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Cationic Nickel Complexes with Weakly Coordinating Counterions and Their Application in the Asymmetric Cycloisomerisation of 1,6-Dienes

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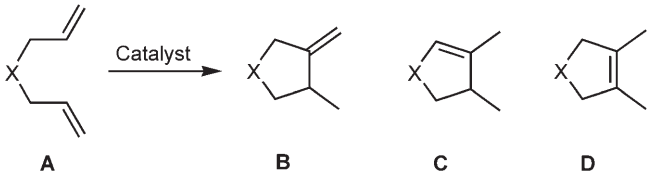
Abstract: The influence of the counterion on cationic nickel catalysts for asymmetric cycloisomerisation of diethyl diallylmalonate (**1a**) and *N*,*N*-diallyltosylamide (**1b**) is investigated. The activity of the catalysts formed from $[Ni(\eta^3\text{-allyl})(\eta^4\text{-cod})]^+$ salts of weakly coordinating anions in combination with Wilke's azaphospholene ligand decreases in the order $[Al\{OC(CF_3)_3\}_4]^- > [B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^- > [Al\{OC(CF_3)_2Ph\}_4]^-$ for **1a** and $[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^- > [Al\{OC(CF_3)_2Ph\}_4]^- > [Al\{OC(CF_3)_3\}_4]^-$ for **1b**, respectively. No significant influence on the enantioselectivity is observed for **1a** whereas a marked increase in ee parallel to a decreasing activity is found for the cyclisation of **1b**.

Keywords: aluminates; asymmetric catalysis; cyclisation; nickel catalysis; olefin dimerisation

Chiral carbo- and heterocycles are widespread structural motifs in biologically active compounds. Hence, the development of efficient stereoselective methods for the synthesis of these frameworks is of continuing interest in catalysis research. The cycloisomerisation of 1,6-dienes (**A**) offers an elegant and atom economic[1] approach to 5- or 6-membered carbo- or heterocycles.[2] Metal complexes based on Pd,[3] Ni,[4] Rh,[5] Ru[6], and Ti,[7] have been identified as promising lead structures for catalyst development. Some of the reported systems are highly chemo- and regioselective towards the formation of the individual 5-membered ring compounds **B**–**D** (Scheme 1). Enantioselective cycloisomerisation, however, has been assessed only sparely so far and remains a challenging task.[8–10]

Recently,[10] we reported for the first time a highly regio- and steroselective catalytic system for the asymmetric cycloisomerisation of diethyl diallylmalonate (**1a**) to



Scheme 1. Cycloisomerisation of 1,6-dienes [X = CH_2, $C(CO_2R)_2$, O, N-R, etc.].

diethyl 3-methylene-4-methylcyclopentane-1,1-dicarboxylate (**2a**) based on cationic nickel complexes of the type $[Ni(\eta^3\text{-allyl})(\eta^4\text{-cod})][Y]$ (**3**) [cod = 1,5-cyclooctadiene; Y = PF_6, AsF_6, SbF_6, barf (barf = $B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4$)] with BINAPHOSQUIN phosphoramidites (R_a,R_c)-**4** and (R_a,S_c)-**5**[11] or Wilke's azaphospholene *all*-(*R*)-**6**[12] as chiral ligands. Up to 80% ee at almost perfect regioselectivity and turnover frequencies of 148 h^{-1} were achieved in an initial screening.

It is well known that the nature of the counterion can have pronounced effects on activity and selectivity of cationic nickel catalysts in olefin dimerisation reactions.[12–14] In the cycloisomerisation of **1a**, which formally corresponds to an *intra*molecular olefin dimerisation, increasing catalyst activities were found in the order $PF_6 < AsF_6 < SbF_6 <$ barf corroborating the common notion that weakly coordinating anions[15] are beneficial for the performance of the nickel catalysts. This has prompted us to investigate the influence of weakly coordinating anions of type $[BAr_4]^-$ and $[Al(OR)_4]^-$ for cycloisomerisation in more detail.

