 1_0 molecule is 62 cm⁻¹ higher than the averaged value of the closely lying IEs of the other three isomers. This prediction agrees very well with the experimental MATI spectrum of 1 in which the two strong peaks are separated by 63 cm⁻¹, the broader signal corresponding to the lower energy. The integrated intensity of the long-wavelength peak is higher due to contribution of the three isomers (1_60, 1_120 and **1 180**).¹⁹

The weaker higher-energy features in the MATI spectra of **1** (Figure 1) and **5**¹⁹ are assigned unambiguously to the vibrational levels of cations **1**⁺ and **5**⁺ on the basis of DFT calculations. These signals arise from excitation of totally symmetric modes S and B. The S vibration involves the metal–ligand stretch and $C_{ring}-C_{Me}$ out-of-plane bend, whereas the B mode corresponds to the ring tilt in combination with the $C_{ring}-C_{Me}$ out-of-plane bend and the Me group torsion vibration (Figure 3). The BPW91/TZVP frequencies of the B mode in the **1_0**⁺, **1_60**⁺, **1_120**⁺, and **1_180**⁺ cations are 217, 201, 172, and 155 cm⁻¹,



Figure 2. Stable rotational isomers of $(\eta^6\text{-MePh})_2\text{Cr}$ with the corresponding ϕ angles between the $C_{\text{ring}}-C_{\text{Me}}$ bond directions and the symmetry point groups (top) and the BPW91/TZVP energy diagram of the ring rotation in the **1** molecule (bottom).



Figure 3. The S (top) and B (bottom) vibrations of the 1_{180}^+ cation resulting from the BPW91/TZVP calculation.

respectively, the B frequency of 1_{120^+} , being close to that of 5^+ (180 cm⁻¹). In contrast to the B vibration, the calculated frequencies of the S mode in the 1^+ rotational isomers are very similar (270–289 cm⁻¹). The peak assignments are given in Table 1.

The ionization energy corresponds to the edge of the shortwavelength wing of a MATI peak. In the two-color MATI spectra of $(\eta^6 - C_6 H_6)_2$ Cr and its deuterated derivatives,¹⁵ the MATI signal descends sharply, providing a narrow blue wing of the MATI band (3 cm⁻¹ between the peak maximum and the signal disappearance region). The MATI maximum and the IE are, therefore, very close. However, on going to the onephoton MATI spectra of the alkylated complexes, this shortwavelength wing becomes much broader (20–25 cm⁻¹), so the ionization energies are presented in Table 1 instead of the peak maximum positions.

On going from compound 1 to the ethylbenzene complex, the isomers resulting from the rotation of the Me fragments bearing by the Et substituents appear in addition to the conformers arising from the different $C_{\text{ring}}-C_{\text{Et}}$ bond orientation. The DFT calculations show that the eclipsed ring conformations $(\phi = 0^{\circ}, 60^{\circ}, 120^{\circ}, 180^{\circ})$ correspond to the energy minima of the 2 molecule, as it was with compound 1. For each ϕ value, at least four nonequivalent positions of the Me groups are possible (Figure 4). One might expect, therefore, that the MATI spectrum of complex 2 will be much more complicated than that of compound 1. However, similar to 1, the 2 MATI spectrum reveals only two intense, long-wavelength 0_0^0 peaks (Figure 5). The corresponding IE values are given in Table 1. The two 0_0^0 maxima separations in the **1** and **2** spectra are close (63 and 84 cm^{-1} , respectively), but the intensity ratios are quite different. In contrast to 1, the spectrum of 2 reveals the stronger 0_0^0 band at higher energies. The explanation comes from the DFT calculations.

