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Studies of electronic effects of modified pyridine-imine ligands utilized in cobalt-catalyzed *meta*-selective *Diels–Alder* reactions

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ABSTRACT

The regioselectivity of cobalt-catalyzed *Diels–Alder* reactions can be controlled by the choice of ligands on the cobalt center. Ligands of the pyridine-imine type favor the formation of the 1,3-disubstitution pattern on the dihydroaromatic product. The investigation was aimed to elucidate the factors for controlling the regioselectivities and reactivity induced by electronic effects of the pyridine-imine ligands in the cobalt-catalyzed *Diels–Alder* reaction. For that, electron-withdrawing as well as electron donating substituents were introduced in the 4-position on the pyridine moiety and on the 4′-position of the aniline derivative used in the imine subunit of the ligands. In close synergy DFT calculations and the comparison with experimental results proved that electronic variation of the substituents at both positions have a negligible influence on the regioselectivity. However, the kinetic data for the cobalt-catalyzed *Diels–Alder* reactions revealed that there are great differences in the lengths of the induction periods when different cobalt pyridine-imine complexes are applied. These results could be elucidated by conductivity experiments showing that ionic homoleptic complexes $Co(L)_2^{2+}/CoBr_4^{2-}$ are in equilibrium with their corresponding neutral heteroleptic complexes of type $Co(L)Br_2$ in solution. The equilibrium position depends on the electronic characteristics of the pyridine-imine ligands (L), thereby influencing the length of the induction period.

1. Introduction

The regiodivergent synthesis of carbocyclic six-membered ring systems via atom economic cobalt-catalyzed *Diels–Alder* reactions is an excellent example of a transformation where the regioselectivity is efficiently controlled by the choice of the ligand system [1] (Scheme 1).

Thereby, the highly selective synthesis of disubstituted dihydroaromatic compounds, such as **1**, can be accomplished when a bidentate phosphine ligand, such as dppe, is applied, leading eventually to arenes of type **3** [2]. On the other hand, the application of pyridine-imine-type ligands in the cobalt-catalyzed *Diels–Alder* reaction leads to the highly selective formation of regioisomer **2** in excellent yields which can be easily oxidized by DDQ (=2,3-dichloro-5,6-dicyano-benzoquinone) to the corresponding arene **4** [3]. In recent applications also silyl- and boron-functionalized alkynes could be applied in the regiodiverse *Diels–Alder* reactions with similarly high regioselectivities leading to very interesting functionalized building blocks for follow-up transformations [4].

In a detailed quantum mechanical investigation the mechanism of the cobalt-catalyzed *Diels–Alder* reaction was evaluated and the regiodivergent behavior of the $Co(dppe)^+$-complex [5] leading to the *para*-substituted product **1**, and of the $Co(pyridine\text{-}imine)^+$-complex [6] predominantly generating the *meta*-substituted product **2** could be explained [7]. A total of eight different reaction pathways were found for the stepwise rather than concerted mechanism yielding the *para*- or the *meta*-product, respectively. The calculated ratios of the primary cycloaddition products **1** and **2** were in excellent agreement with the experimentally observed regioselectivities.

As quintessence from the analysis of the lowest lying transition states for both reaction pathways we came to the conclusion that different steric hindrances of the ligands caused the change in

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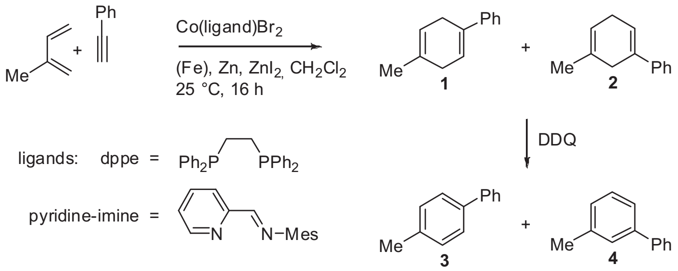


Scheme 1. Regiodivergent synthesis of dihydroaromatic compounds **1** and **2** by cobalt-catalyzed *Diels–Alder* reaction and follow-up oxidation to the arenes **3** and **4**.

regioselectivity. Accordingly, electronic modifications in a remote position of the pyridine-imine ligand should not influence the regioselectivity of the Co(pyridine-imine)-catalyzed cycloaddition process. To test this hypothesis we set out to start this investigation utilizing theoretical methods to evaluate those ligands which cannot be synthesized in a few steps. Thereby, *in silico* evaluations for those hypothetical ligands should be obtained.

