Supporting Information

Laser spectroscopic and computational insights into unexpected structural behaviours of sandwich complexes on ionization

S. Yu. Ketkov*, S.-Y. Tzeng, E. A. Rychagova, G. V. Markin, S. G. Makarov, and W.-B. Tzeng*

Table of content

Experimental details

All manipulations with the air and moisture sensitive compounds were carried out under an inert atmosphere using standard Schlenk tube technique or in evacuated ampoules. (η^7-Cycloheptatrienyl)(η^5-cyclopentadyenyl)chromium (**1**) was synthesized according to the known procedure[S1] by reduction of $CrCl_3 \cdot 3THF$ with *i*-PrMgBr in the presence of cycloheptatriene and freshly distilled cyclopentadiene. The mixed sandwich complex was purified by subsequent vacuum sublimation. The purity of the compound was checked by measuring the NMR and mass spectra. (η^8-Cyclooctatetraene)(η^5-cyclopentadyenyl)titanium (**2**) was prepared using the previously reported route[S2] by reduction of $CpTiCl_3$ with magnesium turnings in the presence of C_8H_8. The complex was purified by repeated vacuum sublimation. Its photoionization mass spectrum revealed no impurities influencing the MATI measurements. The setup described earlier[S3] was used in the MATI experiments. The mixed sandwich compound was placed into the stainless still tube heated up to 170-190 °C and the sample vapour seeded into 1.5 bar of helium was expanded into the vacuum through a heated pulsed valve. A molecular beam was formed from the supersonic jet by a skimmer. Tunable laser pulses in the 215-227 nm region were obtained by the BBO-I crystal frequency doubling of the dye laser output (Lambda-Physik, Scanmate UV) pumped by a Nd:YAG laser (Quanta-Ray PRO-190-10). The wavelengths of the dye lasers were calibrated with a laser wavemeter (Coherent, WaveMaster). A pulsed electric field of ~1 V/cm was applied about 20 ns after the laser pulses to remove the prompt ions. About 11 μs later, a second pulsed electric field of +200 V/cm was applied to ionize the ZEKE-state neutrals. The newly formed threshold ions were directed to the time-of-flight mass spectrometer and detected by a microchannel plate particle detector. The molecular ion signals (m/z = 208 amu ($C_{12}H_{12}Cr^+$) and m/z = 217 amu ($C_{13}H_{13}Ti^+$)) were selected to record the MATI spectra of complexes **1** and **2**, respectively.

Computational details

The geometry optimizations and harmonic vibrational frequency calculations for the neutral and cationic complexes (Ch)(Cp)Cr, (Cot)(Cp)Ti, $(Bz)_2Cr$, $(Bz)_2Ti$, $(Cp)_2Co$ (Ch=η^7-C_7H_7, Cp=η^5-C_5H_5, Cot=η^8-C_8H_8, Bz=η^6-C_6H_6) were carried out at two DFT levels: BPW91/TZVP (DFT1) with the "pure" BPW91 functional[S4] in combination with the triple-ζ valence-split TZVP basis set.[S5] and B3PW91/6-311++G(d,p) (DFT2) with the hybrid B3PW91 functional[S6] and the triple-ζ split valence basis 6-311++G(d,p) including diffuse and polarization functions on hydrogen and the heavy atoms.[S7] The B3PW91/6-311++G(d,p) level of theory was shown to perform well when modeling the MATI spectra of bis-arene complexes.[S8] The BPW91/TZVP combination was successfully used earlier in the MATI study of cobaltocene.[S9] The computations were carried out with the Gaussian 09 program package.[S10] The model MATI spectra were produced on the basis of the Franck-Condon factors calculated with the optimized neutral and ion geometries. The low-frequency torsion ring vibrations were excluded when performing the simulations. The electron density (ED)

topology was analyzed within the frames of the Quantum Theory of Atoms in Molecules[S11] (QT AIM) with the use of the AIM ALL program suit.[S12] The critical points and bond paths were determined. The ED difference (EDD) isosurfaces were built as a result of the ground-state ED subtraction from the ionic ED at the ground-state geometry using the Multiwfn code.[S13]