Among the 2 neutral rotational isomers, the 2_120 configuration with the two CH₃ groups lying at the outer sides of the carbocycles (the $C_{\text{Et}}{-}C_{\text{Et}}{-}C_{\text{ring}}{-}C_{\text{ring}}$ dihedral angle close to 90°) appears to be the most stable. The energies of the 2_0 , 2_60, and 2_180 conformers are higher by 210, 117, and 85 cm⁻¹, respectively. DFT calculations show that the stabilization of the 2_120 neutral relative to the other isomers is accompanied by a decrease in the $C_{ring}-C_{ring}-C_{Et}$ dihedral angle from typical values of 2.3°-2.5° to 0.7°. On ionization, this angle increases to 2.9° and becomes close to that in the 2_{60^+} and 2_180⁺ conformers. This change is indicative of a disappearance of additional stabilizing interactions in the 2_120^+ cation. Indeed, the energies of the 2_{60^+} and 2_{180^+} cations are computed to be even slightly lower (by 10 and 55 cm⁻¹, respectively) than that of 2_120⁺. As a result, the calculated IE value of the 2_120 molecule appears to be close to that of 2_0 (Figure 6). The 2_60 and 2_180 ionization energies are, respectively, 74 and 86 cm⁻¹ lower than the IE of 2_0. The ionizations of 2_0 and 2_120 contribute, therefore, to the shorterwavelength, intense MATI 0_0^0 peak (IE = 42463 cm⁻¹), whereas the long-wavelength, weaker feature (IE = 42379 cm⁻¹) corresponds to the 2_60 and 2_180 isomers. The BPW91/TZVP calculated difference between the $(IE(2_0) + IE(2_{120}))/2$ and $(IE(2_{60}) + IE(2_{180}))/2$ values is 82 cm⁻¹, which is in excellent agreement with the 84 cm^{-1} separation between the two 0_0^0 peaks in the experimental MATI spectrum of **2**. The change in the intensity ratio of the two 0_0^0 bands on going from 1 to 2 arises from the different isomer contributions to the MATI features. In contrast to 2, the long-wavelength 0_0^0 peak in the spectrum of complex 1 (Figure 1) corresponds to three isomers (1_60, 1_120, and 1_180), but only one conformer (1_0) contributes to the high-energy 000 MATI component.¹⁹

Our DFT calculations demonstrate that the rotation of one Et substituent in complex **2** leading to an appearance of a Me group between the carbocycle planes gives two stable isomers

TABLE 1: Ionization Energies (IE (cm⁻¹)), Experimental and Calculated Shifts from the 0_0^0 Transitions Δv (cm⁻¹) and Peak Assignments for Complexes 1–4

compd	IE	$\Delta \nu_{\exp.}{}^a$	$\Delta \nu_{ m calc.}{}^{b}$	assignment
$(\eta^{6}-MePh)_{2}Cr$	42 746	0	27, 5, 0	0_0^0 (1_60 , 1_120 , 1_180)
-	42 809	63/0	73	0_0^0 (1_0)
	42 901	155/92	155	B_0^1 (1_180)
	42 925	179/116	172	B_0^{-1} (1_120)
	42 946	200/137	201	B_0^{-1} (1_60)
	43 033	287/224	277, 270, 272/217	S_0^{-1} (1_60, 1_120, 1_180)/ B_0^{-1} (1_0)
	43 104	358/295	289	S_0^1 (1_0)
$(\eta^6$ -EtPh) ₂ Cr	42 379	0	12, 0	0_0^0 (2_60 , 2_180)
-	42 463	84/0	86, 70	0_0^0 (2_0 , 2_120)
	42 699	320/236	231, 210	S_0^1 (2_0), B_0^1 (2_120)
$(\eta^6 - i - \Pr Ph)_2 Cr$	42 104	0	44, 0, 31	0_0^0 (3_60 , 3_120 , 3_180)
$(\eta^6$ -t-BuPh) ₂ Cr	41 917	0	25, 0	0_0^0 (4_120 , 4_180)

^{*a*} For complexes 1 and 2, the separations from the two intense 0_0^0 components are given. ^{*b*} The calculated shifts from the lowest IE correspond to the assignments given in the last column.