Also, the cobalt-catalyzed reaction starts from a cobalt(II) precursor and a heterogeneous electron transfer from zinc powder generates the proposed catalytically active cobalt(I) species resulting in an induction period. The redox process should be dependent on the electronic characteristics of the Co(pyridine-imine)Br$_2$ complexes resulting in different length of the induction periods dependent from the electron donating/abstracting ability of the ligand on cobalt. Accordingly, electronic modifications of the ligands in remote positions should result in nearly identical thermodynamic and kinetic profiles, almost identical yields and regioselectivities, but in different length of induction periods.

2. Experimental

All reagents were used as purchased from commercial suppliers without further purification. All reactions were carried out using standard Schlenk techniques under dry argon. Solvents were purified and dried according to conventional methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded with an AVANCE 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) or an AVANCE 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C). The kinetic measurements were analysed utilizing GC analyses which were recorded with a Shimadzu GC-2010 Plus Gas Chromatograph. For chromatography the separations were carried out on Macherey–Nagel Silica 60 (0.040–0.063 mm, 230–400 mesh ASTM). For TLC Merck TLC plates (Silica 60, F254) were used.

2.1. Computational details

Geometry optimizations of the molecules without symmetry constraints (C$_1$) were carried out using the Gaussian03 [8] optimizer (Berny-Algorithm) [9] together with TurboMole 5.0 [10] energies and gradients at the gradient corrected DFT level of theory using Becke's exchange functional [11] in conjunction with Perdew's correlation functional [12] (BP86) and Ahlrich's def2-SV(P) basis-sets [13]. The resolution-of-the-identity (RI) approximation [14] was applied using auxiliary basis functions [15]. This level of theory is denoted as RI-BP86/def2-SV(P). Stationary points were characterized as minima (number of imaginary frequencies $i = 0$) or transition states ($i = 1$) by calculating the Hessian matrix analytically (AOFORCE) [16]. The solvent-effect on the calculated energies was estimated with COSMO [17] as single point calculations on the optimized structures. This level of theory is denoted as COSMO//RI-BP86/def2-SV(P). The latter calculations were carried out with a dielectric constant $\varepsilon = 8.93$ for the solvent dichloromethane [18].

2.2. Synthesis of the ligands and cobalt complexes

The ligands **6a**–**6d** were generated by condensation of 2-formylpyridine with aniline derivatives. The cobalt-complexes were synthesized by addition of 1.0 equiv. of the ligand to a solution of cobalt(II) bromide in THF. The mixture was stirred overnight and the solvent was removed. The complexes were stored at ambient temperatures without special preventive measures and used as precatalysts without further purification.

2.3. Representative procedure for the cobalt-catalyzed Diels–Alder reaction

Anhydrous zinc iodide (64 mg, 0.2 mmol, 20 mol%), zinc dust (13 mg, 0.2 mmol, 20 mol%), iron powder (11 mg, 0.2 mmol, 20 mol%) and Co(**5c**)Br$_2$ (45 mg, 0.1 mmol, 10 mol%) were suspended under argon in 1.0 mL dichloromethane. Then isoprene (1.0 mmol) and phenylacetylene (1.0 mmol) were added and the mixture was stirred at room temperature. The conversion of the starting materials was monitored by GC and GC–MS analysis. The reaction mixture was filtered over a short pad of silica gel (pentane) and the solvent was removed under reduced pressure. The residue was dissolved in toluene (10 mL) and stirred with DDQ (1.1 equiv.) for 1 h. The resulting suspension was washed with 10% NaOH/10% Na$_2$S$_2$O$_3$ solution, extracted with diethyl ether, dried over MgSO$_4$ and the solvent was removed under reduced pressure. The product was purified by flash column chromatography on silica gel (eluent: pentane). The analytical data are in accordance with the literature [2,3].

