

A Copper(I)–Arene Complex With an Unsupported η^6 Interaction**

Ashley M. Wright, Benjamin J. Irving, Guang Wu, Anthony J. H. M. Meijer, and Trevor W. Hayton*

Abstract: Addition of PR_3 ($R = Ph$ or OPh) to $[Cu(\eta^6-Me_6C_6)_2][PF_6]$ results in the formation of $[(\eta^6-Me_6C_6)Cu(PR_3)][PF_6]$, the first copper–arene complexes to feature an unsupported η^6 arene interaction. A DFT analysis reveals that the preference for the η^6 binding mode is enforced by the steric clash between the methyl groups of the arene ligand and the phenyl rings of the phosphine co-ligand.

The synthesis of the first metal–arene complex $Cr(\eta^6-C_6H_6)_2$, nearly 100 years ago by Hein and co-workers,^[1] was an important milestone in the development of organometallic chemistry.^[2–4] Since its discovery, metal–arene complexes have been isolated for most of the transition metal elements,^[5–10] and these species have found use in a wide variety of applications. For example, the binding of an arene to a metal activates the ring toward nucleophilic addition, and also renders the ring protons more acidic, making these species synthetically useful.^[11] In addition, metal–arene complexes have found utility as both catalyst precursors and common starting materials.^[12,13] These points are well illustrated by the chemistry of the coinage metals. For example, Cu–arene species are thought to play a role in copper(I)-catalyzed cross-coupling reactions.^[14] Cu–arene complexes are also precursors for catalytic alkoxylation and amination reactions,^[15] and are known to mediate the reaction of Cu^I with oxygen.^[16,17]

Group 11 metal–arene complexes strongly prefer the η^2 binding mode.^[12,18–23] This binding mode is favored as it lessens the interaction between the filled nd orbitals with the filled arene π orbitals.^[24] Consistent with this analysis, the

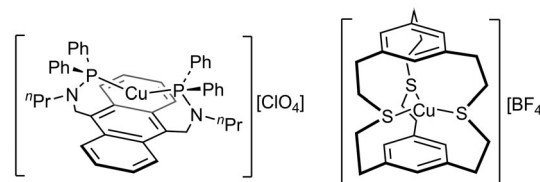
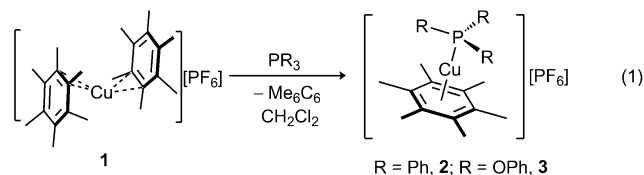


Figure 1. Known examples of Cu(η^6 -arene) interactions.

only reported Cu arene complexes that contain the η^6 binding mode feature tethered arene rings and long Cu–C_{cent} distances (≈ 2.5 – 3.0 Å) indicative of weak interactions (Figure 1).^[25,26] Interestingly, though, the η^6 configuration is proposed to be slightly more stable than the η^2 configuration for the “naked” $[Cu(C_6H_6)]^+$ fragment in the gas phase, but the difference between the η^6 and η^2 modes is less than 1 kJ mol^{−1}.^[27] Inclusion of a counterion, such as a halide or pseudohalide, to the Cu coordination sphere was calculated to increase the stability of the η^2 mode over η^6 ,^[28] which led to the proposal that the unsupported η^6 -arene–copper interaction is unlikely to be observed in the condensed state.^[28]

Herein, we report the synthesis and structural characterization of the first Cu^I–arene complexes that feature unsupported η^6 interactions, demonstrating that complexes of this type are, in fact, isolable.

We previously reported the synthesis of the copper–arene sandwich complex, $[Cu(\eta^2-Me_3C_6H_3)_2][PF_6]$, which was prepared by oxidation of Cu metal with $[NO][PF_6]$ in the presence of mesitylene.^[29] The hexamethylbenzene analogue, $[Cu(\eta^2-Me_6C_6)_2][PF_6]$ (**1**), was prepared in a similar fashion. As determined by X-ray crystallography, complex **1** features two Me_6C_6 ligands coordinated to Cu through η^2 interactions. The Cu–C bond lengths are 2.092(2) and 2.192(2) Å, and are comparable with those previously reported for η^2 -arene,^[13,22,30] alkyne,^[31] and alkene^[32] complexes of copper.



