On the regioselectivity of nucleophilic additions to anisole-Cr(CO)$_3$ and related complexes: a density functional study

Anja Pfletschinger,[a] Wolfram Koch[b] and Hans-Günther Schmalz*[a]

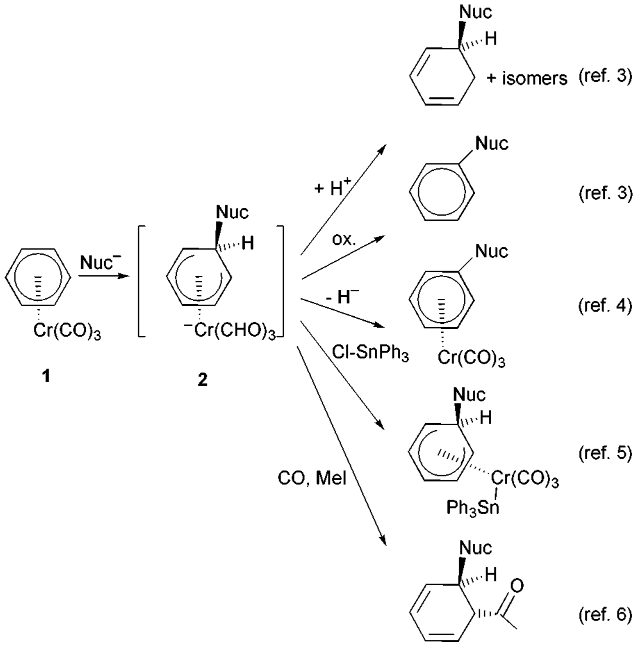
[a] *Institut für Organische Chemie, Universität zu Köln, Greinstrasse 4, D-50939 Köln, Germany. E-mail: schmalz@uni-koeln.de*
[b] *Gesellschaft Deutscher Chemiker, Postfach 900440, D-60444 Frankfurt, Germany*

Received (in Freiburg, Germany) 5th April 2000, Accepted 19th December 2000
First published as an Advance Article on the web 14th February 2001

The *meta* regioselectivity of the nucleophilic addition to methoxy-substituted arene-Cr(CO)$_3$ complexes has been investigated by theoretical methods using density functional calculations employing the hybrid-DFT approach Becke3LYP and a flexible all-electron basis set. By calculating the relative energies and conformational preferences of the competing reactive intermediates (regioisomeric primary addition products) it was, among other things, demonstrated that the preferred reaction pathway proceeds *via* the most stable intermediate. Based on the theoretical results a refined mechanistic picture for a synthetically important metallorganic process was derived.

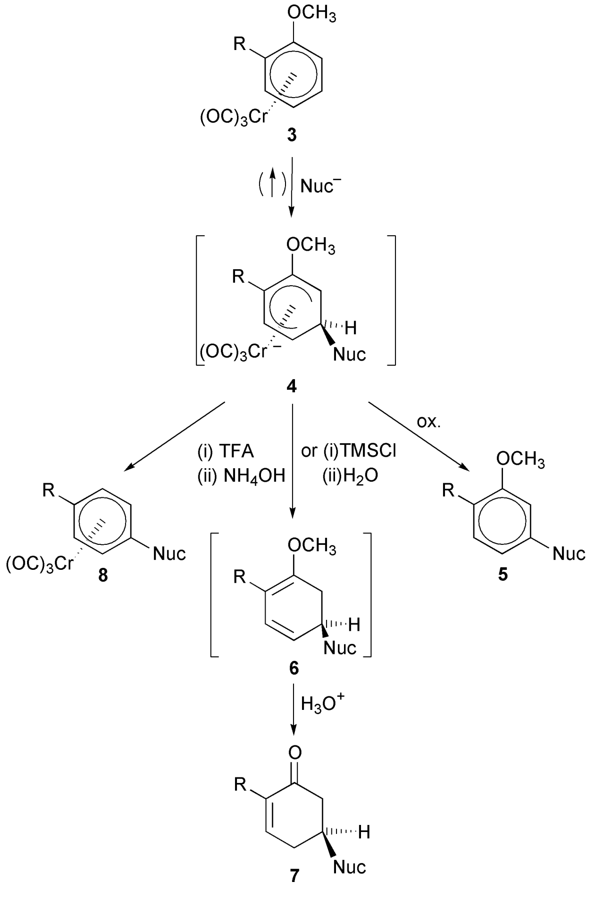
Among the various synthetically useful reactions of arene-Cr(CO)$_3$ complexes,[1] the addition of nucleophiles and subsequent transformations have received broad attention.[2] It is now an established fact that the η^6-complexed arenes, such as the parent benzene complex **1**, are attacked by certain nucleophiles in an *exo*-fashion to form anionic η^5-intermediates of type **2**, which can then further react in different ways depending on the quenching conditions (Scheme 1).[3–6] Without the electron-withdrawing effect of the metal fragment, this chemistry would not take place.