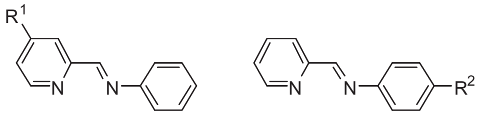
2.4. Kinetic investigations

The *Diels–Alder* reaction was performed as before and samples were taken by syringe under argon in certain time intervals. The progress of the reaction was determined by GC analysis via integration of the peaks.

3. Results and discussion

In order to investigate the electronic influence of a substituent without causing steric hindrance the substituents (R^1 and R^2) were placed on the 4- and 4′-position in *para*-relation to the nitrogen atoms of the pyridine-imine ligand (Fig. 1). Thereby, very little steric hindrance will occur and the electronic modifications will have a strong influence on the electron density at the reactive sites within the cobalt complex via the *trans*-influence. For this purpose the two ligand systems **5a**–**e** and **6a**–**e** were selected with electron-donating as well as electron-withdrawing substituents on position 4 and 4′.

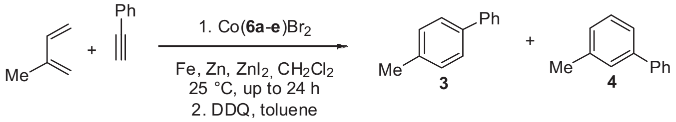
For quantum mechanical investigations the following modifications of the pyridine moiety were selected: substituent R^1 was modified with the electron donating methoxy – (**5a**), the dimethylamino – (**5b**) and the electron withdrawing trifluoromethyl –



5a: R^1 = OMe
5b: R^1 = NMe$_2$
5c: R^1 = H
5d: R^1 = CF$_3$
5e: R^1 = F

6a: R^2 = OMe
6b: R^2 = NMe$_2$
6c (= **5c**): R^2 = H
6d: R^2 = CF$_3$
6e: R^2 = F

Fig. 1. Modification of electronic parameters of the pyridine-imine ligands **5** and **6** (pyridine-imine) for the *meta*-selective cobalt-catalyzed *Diels–Alder* reaction.



Scheme 2. Regioselective synthesis of aromatic compounds **3** and **4** by cobalt-catalyzed *Diels–Alder* reactions/DDQ oxidation.

(**5d**), the fluoro-substituent (**5e**) and the unmodified ligand $R^1 = H$ (**5c**). These modifications are of the highest interest because the first carbon–carbon bond formation in the catalytic cycle of the *Diels–Alder* reaction takes place in *trans*-position to the pyridine moiety of the ligand of type **5**. Electronic modifications at this position should have the strongest influence on the reaction in terms of reactivity and selectivity. We also modified, in a second set of quantum mechanical calculations, the electronic nature of the substituents R^2 in the aniline-type moiety of the pyridine-imine ligand in the same manner: the ligands **6a** and **6b** with the electron donating methoxy-and dimethylamino-substituents as well as the electron deficient ligands **6d** and **6e** with the trifluoromethyl – and fluoro-substituent were selected while **5c**/**6c** again served as a reference compound.

The synthesis of the ligands **6a**–**6e** is trivial as the required 4-substituted aniline derivatives are commercially available, and imine formation with pyridine-2-carbaldehyde proceeds immediately and quantitatively upon mixing the starting materials. For these ligands the corresponding cobalt complexes were synthesized and the *Diels–Alder* reactions were performed according to Scheme 2. The results for the regioselectivity of these reactions are given in Table 1.

On the other hand, the heterocyclic precursors of pyridine-imine ligands of type **5** with modifications in the 4-position of the pyridine subunit are not commercially available and must be generated in multi-step reaction sequences. Therefore, we decided not to synthesize these ligands beforehand but await the outcome of the quantum mechanical investigation and then address the synthesis of the most promising ligand of type **5** hopefully reaping the rewards derived from the calculations and cutting directly to the key ligands.

The results of the quantum mechanical investigations can be summarized as follows:

Table 1
Comparison of the quantum mechanical calculations with the experimental results of the *meta*-selective cobalt-catalyzed *Diels–Alder* reactions.