Figure 4. The stable isomers of **2_180** formed by the rotation of the Et substituents. The hydrogen atoms are omitted for clarity. The corresponding relative energies, $E_{\rm rel}$, and shifts of the adiabatic ionization potentials Δ IE (cm⁻¹) of the neutrals obtained at the BPW91/TZVP level of theory are given below the structures.



Figure 5. One-photon MATI spectrum of $(\eta^6$ -EtPh)₂Cr.

with the $C_{Et}-C_{Et}-C_{ring}-C_{ring}$ dihedral angle close to 30° or 150°. On going to these conformers, the energy of the neutral molecule increases by 600-650 cm⁻¹ (Figure 4), but the ionization potential decreases by 70-150 cm⁻¹. The rotation of the second Et fragment results in a further increase in the molecule energy (Figure 4) and a larger decrease in the IE value. Due to low populations of these ground-state configurations of the jet-cooled molecules, the MATI spectrum of compound 2 reveals no corresponding longer-wavelength features. The higher-energy band (IE = 42 699 cm⁻¹) in the **2** spectrum (Figure 5) arises from the S_0^{1} ionization of the **2_0** isomer and from the B_0^{1} transition in the 2_120 molecule. The calculated S frequency of the 2_0^+ cation (231 cm⁻¹) agrees very well with the 236 cm^{-1} distance from the 0_0^{0} peak (Table 1). According to our DFT calculations, the B_0^{1} ionization transition in the 2_120 molecule lies 26 cm⁻¹ lower than the S_0^{-1} IE of 2 0 and



Figure 6. Changes in the ionization energies ΔIE of the 1 (\blacksquare) and 2 (\blacklozenge) rotational isomers estimated at the BPW91/TZVP level of theory.



Figure 7. One-photon MATI spectra of $(\eta^{6}-i-\text{PrPh})_2\text{Cr}$ (top) and $(\eta^{6}-t-\text{BuPh})_2\text{Cr}$ (bottom).

contributes to the long-wavelength wing of the peak considered. The MATI signals corresponding to the 2_60^+ and 2_180^+ vibrational levels as well as to the 2_120 S_0^{-1} and 2_20 B_0^{-1} ionizations are too weak to be observed in our conditions.

The MATI spectra of complexes **3** and **4** (Figure 7) reveal one intense peak only. The signal-to-noise ratio in these spectra is decreased as compared to the spectra of **1** and **2** because of lower vapor pressure of **3** and **4**. The BPW91/TZVP calculations show that the **3_0**, **3_60**, and **3_180** conformations with two



Figure 8. The isomers of **3_60** bearing two Me groups between the arene planes. The hydrogen atoms are omitted for clarity. Relative energies, $E_{\rm rel}$, and shifts of the first ionization potentials, ΔIE (cm⁻¹), calculated at the BPW91/TZVP level are given near each isomer.

Me groups between the carbocycle planes are, respectively, 569, 28, and 66 cm⁻¹ higher in energy than the most stable **3_120** isomer. The low-populated **3_0** configuration should not give a strong MATI signal. The calculated IE values of the conformers corresponding to the other three ϕ values lie in a relatively narrow range of ~40 cm⁻¹, so the MATI peak observed (Figure 7) can be attributed to the 0_0^0 ionizations of the **3_60**, **3_120**, and **3_180** molecules.

The appearance of additional methyl groups between the arene planes as a result of the *i*-Pr substituent rotation leads to a substantial increase in energy, as was observed with ethylated complex 2 (Figure 4). The 3 isomers with three or four Me fragments between the carbocycle planes give, therefore, no contribution to the MATI spectrum of the jet-cooled complex. On the other hand, compound **3** reveals the isomers bearing two methyl groups between arenes with different Me mutual orientations, similar to the two ethylated species shown in the bottom part of Figure 4. The DFT-estimated ionization potentials of such neutrals with no Me-Me interactions are close, however, so they contribute to the same MATI 0_0^0 band (Figure 7) and result in its broadening. As an example, the calculated relative energies and shifts of the IE values are shown in Figure 8 for the 3_60 isomers. The close Me-Me contact in the 3-60 molecule shown in the bottom part of Figure 8 leads to a substantial increase in energy, so the corresponding MATI signal is too weak to be observed. Therefore, only two rotational isomers of 3_60 contribute to the 3 MATI spectrum.