Additions to anisole-Cr(CO)$_3$ (**3**, R = H) and its derivatives are of particular synthetic relevance (Scheme 2). In such cases, the nucleophile has been shown to regioselectively attack the *meta*-position with respect to the alkoxy substituent.[3f,7] If the intermediate addition product (**4**) is trapped by an oxidising agent, a *meta*-substituted anisole derivative (**5**) is isolated. However, under special work-up conditions dienol ethers **6** are formed, from which in turn cyclohexenones of type **7** are accessible.[8] The latter represent highly valuable (chiral) building blocks for further synthetic applications.[9–11] A third reaction pathway leads to the formation of *meta*-tele-substituted products (**8**),[12] which are favored in the case of *ortho*-substituted substrates.[13]



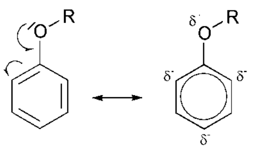
Scheme 1 Nucleophilic addition to benzene-Cr(CO)$_3$ (**1**) and subsequent transformations of the anionic intermediate **2**.

To explain the observed *meta* selectivity of the nucleophilic attack, three models have been used which will be briefly introduced in the following.

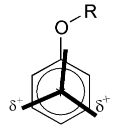


Scheme 2 Nucleophile addition to anisol-Cr(CO)$_3$ derivatives and subsequent transformations.

DOI: 10.1039/b002898n



Scheme 3 Partial charges arising from the mesomeric effect of an oxy substituent on the arene.



Scheme 4 Preferred orientation of the $Cr(CO)_3$ tripod in oxy-substituted benzene-$Cr(CO)_3$ complexes.

Model 1: On a simple level the *meta* selectivity can be rationalized just by electronic effects induced by the substituent already present on the arene. According to Scheme 3 the electron-rich methoxy substituent should deactivate the *ortho* and *para* positions for a nucleophilic attack. This model, however, does not consider any participation of the $Cr(CO)_3$ moiety.

Model 2: A more sophisticated explanation is based on charge control in connection with the conformational arrangement of the $Cr(CO)_3$ tripod (a stereoelectronic effect). From X-ray structures and NMR spectroscopic data it can be assumed that the substrate prefers a conformation with one of the CO ligands eclipsing the methoxy group (Scheme 4). Thus, the *meta* selectivity could be rationalized by the electrostatic activation imposed by the other CO ligands on the eclipsed (*meta*) ring positions.[14] This model considers the partial charges at the arene carbon atoms in the lowest energy conformer of the complex.

Model 3: It has been suggested that certain nucleophilic additions to complexed arenes proceed under orbital control. In such cases, one has to consider the LUMO of the respective complexes. It is not unlikely that a dependency of the orbital coefficients on the orientation of the $Cr(CO)_3$ tripod exists.[15]

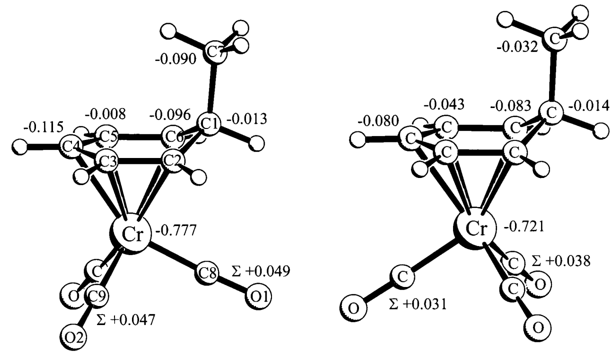
A fundamental problem, however, arises due to the low rotational barrier of the $Cr(CO)_3$ tripod in the neutral starting complexes. Accordingly, the Curtin–Hammet principle[16] should apply for kinetically controlled reactions and the regioselectivity would only be determined by the relative energies of the competing transition states. As several investigations have shown, nucleophilic additions are often reversible (thermodynamically controlled).[7,8c] In such cases, the selectivity would reflect the relative energies of the resulting reactive intermediates. In order to shed light onto the mechanistic problems introduced above, we disclose here a theoretical study based on modern quantum chemical techniques.[17]