No	Ligand	Calc. Regioselectivity[a]		Calc. Regioselectivity (Solv.)[b]		Regioselectivity (Exp.)
		$\Delta\Delta E$[c]	*meta*:*para*[d]	$\Delta\Delta E$[c]	*meta*:*para*[d]	*meta*:*para*
1	**5c**/**6c**	0.5	70:30 (75:25)	0.4	66:34 (74:26)	94:6
2	**5a**	0.6	73:27 (77:23)	0.5	70:30 (77:23)	nd
3	**5b**	0.6	73:27 (77:23)	0.6	73:27 (78:22)	nd
4	**5d**	1.0	84:16 (85:15)	0.6	73:27 (78:22)	nd
5	**5e**	0.5	70:30 (75:25)	0.3	62:38 (74:26)	nd
6	**6a**	0.3	62:38 (73:27)	0.3	62:38 (73:27)	94:6
7	**6b**	0.0	50:50 (65:35)	0.2	58:42 (66:34)	97:3
8	**6d**	0.6	73:27 (77:23)	0.7	77:23 (81:19)	96:4
9	**6e**	0.4	66:34 (74:26)	0.3	62:38 (74:26)	95:5

[a] TURBOMOLE 5.80, RI-BP86/def2-SV(P) including Zero Point Energy correction.
[b] TURBOMOLE 5.80, COSMO//RI-BP86/def2-SV(P).
[c] Energy values in kcal/mol. The energy difference of the lowest activation barriers. For detailed information please check Supporting information.
[d] The first value is calculated only from the lowest activation energies yielding either the *meta* or the *para* product. The values in parentheses give the *meta*:*para* ratio calculated by considering the activation barriers of all eight reaction pathways. nd = not determined.

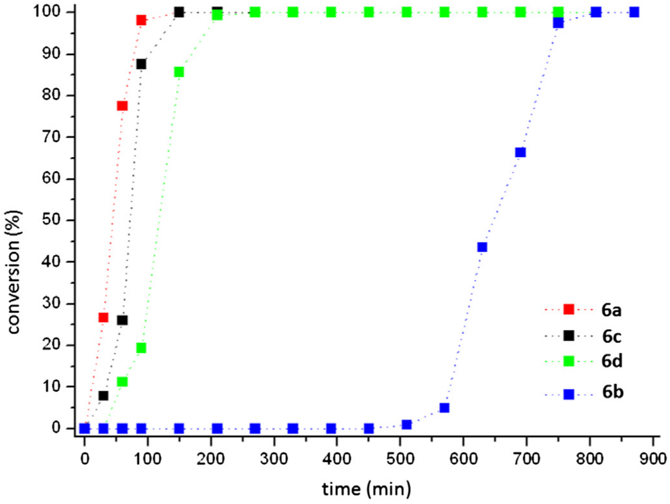


Fig. 2. Kinetic profiles of the *meta*-selective cobalt-catalyzed *Diels–Alder* reaction utilizing cobalt complexes of type Co(**6a**–**d**)Br_2 determined by GC analysis.

Our initial hypothesis that the electronic influence on the regioselectivity is negligible proved to be correct. We found that the calculated values do not indicate a significant change in the regioselectivity of the *meta*-selective cobalt-catalyzed *Diels–Alder* reaction through the variation of the substituents R^1 and R^2 (Table 1). The energy schemes of the *meta*-selective reaction pathways for the ligands **5a**–**e** and ligands **6a**–**d** are merely identical and only very small differences can be found, as shown in Fig. S3 (see, SI).

The results compiled in Table 1 indicate that the calculated regioselectivities for **6a**–**6d** correctly predict that the formation of the *meta* isomer is favoured over the *para* isomer but the absolute values for the *meta*:*para* ratio are smaller than the experimental values. However, theory and experiment agree that there are only small changes in the *meta*:*para* ratio when the electron withdrawing substituents in **6d** and **6e** are replaced by electron donating groups in **6a** and **6b**. Even the greatest difference between the ligands **6b** and **6d** (entry 7/8) with a calculated selectivity increase from 66:34 to 81:19 did not result in any significant change of regioselectivity in the experimentally observed values within their margins of error. Moreover, the calculated changes in regioselectivity for ligands of type **5** (entries 2–5) are even smaller than for those of type **6**. Because the calculations predict a similar negligible change for the regioselectivity for varying the substituents in the 4-position of the pyridine moiety of the pyridine-imine ligand, we decided not to undertake the multiple step syntheses of pyridine-imine ligands with modifications in the 4-position of the pyridine moiety.