The aluminate salts $Li[Al(pftb)_4]^-$ [pftb = $OC(CF_3)_3$] and $Na[Al(hfpp)_4]^-$ [hfpp = $OC(CF_3)_2Ph$] were prepared by reacting the corresponding alcohols with $LiAlH_4$ or $NaAlEt_4$, respectively.[16–18] $Ag[Al(pftb)_4]$[18] was included in the study for comparison. The new nickel complexes $[Ni(\eta^3\text{-allyl})(\eta^4\text{-cod})][Al(pftb)_4]$ (**3a**) and $[Ni(\eta^3\text{-allyl})(\eta^4\text{-cod})][Al(hfpp)_4]$ (**3b**) were synthesised by adding the corresponding lithium or sodium aluminate salts to solutions of allylnickel bromide dimer (**7**) in dichloromethane in the presence of an excess of 1,5-

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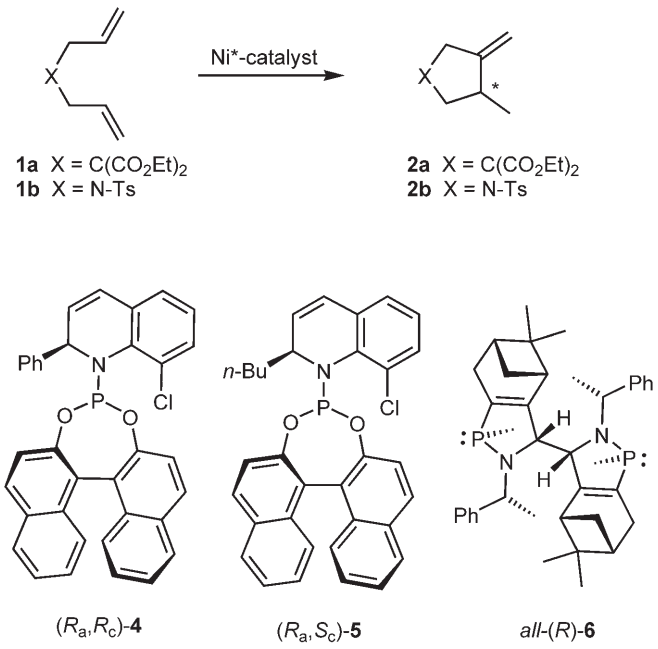

Scheme 2. Chemo-, regio-, and enantioselective cycloisomerisation of diethyl diallylmalonate (**1a**) and *N*,*N*-diallyl tosylamide (**1b**) and chiral ligands effective in this transformation.

cyclooctadiene (Scheme 3).[19] During reaction, the solution turned from dark red to yellow and precipitation of NaBr or LiBr, respectively, took place. After work-up and recrystallisation, the desired complexes were obtained as yellow powders in yields between 70% and 80% under optimised conditions. Complexes **3** decompose rapidly upon contact with air, but they are fairly stable towards water. Representative catalytic results with these complexes and related systems are summarised in Table 1.

In a first set of experiments, the cycloisomerisation of **1a** was used to evaluate the efficacy of the isolated cationic complexes as compared to the use of aluminate salts as activators for *in situ* generation of cationic nickel catalysts starting from allylnickel bromide dimer (**7**). The use of the *in situ* system Li[Al(pftb)$_4$]/**7**/*all*-(*R*)-**6** did not generate an active catalyst and no conversion was observed after 60 minutes (entry 1). However, by replacing Li[Al(pftb)$_4$] with Ag[Al(pftb)$_4$] a productive catalyst system was obtained (entry 2) and a conversion of 62% was achieved within 60 minutes. Even higher activity was achieved using [Ni(η^3-allyl)(η^4-cod)][Al(pftb)$_4$] (**3a**) in combination with *all*-(*R*)-**6** and a conversion of 79% was reached after one hour, corresponding to an average turnover frequency (TOF$_{av}$) of 158 h^{-1} (entry 3). Moreover, the regioselectivity of 89% obtained with the *in situ* activated catalyst could be substantially enhanced to 97% using the halide-free precursor **3a** (*cf.* entry 2 and 3). This observation emphasises again that the generation of catalytically active cationic allylnickel species is not quantitative with the *in situ* protocol. Halide abstraction from [{Ni(η^3-allyl)Br}$_2$] with M[Al(pftb)$_4$] and/or removal of the halide anion as MBr from the reaction mixture is incomplete when M = Ag and does not occur at all when M = Li. Hence, the comparison of intrinsic anion effects should be carried out with the isolated salts only.