Computational details

As in our previous studies[17a] all calculated structures presented in the following sections were fully optimized in the respective point group symmetry employing analytical gradient techniques and the popular hybrid density functional method B3LYP[18] as implemented in GAUSSIAN 98.[19] The one-particle description for the chromium atom was a (14s11p6d) → [8s6p4d] all-electron basis set introduced by Wachters,[20] supplemented with three primitive f-type polarization functions contracted into two. For carbon, hydrogen, and oxygen we employed Dunning's standard split valence D95* basis set, which includes a set of d-type functions on C and O. Spherical harmonic polarization functions (i.e. 5d and 7f components) were used throughout.[21] Harmonic frequencies were computed analytically with the smaller basis set Wachters/D95 in order to estimate the zero point vibrational energies (ZPE) and to identify a stationary point as a minimum or transition structure. The partial charges and orbital hybridizations were calculated employing the natural bond orbital (NBO) scheme as developed by Weinhold and coworkers.[22] All calculations were carried out on either IBM RS/6000 workstations, PC workstations, the workstations available at the RRZK (Universität zu Köln) or the CRAY J932 computer at the Konrad-Zuse-Zentrum, Berlin.

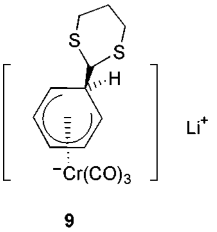
Results and discussion

First, we will discuss reactive intermediates of type **2**. As a model system we investigated the addition product formally derived from the parent benzene complex **1** with a methyl anion as nucleophile (Fig. 1). The optimized minimum structure (**2s**) shows the expected η^5 bonding mode of the chromium tricarbonyl fragment to the π-ligand. To reach the best possible coordination between the chromium and the five carbon atoms, the $Cr(CO)_3$ tripod has moved more closely towards C4 while C1 is bent away from the $Cr(CO)_3$ group. The comparison of our calculated geometry parameters with the experimentally determined structure of **9**[23] (Scheme 5) serves as proof for the quality of the theoretical methodology used. Table 1 shows that there is a satisfying general agreement of the calculated and the experimental data. Deviations



2s **2a**

Fig. 1 Calculated structures and partial charges of the two conformers (**2s** and **2a**) of the anionic complex **2**. The partial charges of the hydrogen atoms are summed into those of the corresponding carbon atoms.



9

Scheme 5 The anionic intermediate **9**, characterized by X-ray crystallography.[3e]

Table 1 Geometrical parameters for the calculated (**2s**) and the experimental (**9**) structure of anionic addition products of type **2**

Parameter	Calculated **2s**	Experimental **9**[a]
C1–C2/Å	1.53	1.49
C2–C3/Å	1.41	1.41
C3–C4/Å	1.44	1.41
C1–C7/Å	1.57	1.53
Cr–(C2–C6)/Å	*ca.* 2.26	*ca.* 2.22
Cr–pentadienyl plane/Å	1.74	1.75
Pentadienyl plane:		
C1–C2–C6/°	37.0	38.6

[a] Ref. 3(*e*)

Table 2 Total energies, zero point energy (ZPE) correction and relative energies for structures **2s**, **2a**, **10s**, **10a**, **11**, **11ts**, **12**, **12ts**, **13**, **13ts**, **14** and **14ts**

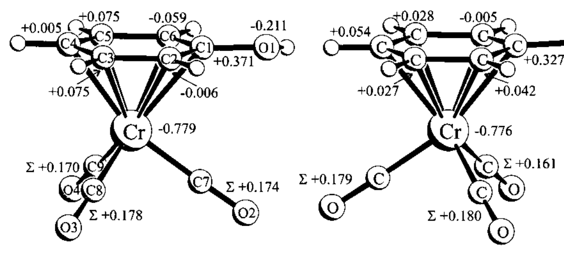
Structure	Total energy/hartree[a]	ZPE/kcal mol^{-1} [b]	Rel. energy/kcal mol^{-1} [c]	Rel. energy/kcal mol^{-1} [d]
2s	−1656.808 72	103.2	0.0	
2a	−1656.796 71	103.1	7.5	
10s	−1692.090 45	82.4	0.0	
10a	−1692.086 29	82.2	2.5	
11	−1771.161 24	123.4	0.0	0.7
11ts	−1771.148 60	123.3	8.0	
12	−1771.162 26	123.3	0.0	0.0
12ts	−1771.149 37	123.1	8.1	
13	−1771.157 23	123.3	0.0	3.2
13ts	−1771.147 20	123.2	6.3	
14	−1771.157 41	123.0	0.0	3.0
14ts	−1771.144 63	122.8	6.9	