The reaction profiles for the different cobalt complexes of type **5** and **6** are very similar for the *Diels–Alder* reaction (see Fig. S3, SI). Accordingly, very little difference should be detectable in their catalytic activity and the overall reaction kinetics.

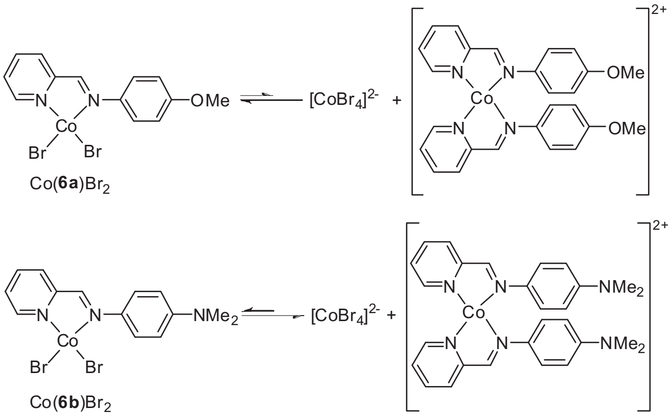
3.1. Kinetic effects of the electronic modifications

The quantum mechanical investigation and the experimental results suggested that electronic modifications on the ligands of type **5** and **6** have little effect on the reaction barriers. However, up to now we concentrated only upon the cobalt complexes in their proposed catalytically active form; the cobalt(I) species. The precursor complexes are activated *in situ* by a reduction of the Co(II) species to their corresponding Co(I) complexes, followed by halide abstraction by the Lewis acid (ZnI_2). For this process an induction period is generally observed. Electronic modifications of the pyridine-imine ligands should result in different induction periods caused by the varied reduction potential of the Co(II) catalyst precursors. Indeed, different induction periods for the activation of the cobalt complexes of type Co(**6**)Br_2 were detected. The kinetic profile of different cobalt complexes (**6a**–**6d**) are shown in Fig. 2.

The shortest induction period was detected for the *Diels–Alder* reaction utilizing the electron-donating methoxy-substituent in ligand **6a**, followed by the unmodified ligand **6c** and the electron-withdrawing ligand **6d**. This order indicates that the electron transfer from zinc powder to the cobalt complex [Co(**6**)Br_2 + e^- → Co(**6**)Br + Br^-] is not the rate limiting step in the induction period, because ease of reduction should be in opposite order following the redox potentials of the complexes. In fact, the order indicates that the abstraction of the halide from the intermediate Co^I(**6**)Br complex to the catalytically active Co(**6**)$^+$ complex by the Lewis acid (ZnI_2) is the rate determining step of the induction period. This is also plausible as the more electron-withdrawing the ligand the stronger the halide is bound to the cobalt atom. Once the active catalyst is formed the reaction is complete within 1–3 h in each of the investigated cases. On the other hand, the induction period for the *Diels–Alder* reaction utilizing the strong electron-donating dimethylamine-substituted ligand **6b** was reproducibly found to be very long (10–14 h), in sharp contrast to our expectations following the arguments given for the other electron-donating methoxy-substituted ligand **6a**. A rationale for this drastically different behaviour of the complex Co(**6b**)Br_2 could be the presence of an pre-equilibrium of cobalt complexes in solution. We envisaged that the complexes Co(**6a**)Br_2 and Co(**6b**)Br_2 are present in different forms when dissolved in dichloromethane (Scheme 3). Complex Co(**6a**)Br_2 could favour the neutral heteroleptic form rather than the ionic homoleptic complexes $[CoBr_4]^{2-}$ and [Co(**6a**)$_2$]$^{2+}$ while the situation for cobalt complex with ligand **6b** was proposed to be quite the opposite with the equilibrium on the site of the homoleptic complexes $[CoBr_4]^{2-}$ and [Co(**6b**)$_2$]$^{2+}$.