With [Ni(η^3-allyl)(η^4-cod)][Al(hfpp)$_4$] (**3b**) the average turnover frequency was significantly lower than with **3a** reaching 110 h^{-1} (entry 4). The benchmark system [Ni(η^3-allyl)(η^4-cod)][barf](**3c**)/*all*-(*R*)-**6** showed an intermediate activity under the standard set of reaction

Table 1. Cycloisomerisation of diethyl diallylmalonate (**1a**) and *N*,*N*-diallyl tosylamide (**1b**).[a]

Entry	Precursor/Activator	Ligand	Sub.	*t* [min]	Cv. [%]	TOF [h^{-1}]	Sel.[b] [%]	ee[c] [%]
1	**7**/Li[Al(pftb)$_4$]	*all*-(*R*)-**6**	**1a**	60	0	–	–	–
2	**7**/Ag[Al(pftb)$_4$]	*all*-(*R*)-**6**	**1a**	60	62	124	89	74 (+)
3	**3a**/–	*all*-(*R*)-**6**	**1a**	60	79	158	97	73 (+)
4	**3b**/–	*all*-(*R*)-**6**	**1a**	60	55	110	91	73 (+)
5	**3c**/–	*all*-(*R*)-**6**	**1a**	60	72	144	91	72 (+)
6[d]	**3d**/–	(R_a,R_c)-**4**	**1b**	30	89	36	88	40 (−)
7[d]	**3d**/–	(R_a,S_c)-**5**	**1b**	30	42	17	95	50 (−)
8[d]	**3d**/–	*all*-(*R*)-**6**	**1b**	30	74	30	92	46 (+)
9[e]	**3b**/–	*all*-(*R*)-**6**	**1b**	60	>99	90	91	47 (+)
10	**3b**/–	*all*-(*R*)-**6**	**1b**	60	34	68	99	48 (+)
11	**3a**/–	*all*-(*R*)-**6**	**1b**	60	11	22	99	54 (+)
12	**3c**/–	*all*-(*R*)-**6**	**1b**	60	64	128	95	33 (+)

[a] T = 20 °C, CH_2Cl_2, substrate/Ni = 200, P(Ligand)/Ni = 1, pftb = Al{OC(CF_3)$_3$}$_4$, hfpp = Al{OC(CF_3)$_2$Ph}$_4$, **3c** = [Ni(η^3-allyl)(η^4-cod)][barf], **3d** = [Ni(η^3-allyl)(η^4-cod)][SbF_6].
[b] Regioselectivity towards **2**.
[c] The ee values were determined by chiral HPLC (**2a**: Chiracel OJ-H, 20 °C, *n*-heptane/2-propanol: 99.975/0.025, 0.5 mL/min, 203 nm; **2b**: Chiracel AD-H, 20 °C, *n*-heptane/2-propanol: 95.0/5.0, 0.5 mL/min, 230 nm).
[d] Substrate/Ni = 20.
[e] Substrate/Ni = 90.