With **1** in hand, we postulated that substitution of one Me_6C_6 ligand with a $2e$ σ -donor ligand would result in a η^2 to η^6 ring slip to generate a pseudotetrahedral $18e^-$ Cu^I complex. Gratifyingly, addition of 1 equiv of PR_3 ($R = Ph$, OPh) to a CH_2Cl_2 solution of **1** results in formation of the half-sandwich complexes $[(\eta^6-Me_6C_6)Cu(PR_3)][PF_6]$ ($R = 2, Ph; 3, OPh$) [Eq. (1)]. Complexes **2** and **3** can be crystallized from

[*] Dr. A. M. Wright, Dr. G. Wu, Prof. Dr. T. W. Hayton
Department of Chemistry and Biochemistry
University of California Santa Barbara
Santa Barbara, CA 93106 (USA)
E-mail: hayton@chem.ucsb.edu

Dr. A. J. H. M. Meijer
Department of Chemistry, University of Sheffield
Sheffield, S3 7HF (UK)

Dr. B. J. Irving
Department of Control Engineering
Faculty of Electrical Engineering
Czech Technical University in Prague
Karlovo náměstí 13, 121 35 Prague 2 (Czech Republic)

[**] Research at UCSB was supported by the University of California, Santa Barbara and the National Science Foundation (CHE 1059097). This publication was also supported by the European social fund within the framework of the project “Support of inter-sectoral mobility and quality enhancement of research teams at Czech Technical University in Prague” (CZ.1.07/2.3.00/30.0034).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201410948>.

CH_2Cl_2 /hexanes at -25°C to give colorless blocks in moderate to good yields (**2**: 40%; **3**: 78%).

Single crystals of **2** and **3** suitable for X-ray crystallography were grown from a dilute CH_2Cl_2 /hexane solution at -25°C . Both complexes feature a copper(I) center bound by a $\eta^6\text{-Me}_6\text{C}_6$ ligand and a single PR_3 ligand, in an overall pseudotetrahedral geometry (Figure 2). The η^6 coordination

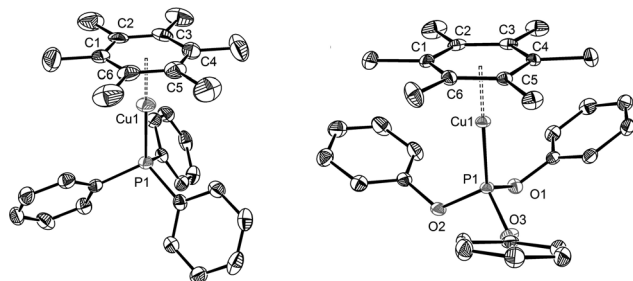


Figure 2. ORTEP drawing of $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{PPh}_3)][\text{PF}_6]$ (**2**) (left) and $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{P}(\text{OPh})_3)][\text{PF}_6]$ (**3**) (right). Hydrogen atoms and a PF_6^- anion have been omitted for clarity. Ellipsoids are shown at 50% probability.

mode of the Me_6C_6 ligand is exemplified by the narrow range of $\text{Cu}-\text{C}_{\text{aryl}}$ bond lengths (**2**: 2.284(5)–2.293(5) Å; **3**: 2.253(1)–2.300(1) Å) and short $\text{Cu}-\text{C}_{\text{cent}}$ distances (**2**: 1.800(3) Å; **3**: 1.775(6) Å). Notably, these $\text{Cu}-\text{C}_{\text{cent}}$ distances are significantly shorter than those previously reported for the tethered $\text{Cu}^1\text{-}\eta^6\text{-arene}$ interactions (Figure 1).^[25,26] For instance, Mascal and co-workers reported a Cu^1 cyclophane complex that features a $\text{Cu}-\text{C}_{\text{cent}}$ distance of 2.97 Å.^[25] Similarly, Zhang and co-workers reported a Cu^1 complex, supported by 9,10-bis[*N,N*-propyl-*N*-(diphenylphosphino)aminomethyl]anthracene, which features a $\text{Cu}-\text{C}_{\text{cent}}$ distance of 2.50 Å.^[26] Finally, the average C–C bond length of the Me_6C_6 ligand in **2** is 1.411 Å (range = 1.395(7)–1.423(7) Å), and is comparable with those of unbound Me_6C_6 , suggesting that there is little net charge transfer in the Cu –arene interaction.^[9] Complex **3** features comparable C–C bond lengths for its Me_6C_6 ligand (1.416(1)–1.421(2) Å). The $\text{Cu}-\text{P}$ bond lengths in **2** (2.158(2) Å) and **3** (2.124(4) Å) are similar to those of $(\eta^5\text{-Cp})\text{Cu}(\text{PPh}_3)$ (2.116(2) Å).^[33,34]