As the steric influences of the pyridine-imine ligands are virtually identical, this assumption must be rationalized in terms of the electronic ligand donor strengths which increases from **6a** to **6b**. The increase in donor strength may thus reduce the amount of available, neutral, heteroleptic and redox–active complexes of Co(**6b**)Br_2, therefore overcompensating the effect of the shift in the redox potential seen for **6a**, **6c**, and **6d**.

The easiest test to determine the proposed equilibrium of the complexes Co(**6a**)Br_2 and Co(**6b**)Br_2 and their ionic homoleptic counterparts in solution are measurements of the conductivity of the solution. The conductivity measurements were performed in dichloromethane (Fig. 3) and a significant difference of Co(**6a**)Br_2 and Co(**6b**)Br_2 was observed. In these measurements the cobalt complex Co(**6b**)Br_2 has a much higher conductivity ($4.41 \cdot 10^{-6}$ S cm^{-1}) compared to Co(**6a**)Br_2 ($0.76 \cdot 10^{-6}$ S cm^{-1}).



Scheme 3. Proposal for the equilibrium of the cobalt complexes in solution.

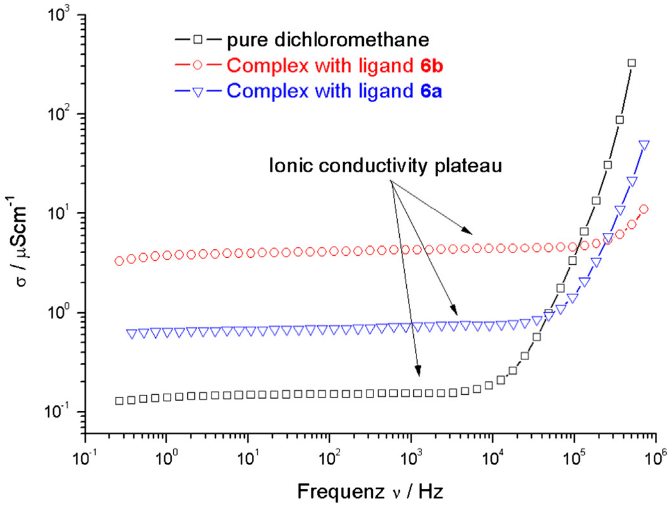


Fig. 3. Broadband conductivity spectra of pure dichloromethane and of the cobalt complexes with ligands **6a** and **6b**, respectively. At intermediate frequencies, conductivity plateaus caused by the ionic conductivity of the solutions are detected. Note that the conductivity of pure dichloromethane results from ionic impurities.

For comparison, we estimated the maximum conductivity of the dichloromethane solution with the given concentrations of the complex Co(**6b**)Br_2 assuming the complete formation of the ionic species [Co(**6b**)$_2$]$^{2+}$ and $[CoBr_4]^{2-}$. The value for the diffusion constants of the ions involved maximum conductivity was estimated based on the *Stokes–Einstein* relation and for the maximum conductivity via the *Nernst–Einstein* equation [19]. The estimated value for the maximum conductivity σ of a mixture of complexes of type [Co(**6b**)$_2$]$^{2+}$/$[CoBr_4]^{2-}$ is $\sigma = (4.0 \pm 0.5) \cdot 10^{-6}$ S cm^{-1}. Accordingly, the methoxy-substituted complex Co(**6a**)Br_2 is the predominant species from which the catalytically active species can be formed directly and only a small fraction exists as ionic species [Co(**6a**)$_2$]$^{2+}$ and $[CoBr_4]^{2-}$. In contrast, the significantly higher conductivity observed for the dimethylamino-substituted complex Co(**6b**)Br_2 indicates that the two ionic species are formed to a high extend and that the neutral Co(**6b**)Br_2 complex is present only in low concentration in solution at best. One must not forget that a contact ion pair [Co(**6b**)$_2$]$^{2+}$ · $[CoBr_4]^{2-}$ does not contribute to the conductivity of the solution and therefore the actual concentration of the complex Co(**6b**)Br_2 as direct catalyst precursor might well be reduced to a minimum thus explaining the long induction period in the preparative *Diels–Alder* reaction. Once the active Co(**6b**)$^+$-species is formed the desired *Diels–Alder* product is formed in a short period of time with a similar rate of conversion and comparable regioselectivities as found for the other cobalt complexes.