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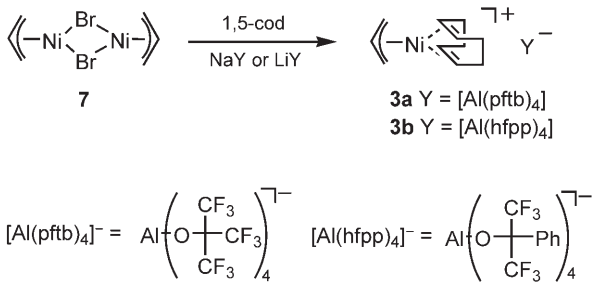

Scheme 3. Synthesis of the cationic nickel complexes.

conditions used here, corresponding to TOF_{av} of 144 h^{-1} (entry 5). Thus, the catalyst activity for the cyclisation of **1a** decreases in the order $[Al(pftb)_4]^- > [barf]^- > [Al(hfpp)_4]^-$ which is in line with the increasing coordination strength of the anions.[15,16]

In order to evaluate the influence of the anion on regio- and enantioselectivities at different conversions, it is again important to ensure that intrinsic effects are observed and selectivities are not affected by secondary isomerisation and/or kinetic resolution of the primary product as occasionally observed in hydrovinylation reactions.[20] Comparing the selectivities obtained with catalyst **3c** at different conversions in the present and previous studies[10] show that no variation occurs within experimental error (cv = 37%: **2a** = 89%, ee = 71%; cv = 72%: **2a** = 91%, ee = 72%; cv = 96%: **2a** = 91%, ee = 71%). Interestingly, the selectivity of the cationic nickel catalyst seems not to be affected by the nature of the counterion in the case of the cyclisation of **1a** in general. Independent of their activity, catalysts **3a**–**c** show largely identical levels of regio- and enantio-selectivity (*cf.* entry 3–5).

In a second set of experiments, the cycloisomerisation of *N*,*N*-diallyltosylamide (**1b**) was investigated as a route to chiral five-membered N-heterocycles. To the best of our knowledge, no enantioselective variant of this cyclisation has yet been achieved. Thus, a brief ligand screening was carried out including (R_a,R_c)-**4**, (R_a,S_c)-**5** and *all*-(*R*)-**6** in combination with [Ni(η^3-allyl)(η^4-cod)][SbF_6] (**3d**) using a catalyst loading of 5 mol % and 30 min reaction time. The formation of the five-membered ring with an exocyclic double bond, 3-methyl-4-methylene-1-tosylpyrrolidine (**2b**), was favoured with all catalyst systems used. In general, the reaction with the nitrogen-containing substrate **1b** tended to be slightly slower than with diethyl diallylmalonate **1a**. In the presence of (R_a,R_c)-**4** high conversion (89%), good regioselectivity (88%) and an ee of 40% were obtained (entry 6). The use of the ligand (R_a,S_c)-**5** led to a more selective (regioselectivity 95%, ee 50%) but a less active (conversion 42%) catalyst (entry 7). A good compromise between activity (conversion 74%) and selectivity (regioselectivity 92%, ee 46%) could be found by using *all*-(*R*)-**6** as the ligand (entry 8).

The counterion variation for substrate **1b** was studied with the cationic complexes **3a**–**c** and *all*-(*R*)-**6** as the ligand. Using **3b** as precursor, full conversion was obtained after 1 hour with a catalyst loading of 1.1 mol % (entry 9), corresponding to a lower limit of the activity of TOF = 90 h^{-1}. By reducing further the catalyst loading to 0.5 mol %, 34% conversion was reached within the same reaction time (entry 10). Unexpectedly, a conversion of only 11% after one hour was obtained with [Ni(η^3-allyl)(η^4-cod)][$Al(pftb)_4$] (**3a**) under identical conditions (entry 11). In sharp contrast, this precursor led to the highest turnover rate in the cycloisomerisation of **1a** (entry 3). The most active catalyst for the cycloisomerisation of **1b** was generated using the barf-containing precursor **3c**. After 60 minutes, 64% of the substrate was consumed, corresponding to an average turnover frequency of 128 h^{-1} (entry 12). The resulting order of activity for the cyclisation of **1b** is $[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^- > [Al\{OC(CF_3)_2Ph\}_4]^- > [Al\{OC(CF_3)_3\}_4]^-$ and differs significantly from the one observed with **1a** as the substrate.