The binding of an arene to a metal can result in a significant shift of its ^{13}C resonances.^[35] However, only small shifts are observed for the aryl carbons in **2** (131.2 ppm) versus those of unbound Me_6C_6 (132.1 ppm). A slight downfield shift of the aryl carbon is observed for **3** (149.2 ppm). Additionally, the methyl carbon resonances in **2** and **3** do not differ significantly from those observed for unbound Me_6C_6 (**2**: 19.06 ppm; **3**: 16.07 ppm; free Me_6C_6 : 16.71 ppm). Overall, these data are consistent with a relatively weak Cu –arene interaction.

To gain further insight into the bonding interactions in **2** and **3**, DFT calculations were performed. For comparison, the “naked” Cu –arene complexes, $[\text{Cu}(\text{C}_6\text{H}_6)]^+$ and $[\text{Cu}(\text{C}_6\text{Me}_6)]^+$, were also studied, as were their C_6H_6 -bearing sister molecules, $[(\text{C}_6\text{H}_6)\text{Cu}(\text{PPh}_3)]^+$ and $[(\text{C}_6\text{H}_6)\text{Cu}(\text{P}(\text{OPh})_3)]^+$. The optimized coordinates for all calculated

Table 1: Calculated relative energies for different binding modes of **2** and **3**.

Complex	$\Delta E(\eta^6-\eta^2)$ [kJ mol^{-1}]	
	Gas phase	CH_2Cl_2
$[\text{Cu}(\text{C}_6\text{H}_6)]^+$	9.79	17.6 ^[a]
$[\text{Cu}(\text{C}_6\text{Me}_6)]^+$	−3.99	4.51
2 / PPh_3 ^[c]	−8.78	−7.19 ^[b]
3 / $\text{P}(\text{OPh})_3$ ^[c]	−13.83	−12.16

[a] The η^6 structure is not a stationary point, so it was calculated as a restricted optimization at a fixed C_{6v} geometry. [b] The η^6 structure in this case is actually slightly off center, that is, η^4 . [c] The η^2 binding mode was calculated using a restricted optimization.

species are given in the Supporting Information (SI). The energy differences between the η^6 and η^2 binding modes for the naked complexes and **2** and **3** are tabulated in Table 1. For the “naked” complexes the calculations reveal that the η^2 structures are generally more stable (apart from $[\text{Cu}(\text{C}_6\text{Me}_6)]^+$ in the gas phase), in accordance with earlier calculations.^[27,28] Structurally, the two η^6 complexes feature similar geometries; however, the Cu^+ ion in $[\text{Cu}(\eta^6\text{-C}_6\text{Me}_6)]^+$ is closer to the arene than in $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ ($\text{Cu}-\text{C}_{\text{cent}}$ = 1.66 Å and 1.73 Å, respectively). The two η^2 structures are also similar, but the distance between Cu^+ and the C=C bond has increased to 1.89 Å and 1.92 Å for $[\text{Cu}(\eta^2\text{-C}_6\text{Me}_6)]^+$ and $[\text{Cu}(\eta^2\text{-C}_6\text{H}_6)]^+$, respectively.