[a] Optimization with B3LYP and the basis set Wachters + f/D95*. [b] B3LYP, Wachters/D95. [c] Relative energies for the rotational barriers. [d] Relative energies of the four reactive intermediates in their most favored geometries.

may result from the different kind of nucleophile, which attacked the benzene-$Cr(CO)_3$ complex, and from the fact that the calculations mirror only the naked anion in the gas phase while in the crystal a counter ion is also present. Nevertheless, the pronounced features of an anionic addition product are very well reproduced by the calculations.

The NBO analysis reveals that the negative charge in **2s** is strongly delocalized, in particular to the $Cr(CO)_3$ moiety.[24] In order to estimate the rotational barrier of the $Cr(CO)_3$ group, the two conformers **2s** and **2a** were calculated (see Table 2). **2a** turns out to be the transition state for this rotation process connected to an imaginary frequency of 55.8 cm^{-1}. The *syn*-eclipsed conformer **2s** is 7.5 kcal mol^{-1} more stable than the *anti*-eclipsed conformer **2a**. This barrier is remarkably high in contrast to the negligible rotational barrier of 0.2 kcal mol^{-1} in the neutral benzene-$Cr(CO)_3$ complex **1**.[17a] From these calculations it is concluded that anionic intermediates of type **2** generally prefer a single (*syn*-eclipsed) conformation with respect to the rotation of the $Cr(CO)_3$ tripod.[25]

We next turned our attention to the structure and electronic properties of oxygen-substituted arene-$Cr(CO)_3$ complexes. As a model system we first calculated the phenol-$Cr(CO)_3$ complex **10**. In addition to the ground state minimum structure (**10s**), we also calculated the transition state (**10a**) for the rotation of the $Cr(CO)_3$ tripod in order to quantify the influence of the conformation on the partial charges of the arene carbons and to get information about the height of the rotational barrier. The calculated structures and the partial charges of **10s** and **10a** are depicted in Fig. 2; selected bond lengths of **10s** are shown in Table 3. Due to the fact that the hydrogen atom of the hydroxy group is oriented nearly in the plane of the arene ring, the symmetry of the complex **10s** is reduced to C_1. The CO groups of the $Cr(CO)_3$ tripod are eclipsed with three carbon atoms of the arene, including the OH-substituted carbon center. This orientation corresponds to the lowest energy conformer. The rotational barrier of the $Cr(CO)_3$ group is calculated to be 2.5 kcal mol^{-1}, which is higher than in benzene-$Cr(CO)_3$, **1** (0.2 kcal mol^{-1}) or toluene-$Cr(CO)_3$ (0.8 kcal mol^{-1}).[16a]



10s **10a**

Fig. 2 Calculated structures and partial charges of the two conformers (**10s** and **10a**) of the phenol-$Cr(CO)_3$ complex **10**. The partial charges of the hydrogen atoms are summed into those of the corresponding carbon atoms.

Table 3 Selected bond lengths of the calculated structure **10s**

Bond	Calc. bond length/Å[a]
C1–C2	1.421
C2–C3	1.421
C3–C4	1.425
C4–C5	1.422
C5–C6	1.426
C6–C1	1.423
C1–O1	1.384
Cr–C1	2.361
Cr–C2	2.345
Cr–C3	2.305
Cr–C4	2.320
Cr–C5	2.293
Cr–C6	2.337
Cr–C7	1.843
Cr–C8	1.841
Cr–C9	1.840
C7–O2	1.188
C8–O3	1.188
C9–O4	1.189

[a] B3LYP, Wachters + f/D95*

The two *ortho* carbon atoms in **10s** (with respect to the hydroxy group) carry a very small negative partial charge in contrast to the *meta* positions, which indeed possess a slightly positive partial charge. This may be an indication for the kinetic preference of the *meta* attack by a nucleophile.