Similarly, a remarkable difference in the sensitivity of the two substrates **1a** and **1b** in terms of selectivity was noted. For substrate **1b**, almost perfect regioselectivity was obtained with all cationic nickel precursors **3a**–**c**. The level of enantioselectivity achieved for **1b** was generally lower than with **1a**. Most intriguingly, however, the choice of the counterion in complexes **3a**–**c** has a marked effect on the enantioselectivity in the cycloisomerisation of **1b**. The enantioselectivity increased from 33% to 54% in the opposite order as observed for the activity (entries 10–12). This is again in marked contrast to the insensitivity of the enantioselectivity in the cyclisation of **1a**.

In summary, the synthesis of the cationic allylnickel complexes [Ni(η^3-allyl)(η^4-cod)][$Al(pftb)_4$] (**3a**) and [Ni(η^3-allyl)(η^4-cod)][$Al(hfpp)_4$] (**3b**) has been realised. In combination with the ligand *all*-(*R*)-**6**, they lead to highly active catalysts in the chemo-, regio-, and enantioselective cycloisomerisation of diethyl diallylmalonate (**1a**) and *N*,*N*-diallyltosylamide (**1b**). Turnover rates up to 158 h^{-1} and 128 h^{-1} for substrates **1a** and **1b**, respectively, were reached at room temperature with a catalyst loading of 0.5 mol %. These turnover rates compare favourably even with those of the most active achiral catalysts for the cycloisomerisation of diallyl malonates,[3–5] whereas much lower activities are reported for **1b**.[4b,6] At almost perfect regioselectivity, enantioselectivities of 73% and 54% were achieved for the (+)-enantiomers of **2a** and **2b**, respectively. A comparison of the activities and selectivities including the barf-containing benchmark catalyst **3c** revealed that the counterion plays a significant role in defining the catalyst performance, whereby the exact nature and magnitude of the effect depends critically on the structure of the substrate.

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Experimental Section

General Remarks

All reactions were carried out under an atmosphere of dry and oxygen-free argon using standard Schlenk techniques. All solvents were dried and distilled prior to use. NMR spectra were measured at room temperature on a Bruker AV-600 (^{1}H, ^{13}C) and on a Bruker DPX-300 (^{19}F) spectrometer. Chemical shifts are given relative to TMS using the solvent signals as internal reference for ^{1}H and ^{13}C and $BF_3 \cdot OEt_2$ as external reference for ^{19}F.

[Ni(η^3-allyl)(η^4-cod)][Al{OC(CF_3)$_3$}$_4$] (3a)

[{Ni(η^3-allyl)Br}$_2$] (201 mg, 0.56 mmol) was dissolved in CH_2Cl_2 (10 mL) and 1,5-cyclooctadiene (484 mg, 0.32 mL, 4.48 mmol) was added at $-20\,^\circ$C. To this solution Li[Al{OC(CF_3)$_3$}$_4$] (1.20 g, 1.23 mmol) dissolved in CH_2Cl_2 (15 mL) was added dropwise. The reaction mixture was stirred for 2 h at $-20\,^\circ$C and for 1 h at room temperature. After filtration through a pad of Celite, the volatile compounds were removed under reduced pressure. Recrystallisation from CH_2Cl_2/*n*-pentane afforded the desired product as a yellow powder. Yield: 1.08 g (82%); ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 2.54$ (4H, bd, C*H*H$_{cod}$), 2.82 (4H, bd, CH*H*$_{cod}$), 3.13 (2H, d, $^3J = 14.5$ Hz, CH$_{trans,allyl}$), 4.58 (2H, d, $^3J = 7.4$ Hz, CH$_{cis,allyl}$), 5.85 (2H, bs, CH$_{cod}$), 6.05 (3H, m, CH$_{cod}$ + CH$_{central,\ allyl}$); ^{13}C{^{1}H}-NMR (150 MHz, CD_2Cl_2): $\delta = 29.3$ (C$_{cod}$), 30.1 (C$_{cod}$), 74.4 (C$_{allyl}$), 114.2 (C$_{cod}$), 114.3 (C$_{cod}$), 121.6 (q, $^1J_{C,F} = 292.5$ Hz, CF_3), 124.7 (C$_{central,\ allyl}$); ^{19}F{^{1}H}-NMR (282 MHz, CD_2Cl_2): $\delta = -77.4$ ppm.