Interestingly, the addition of PPh_3 or $\text{P}(\text{OPh})_3$ to the $[\text{Cu}(\text{arene})]^+$ motif results in a reversal of the favored arene binding mode. The η^6 motif becomes favored by 8.78 and 13.83 kJ mol^{-1} for **2** and **3** (in the gas phase), respectively (Table 1). Inclusion of solvent (CH_2Cl_2) in the calculation results in a slight destabilization of the η^6 binding mode relative to the η^2 mode, which we attribute to the attenuation of the electrostatic interaction due to the change in dielectric constant from vacuum to CH_2Cl_2 , but the η^6 mode is still favored. We attribute the lower stability of the η^2 mode to the steric clash between the CH_3 groups on Me_6C_6 and the $[\text{Cu}(\text{PR}_3)]^+$ moiety. The larger $\Delta E(\eta^6-\eta^2)$ values calculated for compound **3**, which features the phenyl groups on the $\text{P}(\text{OPh})_3$ moiety pointing toward the methyl groups of the Me_6C_6 ligand (see Table 1, Figure S18), also support the notion that sterics dictate the binding mode. Moreover, we calculate that $[(\text{C}_6\text{H}_6)\text{Cu}(\text{PPh}_3)]^+$, which features the smaller C_6H_6 ligand, prefers the η^2 motif, whereas $[(\text{C}_6\text{H}_6)\text{Cu}(\text{P}(\text{OPh})_3)]^+$ exhibits a preference for a η^1 motif, consistent with a diminished steric clash between the C_6H_6 ring and the $[\text{Cu}(\text{PR}_3)]^+$ fragment (see SI). The isolation of **1** is also consistent with this argument, as it shows that a η^2 binding mode of the Me_6C_6 ligand is preferred in the absence of a phosphine co-ligand. Thus, several lines of evidence support the argument that sterics do play a dominating role in the choice of final binding mode.

Inspection of the molecular orbitals (both for B3LYP and for a Hartree–Fock calculation, based on the DFT-optimized geometry) does not give a clear molecular orbital picture for the Cu –arene interaction. Moreover, the effect of solvent on the relative stabilities of the η^2 and η^6 binding modes, along with the importance of sterics in determining the hapticity,

suggest a significant electrostatic component to the interaction. Thus, to elucidate the bonding interaction further, the complexes were studied using a Mulliken partitioning scheme, permitting the Mulliken charges of the Cu^+ ions in **2** and **3** to be calculated. The calculated Cu^+ charges for **2** and **3** are 0.86 and 0.81 (in CH_2Cl_2), respectively (Table 2). Both of these

Table 2: Mulliken charges on the central Cu^+ ion for complexes **2** and **3** with a η^6 bound arene.

Complex	Gas phase	CH_2Cl_2
2 / PPh_3	0.83	0.86
3 / $\text{P}(\text{OPh})_3$	0.78	0.81

values are close to 1, which supports a largely electrostatic bonding interaction with very little covalency. The electrostatic bonding arrangement is further supported by analysis of the total electron density isosurfaces of **2** and **3** (see SI for details).^[36] We used H_2 (0.24 a.u.) and LiF (0.005 a.u.) as benchmarks for covalent and ionic bonding, respectively (see SI). The calculated values for **2** and **3** (in vacuo) are: **2**: $\eta^2 = 0.07$ a.u., $\eta^6 = 0.05$ a.u.; **3**: $\eta^2 = 0.07$ a.u., $\eta^6 = 0.05$ a.u. Notably, these values are similar to that calculated for LiF , which supports the conclusion that arene binding in **2** and **3** is largely electrostatic. These data also suggest that the character of the Cu–arene interaction is insensitive to the choice of PR_3 ligand, but is sensitive to the coordination mode: i.e., the lower electron density cutoff values for the η^6 coordination mode indicate a less covalent interaction than the η^2 mode. Similar results are also observed for the ‘naked’ systems. For example, for $[\text{Cu}(\text{C}_6\text{H}_6)]^+$, the maximum values of the electron densities are 0.08 a.u. for the η^2 mode and 0.055 for the η^6 mode. Our calculations also show that the η^2 motif for the ‘naked’ systems becomes relatively more stable with the introduction of the CH_2Cl_2 solvent into the calculation, which indicates that the binding between naked Cu^+ and the arene is also largely electrostatic in character, in accordance with previous results.^[27,28]