No such conformers resulting from the substituent rotation around the $C_{ring}-C_R$ bond are possible for (*t*-BuPh)₂Cr. The DFT calculations reveal only **4_74**, **4_120**, and **4_180** stable neutrals and cations. Because of Me–Me repulsion, the ϕ angle between the $C_{ring}-C_{t-Bu}$ directions increases from 60° to 74°. The lowest energy corresponds to the **4_120** molecule ($E_{rel} = 0$). The E_{rel} values of the **4_74** and **4_180** neutrals are higher by 464 and 113 cm⁻¹, respectively. The strong peak observed in the **4** MATI spectrum (Figure 7) arises, therefore, mainly from the ionization of the **4_120** population ratio at 100 K is ~1.3 × 10⁻³, so the **4_74** isomer is expected to give no contribution to the MATI spectrum of jet-cooled complex 4. Thus, DFT calculations provide a basis for the full interpretation of the 1-4 MATI spectra.

The high-resolution data obtained from the MATI spectra of jet-cooled molecules 1-4 reveal a nonadditive influence of the methyl substituents on the ionization energies of $(\eta^{6}-\text{Me}_{n}\text{CH}_{3-n}\text{Ph})_{2}\text{Cr}$ (n = 0, 1, 2, 3). The introduction of each methyl group decreases IE in the row $1_180-2_180-3_180-4_180$ by 367, 275, and 187 cm⁻¹, respectively. The methylation influence therefore becomes weaker as n increases. One could connect this effect with the appearance of two and four Me groups between the arene planes in the **3** and **4** molecules, respectively. However, our DFT calculations show that the IE decreases as the number of methyls between the rings increases (Figure 4). Then the methylation influence would become stronger on going from n = 0 to n = 3.

The opposite trend in the IE change observed in the MATI experiment can be explained as a result of an increase in the zero-point energy (ZPE) on introduction of additional Me groups. The ZPE in the chromium bisarene cation is higher than that in the corresponding neutral.^{15,19} The increase in the ZPE on methylation is, therefore, also larger for the cation. This would give a positive contribution to the IE shift. For instance, according to the BPW91/TZVP calculations, the ZPE-(cation)–ZPE(neutral) difference increases from 385 to 531 cm⁻¹ when one goes from **2_180** to **3_180**, so this effect can well be responsible for the observed deviations from the linear dependence of the IE on the number of methyl groups in the alkyl substituents of complexes 1-4.

Conclusions

MATI spectroscopy in combination with DFT calculations appears to be an extremely efficient method for investigations of alkylated derivatives of $bis(\eta^6$ -benzene)chromium. The spectra of the jet-cooled MePh and EtPh complexes reveal two intense 000 MATI peaks arising from ionizations of rotational isomers. For complex 1, the long-wavelength band is more intense because it arises from ionizations of three rotational isomers (1_60, 1_120, and 1_180), and the higher-energy peak corresponds to the 1_0 molecules. A higher relative intensity of the short-wavelength 0_0^0 feature in the spectrum of the ethylated compound is explained by the contribution of the most stable 2_120 conformer, together with the 2_0 species. The 1 and 2 spectra also reveal weaker bands corresponding to the cationic vibrational levels that have been interpreted on the basis of DFT calculations. The MATI spectra provide accurate experimental frequencies of the low-energy vibrations of the gas-phase bisarene cations. The spectra of the compounds bearing *i*-Pr and *t*-Bu groups show one 0_0^0 component because of close ionization potentials of the contributing isomers, as indicated by DFT. The precise values of ionization energies obtained from the MATI spectra reveal a nonlinear dependence of the IE on the number of Me groups in the alkyl substituents of $(\eta^6$ -RPh)₂Cr. This can be explained by an increase in the zero point energy difference between the cation and the neutral molecule on methylation of the substituents.

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