Figures

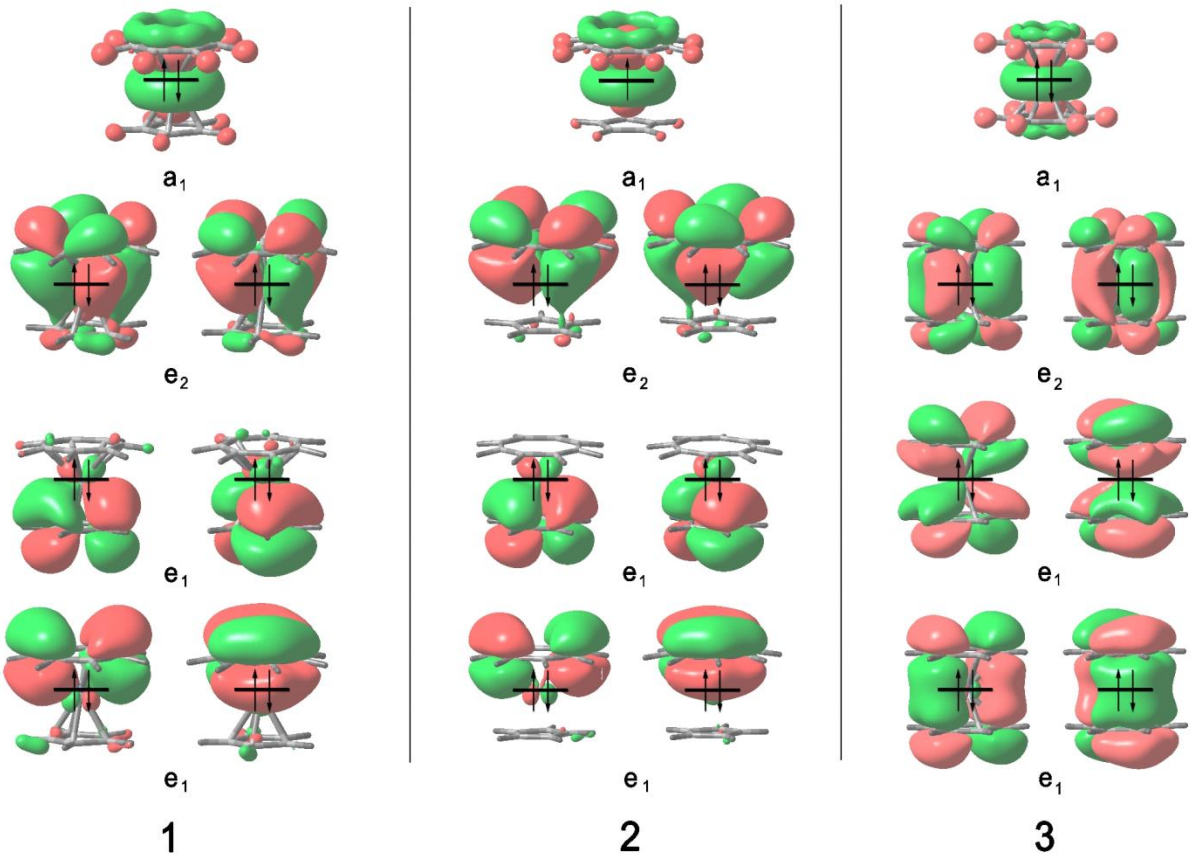
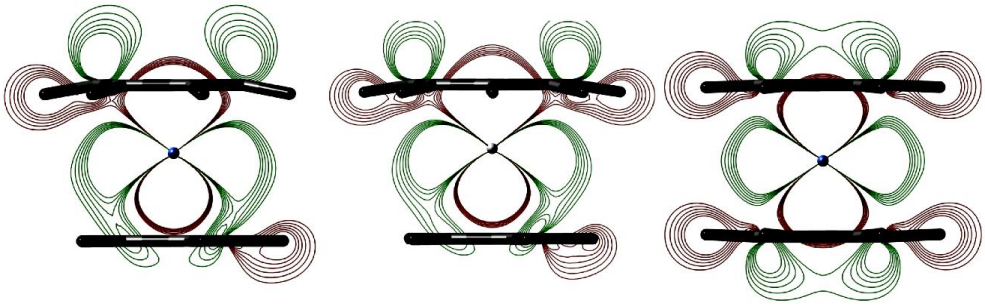


Fig. S1 The isosurfaces (isovalue ±0.02) of the higher occupied orbitals of neutral complexes (Ch)(Cp)Cr(**1**), (Cot)(Cp)Ti(**2**) and $(Bz)_2Cr$(**3**). The orbital populations are indicated.