While a positive partial charge is located on the *meta* positions in **10s**, the activation of the *meta* position in **10a** is not only less pronounced, but even one of the *ortho* positions is significantly positively charged. The difference of the partial charges of the two *ortho* positions in **10a** can be attributed to the bent orientation of the hydroxy group. While the *para* carbon atom is not activated in **10s**, it carries a significant positive partial charge in **10a** and therefore would be prone towards nucleophilic attack. On comparing the partial charges of **10s** and **10a** it becomes obvious that *the stereoelectronic influence of the* $Cr(CO)_3$ *tripod overcompensates for the simple electronic effect of the oxy substituent.*

In accordance with the charge distribution discussed above, the calculated LUMOs[26] of the eclipsed and staggered phenol-$Cr(CO)_3$ complexes **10s** and **10a** show no coefficient in the *para* and *ipso* positions. This corresponds to the experimental observation that usually no *para* addition occurs. Interestingly, the LUMOs of both conformers (**10s** and **10a**) do not differ significantly with respect to their coefficients at the *ortho* and *meta* positions (Fig. 3).

The calculation of the ground state structure **10s** indicates that model 2 reflects much better than model 1 the disposition of the substrate towards nucleophilic addition under charge control, the main effect being the activation of the *meta* position by the eclipsed carbonyl groups in the preferred conformer **10s**. Furthermore, the calculations suggest that the *meta* selectivity cannot be explained in terms of model 3 (orbital control).

As mentioned in the introduction, model 2 still has some fundamental limitations. A better model should consider the relative energy of the competing reactive intermediates in the case of reversible reactions (thermodynamic control). To rationalize the selectivity of kinetically controlled reactions, however, the relative energies of competing transition states need to be analyzed. Therefore, a theoretical investigation of the four regioisomeric intermediates **11**–**14**, formally derived by addition of a methyl anion to the *ortho*, *meta*, *para* or *ipso* position of the anisole-$Cr(CO)_3$ complex **3** (R = H), was carried out (Scheme 6).[27] The calculated ground state structures of these anionic complexes (Fig. 4) verify the assumption that the *syn*-eclipsed conformation (with one CO group eclipsing the newly formed sp^3 center) is always preferred. This effect is stronger than any directing influence of the oxy substituent on the conformation of the metal carbonyl fragment.

The relative energies of the four competing intermediates in their lowest energy conformation (Fig. 5) reflect qualitatively the experimentally well-documented preference for the *meta*-addition product, although the calculated energy difference between **11** and **12** is rather small. The *para and ipso* products **13** and **14** are clearly disfavored. A possible explanation for the greater stability of **12** in comparison to the other isomers may be the fact that only in **12** is a favorable eclipsed orientation of one CO ligand to the methoxy-substituted ring carbon and the newly formed sp^3 center realized.

The calculation of the rotational barriers of the $Cr(CO)_3$ group in the four anionic intermediates **11**–**14** (energies of the transition states, ts, see Table 2) again reveals rather high barriers: 8.0 for **11**, 8.1 for **12**, 6.3 for **13** and 6.9 for **14**.[28] This means that in contrast to the neutral substrates the rotation of the $Cr(CO)_3$ tripod is significantly restricted in the reactive intermediates.

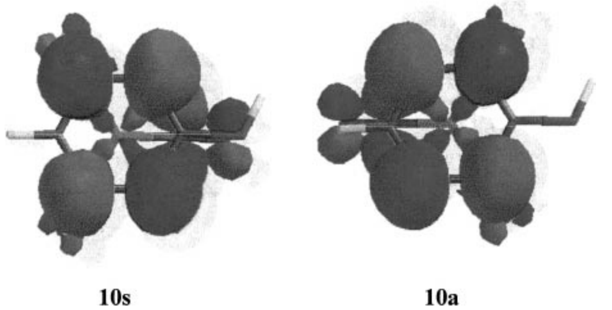
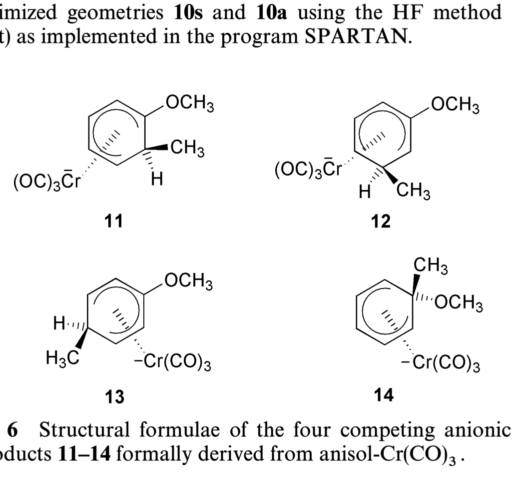