Finally, the isolation of complexes **2** and **3** allows for a structural comparison with other first-row $\text{M}(\eta^6\text{-arene})$ complexes. A search of the Cambridge structural database reveals the existence of 77 $18e^- \text{M}(\eta^6\text{-C}_6\text{R}_6)$ ($\text{R} = \text{H}$ or Me) complexes of the first-row transition metals (Cr to Ni). Figure 3 depicts the average $\text{M}-\text{C}_{\text{cent}}$ distance for each element for this series of complexes. Most importantly, **2** and **3** feature the longest $\text{M}-\text{C}_{\text{cent}}$ distances, which supports our contention that the Cu–arene interaction is weak and predominantly electrostatic in nature, a consequence of the contracted nature of the $3d^{10}$ shell. This contention is further supported by the observed decrease in $\text{M}-\text{C}_{\text{cent}}$ distances on moving from Cu to Fe. This decrease can be rationalized by the better energy match of the $3d$ orbitals with the arene π^* orbitals as one moves from right to left across the row, which permits a more effective back-bonding interaction.

In summary, we have isolated and structurally characterized the first copper complexes with an unsupported η^6 arene interaction. This completes the series of known unsupported

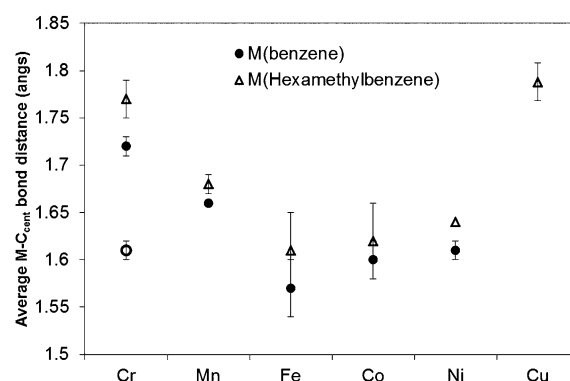


Figure 3. Average $\text{M}-\text{C}_{\text{cent}}$ distances for $18e^- \text{M}(\eta^6\text{-C}_6\text{R}_6)$ complexes ($\text{R} = \text{H}$, closed circles, or Me , open triangles) in the Cambridge Structural Database.^[19] The open circle represents $\text{Cr}(\text{benzene})\text{L}_3$ -type complexes, in which L is not a carbonyl ligand (9 examples).

$[\text{M}(\eta^6\text{-C}_6\text{R}_6)]^+$ first-row transition metal complexes. These copper–arene complexes have much shorter $\text{Cu}-\text{C}_{\text{cent}}$ distances (≈ 1.80 Å) than those previously reported for $\text{Cu}(\eta^6\text{-arene})$ compounds. Despite this structural difference, density functional theory calculations show that the Cu^+ –arene interaction is largely electrostatic in nature, whereas the preference for the η^6 binding mode is enforced by the steric clash between the methyl groups of the arene ligand and the phenyl rings of the phosphine co-ligand.

Received: November 11, 2014

Published online: January 21, 2015

Keywords: bonding analysis · copper · metal arenes · organometallic compounds · π complexes

- [1] F. Hein, *Ber. Dtsch. Chem. Ges.* **1919**, 52, 195–196.
- [2] E. O. Fischer, W. Hafner, *Z. Naturforsch. Part B* **1955**, 10, 665–668.
- [3] G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, 74, 2125–2126.
- [4] P. Powell, *Principles of Organometallic Chemistry*, 2nd ed., Chapman and Hall, New York, **1988**.
- [5] H. G. Smith, R. E. Rundle, *J. Am. Chem. Soc.* **1958**, 80, 5075–5080.
- [6] R. K. McMullan, T. F. Koetzle, C. J. Fritchie Jr, *Acta Crystallogr. Sect. B* **1997**, 53, 645–653.
- [7] E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, T. Albright, *Chem. Rev.* **1982**, 82, 499–525.
- [8] M. N. Bochkarev, *Chem. Rev.* **2002**, 102, 2089–2118.
- [9] S. M. Hubig, S. V. Lindeman, J. K. Kochi, *Coord. Chem. Rev.* **2000**, 200, 831–873.
- [10] G. Pampaloni, *Coord. Chem. Rev.* **2010**, 254, 402–419.
- [11] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd ed., Wiley, New York, **2001**.
- [12] M. B. Dines, P. H. Bird, *J. Chem. Soc. Chem. Commun.* **1973**, 12–12.
- [13] G. Santiso-Quinones, A. Higelin, J. Schaefer, R. Brückner, C. Knapp, I. Krossing, *Chem. Eur. J.* **2009**, 15, 6663–6677.
- [14] D. Ma, Y. Zhang, J. Yao, S. Wu, F. Tao, *J. Am. Chem. Soc.* **1998**, 120, 12459–12467.
- [15] R. T. Gephart, C. L. McMullin, N. G. Sapiezynski, E. S. Jang, M. J. B. Aguilá, T. R. Cundari, T. H. Warren, *J. Am. Chem. Soc.* **2012**, 134, 17350–17353.