(Ch)(Cp)Cr **(1)** 87% Cr(d)

(Cot)(Cp)Ti **(2)** 87% Ti(d)

$(Bz)_2Cr$ **(3)** 89% Cr(d)

Fig. S2 The B3PW91/6-311++G(d,p) contour maps (isolines ±(0.01-0.02), step 0.002) of MO $a_1(d_{z2})$ in the CMC (M=Cr, Ti) plane orthogonal to the carbocycles of neutral complexes **1** – **3**. The metal 3d contributions are given.

References

[S1] H. O. van Oven, C. J. Groenenboom, H. J. de Liefde Meijer, *J. Organomet. Chem*. **1974**, *81*, 379-384.

[S2] L. B. Kool, M. D. Rausch, R. D. Rogers, *J. Organomet.Chem.*, **1985**, *297*, 289.

[S3] Y. Xu, S. Y. Tzeng, V. Shivatare, K. Takahashi, B. Zhang, W. B. Tzeng, *J. Chem. Phys*., **2015**, *142*, 124314.

[S4] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B: Condens. Matter* **1992**, *46*, 6671-6687.

[S5] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835.

[S6] a) A. D. Becke, *J. Chem. Phys.* **1992**, *98*, 5648-5652; b) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B: Condens. Matter* **1996**, *54*, 16533-16539.

[S7] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654; b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem*. **1983**, *4*, 294-301.

[S8] S. Y. Ketkov, S.-Y. Tzeng, P.-Y. Wu, G. V. Markin, W.-B. Tzeng, *Chem. Eur. J.* **2017**, *23*, 13669-13675; b) S. Y. Ketkov, *Dalton Trans.* **2020**, *49*, 569-577.

[S9] S. Y. Ketkov, H. L. Selzle, *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 11527-11530.

[S10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, 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 B.01), Wallingford, CT: Gaussian Inc., **2010**.

[S11] 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*, 633-662.

[S12] T. A. Keith, *AIMAll* (Version 13.05.06), TK Gristmill Software, Overland Park KS, USA, **2013**, http://aim.tkgristmill.com.

[S13] a) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592; b) T. Lu, F. Chen, *J. Mol. Graphics Model.* **2012**, *38*, 314-323.

Atomic coordinates for the optimized sandwich molecules

25

$(C_7H_7)(C_5H_5)Cr$; BPW91/TZVP

Cr	0.049900	-0.000300	-0.000100
C	1.878900	-0.858300	0.860200
C	1.878600	-1.085500	-0.549300
C	1.879100	0.184900	-1.200700
H	1.881800	-1.624800	1.630400
H	1.881500	-2.055300	-1.039300
H	1.881000	0.352500	-2.274200
C	1.880400	0.552200	1.080000
C	1.880500	1.197000	-0.193800
H	1.884500	2.269800	-0.366200
H	1.884300	1.048500	2.046600
C	-1.391000	-0.932600	1.337500
C	-1.398600	-1.625700	0.104100
C	-1.398500	-1.094100	-1.206700
C	-1.390300	0.262700	-1.609200
H	-1.214500	-1.550400	2.221800
H	-1.222600	-2.702600	0.171400
H	-1.222000	-1.820200	-2.004900
H	-1.213500	0.434800	-2.674100
C	-1.389500	0.464800	1.563900
C	-1.391600	1.512600	0.613000
C	-1.389400	1.423200	-0.798800
H	-1.209300	2.511500	1.018500
H	-1.209400	2.363800	-1.326100