The proposed pre-equilibrium is most likely solvent dependent and in principle a solvent-induced shift of the pre-equilibrium from [Co(**6b**)$_2$]$^{2+}$ · $[CoBr_4]^{2-}$ towards the desired pre-catalyst Co(**6b**)Br_2 would be desirable. Unfortunately, we experienced in the past, that the cobalt-catalysed *Diels–Alder* reactions utilising pyridine-imine type-ligands are solvent-dependent. The reactions are best performed in dichloromethane while in other solvents, such as toluene, tetrahydrofuran or acetone, the reactions proceeded sluggishly. Therefore, the aspects of influencing the pre-equilibrium by other solvents would be interesting, but out of scope of this investigation.

4. Conclusion

The results of the quantum mechanical investigation of different pyridine-imine ligands of type **6** applied in cobalt-catalyzed *Diels–Alder* reaction are in relatively good agreement with the experimental results indicating the correct regioselectivities although not with the needed high precision. However, the calculations and experimental data are in line for ligands of type **6** which result in almost identical regioselectivity of the *meta*-selective *Diels–Alder* reaction. Accordingly, electronic modifications in the ligands do not influence the regioselectivity significantly. The quantum mechanical investigation of different pyridine-imine ligands of type **5** were undertaken to predict changes in the regioselectivity. In this case even smaller changes in the energy of the transition states were found resulting in almost identical predictions for the regioselectivities. These results prompted us not to undergo the multi-step synthesis of such ligands of type **5**. The thermodynamic data for the reaction pathways and the expected kinetic outcome suggested that the cobalt catalysts of type Co(**6**)Br_2 should have performed very similarly in the cobalt-catalyzed *meta*-selective *Diels–Alder* reaction. However, the investigation of the kinetic data of ligands of type **6** in the *Diels–Alder* reaction led to two results. First, we identified the halide abstraction step by the Lewis acid to be rate determining for the activation of the complex and second, that the unexpected long induction period for the cobalt complex [Co(**6b**)Br_2] could only be explained by a pre-equilibrium diminishing the concentration of the catalyst precursor complex [Co(**6b**)Br_2] in solution. Conductivity measurements of the dichloromethane solution revealed that complex [Co(**6b**)Br_2] is essentially not present in solution and that the equilibrium is shifted towards the homoleptic complexes $[Co(\mathbf{6b})_2]^{2+}$ and $[CoBr_4]^{2-}$ which are not direct catalyst precursors for the catalytically active cobalt species. The electronic modifications led to an altered length of the induction periods for the activation of the cobalt complexes caused by different positions of the pre-equilibria of the cobalt complexes of type Co(**6**)Br_2 species in solution. Accordingly, the main message to learn from this contribution is that catalysts with different electronically modified ligands which are activated *in situ* exhibit induction periods which depends not only of the mode of activation but could also depend on pre-equilibria. The evaluation of such ligand screenings should also include the length of the induction periods and in the next phase the catalytic performance of the catalysts.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.09.020.

References

[1] For general reviews concerning cobalt-catalyzed carbon–carbon bond formations see: (a) G. Hilt, Eur. J. Org. Chem. (2012) 4441;
(b) G. Dominguez, Perez-Castells, J. Chem. Soc. Rev. 40 (2011) 3430;
(c) C. Gosmini, A. Moncomble, Isr. J. Chem. 50 (2010) 568;
(d) G. Cahiez, A. Moyeux, Chem. Rev. 110 (2010) 1435;
(e) F. Hebrard, P. Kalck, Chem. Rev. 109 (2009) 4272;
(f) D. Leboeuf, V. Gandon, M. Malacria, in: S. Ma (Ed.), Handbook of Cyclization Reactions, vol. 1, Wiley-VCH, Weinheim, 2009, p. 367;
(g) B.R. Galan, T. Rovis, Angew. Chem. Int. Ed. 48 (2009) 2830;
(h) I. Omae, Appl. Organomet. Chem. 22 (2008) 149;
(i) W. Hess, J. Treutwein, G. Hilt, Synthesis (2008) 3537;
(j) I. Omae, Appl. Organomet. Chem. 21 (2007) 318;
(k) S. Kotha, E. Brahmachary, K. Lahiri, Eur. J. Org. Chem. (2005) 4741;
(l) M. Malacria, C. Aubert, J.L. Renaud, in: M. Lautens, B.M. Trost (Eds.), Science of Synthesis: Houben-Weyl Methods of Molecular Transformations, vol. 1, Thieme, Stuttgart, 2001, p. 439;
(m) S. Saito, Y. Yamamoto, Chem. Rev. 100 (2000) 2901.