[Ni(η^3-allyl)(η^4-cod)][Al{OC(CF_3)$_2$Ph}$_4$] (3b)

[{Ni(η^3-allyl)Br}$_2$] (235 mg, 0.65 mmol) was dissolved in CH_2Cl_2 (10 mL) and 1,5-cyclooctadiene (519 mg, 0.35 mL, 4.80 mmol) was added at $-20\,^\circ$C. To this solution Na[Al{OC(CF_3)$_2$Ph}$_4$] (1.34 g, 1.31 mmol) dissolved in CH_2Cl_2 (15 mL) was added dropwise. The reaction mixture was stirred for 2 h at $-20\,^\circ$C and for 1 h at room temperature. After filtration through a pad of Celite, the volatile compounds were removed under reduced pressure. The residue was washed with Et_2O (2×5 mL) and recrystallised from CH_2Cl_2/*n*-pentane affording the desired product as a yellow powder. Yield: 1.25 mg (79%); ^{1}H-NMR (600 MHz, CD_2Cl_2): $\delta = 2.45$ (4H, bd, C*H*H$_{cod}$), 2.75 (4H, bd, CH*H*$_{cod}$), 3.00 (2H, d, $^3J = 14.5$ Hz, CH$_{trans,allyl}$), 4.45 (2H, d, $^3J = 6.9$ Hz, CH$_{cis,allyl}$), 5.75 (2H, bs, CH$_{cod}$), 5.94 (3H, m, CH$_{cod}$ + CH$_{central,\ allyl}$), 7.20 (8H, bs, CH$_{arom}$), 7.31 (4H, bs, CH$_{arom}$), 7.88 (8H, bs, CH$_{arom}$); ^{13}C{^{1}H}-NMR (150 MHz, CD_2Cl_2): $\delta = 29.2$ (C$_{cod}$), 30.0 (C$_{cod}$), 74.5 (C$_{allyl}$), 114.0 (C$_{cod}$), 114.2 (C$_{cod}$), 124.0 (q, $^1J_{C,F} = 291.0$ Hz, CF_3), 124.4 (C$_{central,\ allyl}$), 127.5 (C$_{arom}$), 128.1 (C$_{arom}$), 128.6 (C$_{arom}$), 135.4 (C$_{arom,ipso}$); ^{19}F{^{1}H}-NMR (282 MHz, CD_2Cl_2): $\delta = -74.8$ ppm.

Typical Procedure for a Catalytic Reaction

A solution of the ligand (0.03 mmol P) in CH_2Cl_2 (5 mL) was added at room temperature to a solution of the nickel precursor (0.03 mmol Ni) in CH_2Cl_2 (5 mL) under inert gas conditions. After 15 minutes of stirring, the substrate (6.0 mmol) was added *via* syringe to the yellow catalyst solution. If required, the activator (*ca.* 0.1 mmol) was added at this stage. The mixture was stirred for the desired reaction time and the reaction was then stopped by adding aqueous ammonia (1 mL). The organic phase was washed with water ($3 \times$ 2 mL), dried over $NaSO_4$, and analysed by GC and GC-MS. For analysis by chiral HPLC the chlorinated solvent was replaced by *n*-heptane/2-propanol and the solution filtered through a pad of silica. Further details and modifications of the conditions are given in Table 1.

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