H -1.209900 0.772300 2.597500

25

$(C_7H_7)(C_5H_5)Cr^+$; BPW91/TZVP

Cr 0.058200 -0.000400 -0.000300

C 1.883200 -0.859800 0.860300

C 1.882700 -1.086300 -0.550200

C 1.884300 0.185100 -1.201900

H 1.873500 -1.625700 1.629400

H 1.874400 -2.054600 -1.040900

H 1.876400 0.352100 -2.274500

C 1.884300 0.551800 1.080500

C 1.885500 1.197600 -0.194000

H 1.878600 2.269400 -0.366000

H 1.877100 1.047000 2.046400

C -1.381500 -0.934400 1.341600

C -1.388200 -1.629900 0.104900

C -1.385900 -1.097300 -1.209600

C -1.380100 0.263600 -1.613300

H -1.224000 -1.552000 2.225600

H -1.230800 -2.706400 0.173600

H -1.230500 -1.822600 -2.008300

H -1.223000 0.435500 -2.677900

C -1.379300 0.466800 1.568500

C -1.381800 1.517400 0.615000

C -1.381200 1.427300 -0.800600

H -1.220100 2.516400 1.020100

H -1.221200 2.367100 -1.329200

H -1.220400 0.773200 2.602300

27

$(C_8H_8)(C_5H_5)Ti$; BPW91/TZVP

C 1.390600 1.219100 1.385500

C 1.390000 -0.117500 1.841900

C 1.389000 -1.385700 1.219300

C 1.389700 -1.842200 -0.117500

H 1.224400 1.932500 2.196000

H 1.223900 -0.186200 2.919400

H 1.223600 -2.196200 1.932800

H 1.222500 -2.919600 -0.186100

C 1.389800 1.841700 0.117400

C 1.390700 1.385200 -1.219500

C 1.389200 -1.219700 -1.385300

H 1.224300 2.195700 -1.932800

H 1.223600 -1.933000 -2.196000

H 1.225100 2.919400 0.186100

C 1.389900 0.117400 -1.841800

H 1.224300 0.186000 -2.919400

C -2.131200 -0.999100 0.684500

C -2.131200 -0.959600 -0.738900

H -2.135300 -1.820300 -1.401500

C -2.131200 0.406400 -1.141200

H -2.135400 0.770600 -2.164600

C -2.131100 0.342500 1.162000

H -2.135300 0.649300 2.204000

C -2.131200 1.211100 0.033600

H -2.135300 2.297000 0.063800

H -2.135000 -1.895300 1.298400

Ti -0.086100 0.000100 -0.000000

27

$(C_8H_8)(C_5H_5)Ti^+$; BPW91/TZVP

C 1.327600 1.206600 1.402700

C 1.327600 -0.138900 1.845200

C 1.325800 -1.403800 1.206500

C 1.326300 -1.846500 -0.139400

H 1.162200 1.909400 2.219400

H 1.162300 -0.219800 2.919700

H 1.161600 -2.220600 1.909400

H 1.159400 -2.920900 -0.219900

C 1.326200 1.845300 0.137800

C 1.326900 1.402700 -1.208100

C 1.324900 -1.208000 -1.403800

H 1.160300 2.219500 -1.910600

H 1.159300 -1.910500 -2.220700

H 1.162100 2.919900 0.218600

C 1.325100 0.138200 -1.846600

H 1.159700 0.218700 -2.921000

C -2.038100 -0.976700 0.717500

C -2.038900 -0.982600 -0.707200

H -2.035800 -1.863700 -1.341800

C -2.038300 0.370600 -1.153200

H -2.034600 0.701800 -2.187300

C -2.036900 0.380200 1.152200

H	-2.031900	0.720000	2.183500
C	-2.037100	1.212900	-0.004000
H	-2.032400	2.298700	-0.008500
H	-2.034400	-1.852500	1.359400
Ti	-0.046800	-0.000200	-0.000000

25

$(C_7H_7)(C_5H_5)Cr$; B3PW91/6-311++g(d,p)

C	0.114500	0.045800	-0.134200
C	-0.092400	0.044800	1.270300
C	1.179400	0.041900	1.901300
C	2.172500	0.041300	0.886800
C	1.514300	0.044000	-0.371200
Cr	0.980500	1.871000	0.712300
H	1.995100	0.041300	-1.339800
H	3.242300	0.036100	1.044500
H	-0.658500	0.046000	-0.890400
H	-1.050600	0.042200	1.771600
H	1.359800	0.038700	2.967600
C	2.510700	3.285700	0.170100
C	1.510200	3.284300	-0.820600
C	0.111200	3.286200	-0.655600
C	2.360400	3.283700	1.569500
C	-0.631400	3.289200	0.540300
C	1.171900	3.280000	2.325100
H	3.519600	3.099400	-0.189100
H	1.858900	3.101900	-1.833700
H	-0.463600	3.102600	-1.559500