- [16] T. Osako, Y. Tachi, M. Doe, M. Shiro, K. Ohkubo, S. Fukuzumi, S. Itoh, *Chem. Eur. J.* **2004**, *10*, 237–246.
- [17] T. Osako, Y. Tachi, M. Taki, S. Fukuzumi, S. Itoh, *Inorg. Chem.* **2001**, *40*, 6604–6609.
- [18] R. W. Turner, E. L. Amma, *J. Am. Chem. Soc.* **1966**, *88*, 1877–1882.
- [19] Cambridge Structural Database, 6.16 ed., **2014**.
- [20] R. R. Conry, *Chem. Commun.* **1998**, 555–556.
- [21] R. R. Conry, W. S. Striejske, A. A. Tipton, *Inorg. Chem.* **1999**, *38*, 2833–2843.
- [22] A. M. Dattelbaum, J. D. Martin, *Inorg. Chem.* **1999**, *38*, 6200–6205.
- [23] S. Y. Lee, S. J. Na, H. Y. Kwon, B. Y. Lee, S. O. Kang, *Organometallics* **2004**, *23*, 5382–5385.
- [24] F. Meyer, F. A. Khan, P. B. Armentrout, *J. Am. Chem. Soc.* **1995**, *117*, 9740–9748.
- [25] M. Mascal, J.-L. Kerdelhué, A. J. Blake, P. A. Cooke, *Angew. Chem. Int. Ed.* **1999**, *38*, 1968–1971; *Angew. Chem.* **1999**, *111*, 2094–2096.
- [26] F.-B. Xu, Q.-S. Li, L.-Z. Wu, X.-B. Leng, Z.-C. Li, X.-S. Zeng, Y. L. Chow, Z.-Z. Zhang, *Organometallics* **2003**, *22*, 633–640.
- [27] T. K. Dargel, R. H. Hertwig, W. Koch, *Mol. Phys.* **1999**, *96*, 583–591.
- [28] S.-L. Zhang, L. Liu, Y. Fu, Q.-X. Guo, *J. Mol. Struct.* **2005**, 757, 37–46.
- [29] A. M. Wright, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 14336–14337.
- [30] D. S. Laitar, C. J. N. Mathison, W. M. Davis, J. P. Sadighi, *Inorg. Chem.* **2003**, *42*, 7354–7356.
- [31] A. Das, C. Dash, M. A. Celik, M. Yousufuddin, G. Frenking, H. V. R. Dias, *Organometallics* **2013**, *32*, 3135–3144.
- [32] G. Santiso-Quiñones, A. Reisinger, J. Slattey, I. Krossing, *Chem. Commun.* **2007**, 5046–5048.
- [33] F. A. Cotton, J. Takats, *J. Am. Chem. Soc.* **1970**, *92*, 2353–2358.
- [34] J. A. Tang, B. D. Ellis, T. H. Warren, J. V. Hanna, C. L. B. Macdonald, R. W. Schurko, *J. Am. Chem. Soc.* **2007**, *129*, 13049–13065.
- [35] J. A. Chudek, G. Hunter, R. L. MacKay, P. Kremminger, K. Schlogl, W. Weissensteiner, *J. Chem. Soc. Dalton Trans.* **1990**, 2001–2005.
- [36] B. J. Irving, F. Y. Naumkin, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7697–7709.