Fig. 3 Lowest unoccupied molecular orbitals (LUMO) calculated for the optimized geometries **10s** and **10a** using the HF method (3-21g basis set) as implemented in the program SPARTAN.



Scheme 6 Structural formulae of the four competing anionic addition products **11–14** formally derived from anisol-$Cr(CO)_3$.

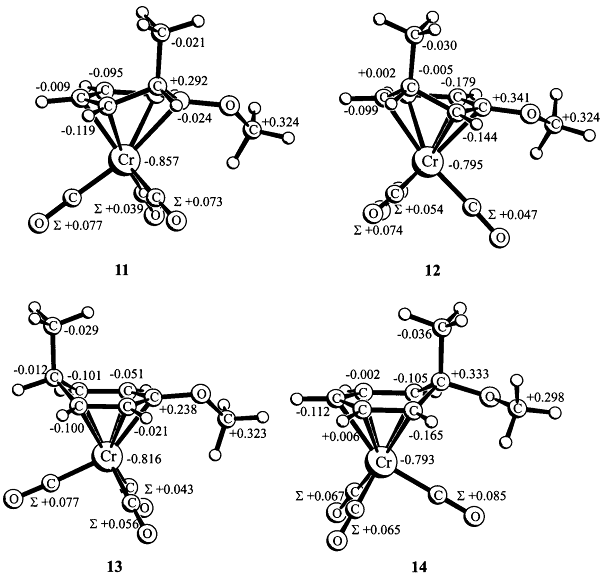


Fig. 4 Calculated structures of the four isomeric anionic addition products **11**–**14** in their lowest energy conformations.

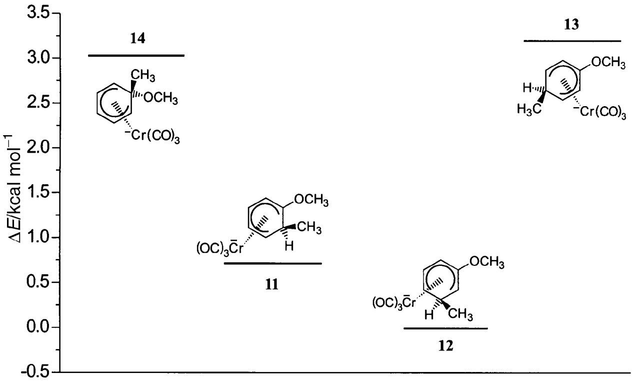


Fig. 5 Relative energies of the four isomeric anionic intermediates **11**–**14**.

Following the Hammond postulate,[29] the transition state of the nucleophilic addition should be more similar to the reactive intermediates than to the substrate. Therefore, the calculated relative energies of **11**–**14** should reflect the rates of the four competing reaction pathways. This leads indeed to a better qualitative understanding of the regioselectivity of the reaction, both under kinetic and thermodynamic control. This refined model correlates nicely with the stereoelectronic interpretation according to model 2. Obviously, the kinetically (charge) controlled nucleophile attack at the activated *meta* position of the substrate **3** (R = H) in its lowest energy conformation leads to the most stable intermediate (**12**) in its lowest energy conformation. Thus, the kinetically preferred reaction pathway is that which requires a minimum of structural reorganization, according to the principle of least motion.[30]

Conclusion

We have used modern DFT techniques to calculate structures and relative energies of oxy-substituted arene $Cr(CO)_3$ complexes and anionic intermediates formally derived therefrom by nucleophilic addition of a methyl anion. The reliability of the DFT calculations had been shown in the past by calculating reactive intermediates derived from toluene-$Cr(CO)_3$.[17a]

As a result of our theoretical study, an improved rationale for the *meta* selectivity of synthetically important nucleophilic additions to anisole-Cr(CO)$_3$ and related complexes has been developed. In contrast to older models, the new picture does not ignore the Curtin–Hammet principle as it considers the (relative) energy and the preferred conformation of competing reactive intermediates and not only the ground state structure of the starting material.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work. Parts of this research was performed while the authors were staying at TU, Berlin, and we thank the Konrad-Zuse Zentrum für Informationstechnik, Berlin, as well as the Regionales Rechenzentrum der Universität zu Köln (RRZK) for providing a generous amount of computer time. We also acknowledge valuable referee comments, which helped us to significantly improve this manuscript.