H 3.270100 3.095800 2.133900

H -1.696300 3.103800 0.425600

H 1.297200 3.094400 3.388600

C -0.159900 3.284000 1.866600

H -0.914100 3.099700 2.627300

25

$(C_7H_7)(C_5H_5)Cr^+$; B3PW91/6-311++g(d,p)

C 0.121500 -0.000600 -0.144200

C -0.099100 -0.000900 1.259000

C 1.167200 -0.000800 1.902800

C 2.170600 -0.000100 0.897300

C 1.524200 0.000200 -0.367700

Cr 0.976300 1.809100 0.710100

H 2.013900 0.006300 -1.331200

H 3.238400 0.007000 1.065000

H -0.643500 0.006700 -0.907600

H -1.061600 0.004300 1.750700

H 1.337100 0.005700 2.970200

C 2.350400 3.231800 -0.158200

C 1.154300 3.228700 -0.906100

C -0.177100 3.223900 -0.436900

C 2.511900 3.228200 1.243600

C -0.640000 3.227400 0.896600

C 1.515900 3.227500 2.244200

H 3.257300 3.068700 -0.730900

H 1.272400 3.066500 -1.972100

H -0.937300 3.063300 -1.193700

H 3.525200 3.068000 1.595600

H -1.705400 3.064200 1.019600

H 1.872800 3.066800 3.255800

C 0.113400 3.230100 2.089300

H -0.454900 3.065900 2.998700

27

$(C_8H_8)(C_5H_5)Ti$; B3PW91/6-311++g(d,p)

C 0.109500 0.555200 -0.092200

C -0.094100 0.510800 1.309300

C 1.176200 0.465300 1.935200

C 2.165000 0.481500 0.920400

C 1.505700 0.536900 -0.332500

H 1.984100 0.556900 -1.302200

H 3.235000 0.451700 1.074900

H -0.664900 0.591200 -0.846200

H -1.051200 0.507200 1.812800

H 1.359000 0.421300 3.000100

C 2.790900 3.973700 0.316900

C -0.589900 4.047800 0.018600

C 2.666600 3.927600 1.716500

C -0.714400 4.001700 1.418800

C 1.588200 3.916600 2.619300

H 3.811500 3.795600 -0.010900

H -1.544400 3.913500 -0.483000

H 3.614400 3.722900 2.206700

H -1.741500 3.841300 1.734800

H 1.906400 3.706600 3.636700

C	0.187900	3.948300	2.495900
H	-0.312000	3.755000	3.441100
C	0.488100	4.058900	-0.883800
H	0.163600	3.930400	-1.912800
C	1.888600	4.027300	-0.760400
H	2.382200	3.882200	-1.717400
Ti	1.010800	2.541200	0.817900

27

$(C_8H_8)(C_5H_5)Ti^+$; B3PW91/6-311++g(d,p)

C	0.018600	0.235100	-0.030000
C	-0.008200	0.233200	1.387100
C	1.331100	0.219100	1.850600
C	2.185800	0.212000	0.719900
C	1.374600	0.221800	-0.442400
H	1.728100	0.223400	-1.464100
H	3.266700	0.204800	0.740400
H	-0.843700	0.248500	-0.681900
H	-0.894700	0.245400	2.005900
H	1.645700	0.218300	2.884900
C	2.489000	3.516500	-0.401400
C	-0.807900	3.549700	0.438900
C	2.837000	3.509400	0.964200
C	-0.459700	3.542900	1.804700
C	2.117400	3.516200	2.176300
H	3.344500	3.333200	-1.043000
H	-1.869500	3.386100	0.286100
H	3.895200	3.325000	1.116800

H	-1.319100	3.378300	2.446100
H	2.757200	3.334100	3.033400
C	0.752200	3.530400	2.524300
H	0.597400	3.355900	3.583900
C	-0.088600	3.543100	-0.772600
H	-0.731600	3.377300	-1.630500
C	1.277500	3.529000	-1.120800
H	1.428200	3.355600	-2.181000
Ti	1.000600	2.189900	0.699900