[2] (a) A.-L. Auvinet, J.P.A. Harrity, G. Hilt, J. Org. Chem. 75 (2010) 3893;
(b) G. Hilt, C. Hengst, J. Org. Chem. 72 (2007) 7337;
(c) G. Hilt, C. Hengst, Synlett (2006) 3247;
(d) G. Hilt, W. Hess, F. Schmidt, Eur. J. Org. Chem. (2005) 2526;
(e) G. Hilt, S. Lüers, K.I. Smolko, Org. Lett. 7 (2005) 251;
(f) G. Hilt, S. Lüers, K. Harms, J. Org. Chem. 69 (2004) 624;
(g) G. Hilt, K.I. Smolko, Angew. Chem. Int. Ed. 42 (2003) 2795;
(h) G. Hilt, K.I. Smolko, B.V. Lotsch, Synlett (2002) 1081;
(i) G. Hilt, S. Lüers, K. Polborn, Isr. J. Chem. 41 (2001) 317;
(j) G. Hilt, F.-X. du Mesnil, Tetrahedron Lett. 41 (2000) 6757.

[3] (a) F. Erver, G. Hilt, Org. Lett. 14 (2012) 1884;
(b) M. Arndt, G. Hilt, A.F. Khlebnikov, S.I. Kozhushkov, A. de Meijere, Eur. J. Org. Chem. (2012) 3112;
(c) G. Hilt, M. Danz, Synthesis (2008) 2257;
(d) G. Hilt, J. Janikowski, W. Hess, Angew. Chem. Int. Ed. 45 (2006) 5204.

[4] (a) J.R. Kuttner, S. Warratz, G. Hilt, Synthesis 44 (2012) 1293;
(b) G. Hilt, J. Janikowski, Org. Lett. 11 (2009) 773.

[5] dppe = 1,2-bis(diphenylphosphino)ethane.

[6] Pyridine-imine = abbreviation for ligands such as *N*-(pyridin-2-ylmethylene) aniline.

[7] P. Mörschel, J. Janikowski, G. Hilt, G. Frenking, J. Am. Chem. Soc. 130 (2008) 8952.

[8] M. Frisch, et al., Gaussian03, Revision E.01, Gaussian, Inc, Wallingford CT, 2004.

[9] H.B. Schlegel, J. Comput. Chem. 3 (1982) 214.

[10] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165.

[11] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[12] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.

[13] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297.

[14] R. Ahlrichs, Phys. Chem. Chem. Phys. 6 (2004) 5119.

[15] (a) K. Eichkorn, O. Treutler, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 242 (1995) 652;
(b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 97 (1997) 119;
(c) F. Weigend, Phys. Chem. Chem. Phys. 8 (2006) 1057.

[16] (a) P. Deglmann, F. Furche, J. Chem. Phys. 117 (2002) 9535;
(b) P. Deglmann, F. Furche, R. Ahlrichs, Chem. Phys. Lett. 362 (2002) 511;
(c) P. Deglmann, K. May, F. Furche, R. Ahlrichs, Chem. Phys. Lett. 384 (2004) 103.

[17] A. Klamt, G. Schüürmann, J. Chem. Soc. Perkin Trans. 2 (5) (1993) 799.

[18] Used radii/Å;: r(H) = 1.4040; r(C) = 1.9890; r(N) = 1.8135; r(O) = 1.7784; r(F) = 1.7199; r(Co) = 2.2230.

[19] For the calculation of the expectable maximum conductivity, see SI.