References and notes

1 Selected reviews: (*a*) H.-G. Schmalz and S. Siegel, in *Transition Metals for Fine Chemicals and Organic Synthesis*, ed. C. Bolm and M. Beller, VCH, Weinheim, 1998; (*b*) L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd edn., University Science Books, Mill Valley, CA, 1999, ch. 10; (*c*) S. G. Davies and T. D. McCarthy, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, pp. 1039–1070; (*d*) M. Uemura, in *Advances in Metal Organic Chemistry*, ed. L. S. Liebeskind, JAI Press, Greenwich, CT, 1991, vol. 2, pp. 195–245; (*e*) V. N. Kalinin, *Russ. Chem. Rev.*, 1987, **56**, 682.

2 Reviews: (*a*) M. F. Semmelhack, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 4, p. 517; (*b*) M. F. Semmelhack, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, p. 979; (*c*) E. P. Kündig, D. Amurrio, D. Beruben, K. Khan, A. Ripa and L. Ronggang, *Pure Appl. Chem.*, 1997, **69**, 543; (*d*) A. R. Papae, K. P. Kaliappan and E. P. Kündig, *Chem. Rev.*, 2000, **100**, 2917.

3 (*a*) M. F. Semmelhack, H. T. J. Hall, M. Yoshifuji and G. Clark, *J. Am. Chem. Soc.*, 1975, **97**, 1247; (*b*) M. F. Semmelhack, H. T. J. Hall, M. Yoshifuji and G. Clark, *J. Am. Chem. Soc.*, 1976, **98**, 6387; (*c*) M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, 1977, **99**, 1675; (*d*) M. F. Semmelhack, Y. Thebtaranonth and L. Keller, *J. Am. Chem. Soc.*, 1977, **99**, 959; (*e*) M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; (*f*) M. F. Semmelhack, G. Clark, J. L. Garcia, J. J. Harrison, Y. Thebtaranonth, W. Wulff and A. Yamashita, *Tetrahedron*, 1981, **37**, 3957.

4 A. Fretzen, A. Ripa, R. Liu, G. Bernardinelli and E. P. Kündig, *Chem. Eur. J.*, 1998, **4**, 251.

5 E. P. Kündig, A. F. Cunningham, J. R. P. Paglia, D. P. Simmons and G. Bernardinelli, *Helv. Chim. Acta*, 1990, **73**, 386.

6 E. P. Kündig and D. P. Simmons, *J. Chem. Soc., Chem. Commun.*, 1983, 1320.

7 E. P. Kündig, V. Desobry, D. P. Simmons and E. Wenger, *J. Am. Chem. Soc.*, 1989, **111**, 1804.

8 (*a*) M. F. Semmelhack, J. J. Harrison and Y. Thebtaranonth, *J. Org. Chem.*, 1979, **44**, 3275; (*b*) H. G. Schmalz and K. Schellhaas, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2146; (*c*) M. F. Semmelhack and H. G. Schmalz, *Tetrahedron Lett.*, 1996, **37**, 3089; (*d*) A. J. Pearson, A. V. Gontcharov and P. D. Woodgate, *Tetrahedron Lett.*, 1996, **37**, 3087; (*e*) A. J. Pearson and A. V. Gontcharov, *J. Org. Chem.*, 1998, **63**, 152.

9 (*a*) M. F. Semmelhack and A. Yamashita, *J. Am. Chem. Soc.*, 1980, **102**, 5924; (*b*) M. Uemura, T. Kobayashi, T. Minami and Y. Hayashi, *Tetrahedron Lett.*, 1986, **27**, 2479.

10 See for instance: K. Schellhaas, H.-G. Schmalz and J. W. Bats, *Chem. Eur. J.*, 1998, **4**, 57.

11 A. Quattropani, G. Anderson, G. Bernardinelli and E. P. Kündig, *J. Am. Chem. Soc.*, 1997, **119**, 4773.

12 For a review on indirect nucleophilic substitutions at arene-Cr(CO)$_3$ complexes, see: F. Rose-Munch, V. Gagliardini, C. Renard and E. Rose, *Coord. Chem. Rev.*, 1998, **178–180**, 249.

13 (*a*) H.-G. Schmalz and K. Schellhaas, *Tetrahedron Lett.*, 1995, **36**, 5511; (*b*) see also ref. 8(*b*).

14 (*a*) A. Solladie-Cavallo and J. Suffert, *J. Org. Magn. Res.*, 1980, **14**, 426; (*b*) A. Solladie-Cavallo, *Polyhedron*, 1985, **11**, 901; (*c*) T. A. Albright and B. K. Carpenter, *Inorg. Chem.*, 1980, **19**, 3092; (*d*) W. R. Jackson, I. D. Rae and M. G. Wong, *Aust. J. Chem.*, 1986, **39**, 303.

15 (*a*) M. F. Semmelhack, G. R. Clark, R. Farina and M. Saeman, *J. Am. Chem. Soc.*, 1979, **101**, 217; (*b*) M. F. Semmelhack, J. L. Garcia, D. Cortes, R. Farina, R. Hong and B. K. Carpenter, *Organometallics*, 1983, **2**, 467; (*c*) B. Ohlsson and C. Ullenius, *J. Organomet. Chem.*, 1988, **350**, 35.

16 (*a*) D. Y. Curtin, *Rec. Chem. Prog.*, 1954, **15**, 111; (*b*) for an excellent discussion, see also: E. L. Eliel, *Stereochemistry of Carbon Compounds*, Wiley, New York, 1994, p. 647ff.

17 For previous theoretical work on arene-Cr(CO)$_3$ complexes using DFT methods, see: (*a*) A. Pfletschinger, T. K. Dargel, H.-G. Schmalz and W. Koch, *Chem. Eur. J.*, 1999, **5**, 537 and references cited therein; (*b*) C. A. Merlic, J. C. Walsh, D. J. Tantillo and K. N. Houk, *J. Am. Chem. Soc.*, 1999, **121**, 3596.

18 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (*c*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623; (*d*) W. Koch and M. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, 2000.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudink, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, rev. A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

20 A. J. H. Wachters, *J. Chem. Phys.*, 1970, **52**, 1033.

21 T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H. F. Schaefer III, Plenum Press, New York, 1977, vol. II, p. 1ff.

22 (*a*) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899; (*b*) E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO, ver. 3.1. The partial charges of the hydrogen atoms are summed into the heavy atoms in Fig. 1, 2 and 4.

23 The only X-ray crystal structure of an anionic addition product has been reported by M. F. Semmelhack *et al.*, see ref. 3(*e*).

24 The Cr(CO)$_3$ unit carries about two thirds ($0.63|e|$) of the negative charge.

25 This conclusion fits the picture derived from previous experimental and theoretical investigations of other types of (cyclohexadienyl)ML$_3$ complexes, see: (*a*) T. H. Whitesides and R. A. Budnik, *Inorg. Chem.*, 1975, **14**, 664; (*b*) S. A. R. Knox, R. P. Phillips and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1976, 552; (*c*) T. A. Albright, P. Hofmann and R. Hoffmann, *J. Am. Chem. Soc.*, 1977, **99**, 7546.

26 The frontier orbitals were calculated using the program SPARTAN 1.4, Wavefunction, Inc., Irvine, CA, USA, 1997.

27 Initial attempts to calculate similar reactive intermediates derived from **10** were complicated by the fact that the hydroxy group tended to form hydrogen bridges to one of the carbonyl oxygen atoms (in the case of *ipso* and *para* addition). However, these calculations showed an even more pronounced energetic preference for the intermediate resulting from *meta* addition ($\Delta E_{ortho/meta} = 2.1$ kcal mol^{-1}).

28 A similar value for the rotation of the Cr(CO)$_3$ group in addition products of this type has been predicted by EHT calculations: see ref. 15(*c*).

29 G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.

30 The regioselective benzylic deprotonation of arene-Cr(CO)$_3$ complexes has been rationalized in a similar way, see: T. Volk, D. Bernicke, J. W. Bats and H.-G. Schmalz, *Eur. J. Inorg. Chem.*, 1998, 1883; see also ref. 17(*a*).