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Concave Reagents 25: Transition Metal Complexes of Concave 1,10-Phenanthrolines as Catalysts for [4 + 2]-Cycloadditions. Ligand Effects on the *Exo/Endo*-Selectivity*

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Acryloyl pyrazoles **5** undergo cycloaddition with cyclopentadienes **6** to give new norbornenes **7** if the reaction is catalyzed by transition metal ions like Co^{2+} or Ni^{2+}. The *exo/endo*-selectivity can be shifted towards *exo* by supramolecular control of the transition state using (concave) 1,10-phenanthrolines **1** or **2** as ligands. The products have been fully characterized.

Transition metal complexes are often used as catalysts in organic reactions [1]. One reaction which may be catalyzed by Lewis-acids is the pericyclic [4 + 2]-cycloaddition (Diels-Alder reaction). Because the products of Diels-Alder reactions are often mixtures of isomers, many investigations have been carried out to influence and optimize the isomeric excesses [2]. For a limited number of dienes (mostly cyclopentadiene) and dienophiles (usually acrolein and acrylate derivatives), excellent enantioselectivities have been obtained [3, 4] for a variety of metal ions as Lewis acids (e.g. Mg-(II) [5], Al-(III) [6], Ti-(IV) [7], Fe-(II) and (III) [5, 8], Mn-(II) [9] or Cu-(II) [5, 10]). Bisdentate ligands as 3-acryloyl-1,3-oxazolidin-2-ones gave especially good results. As expected [11] α-unsubstituted acrolein and acrylate derivatives gave *endo*-norbornenes preferentially.

In this work we extend the Lewis acid catalyzed Diels-Alder reaction to acryloyl pyrazoles **5** as new dienophiles with cobalt and nickel ions as Lewis acids. By using (concave) 1,10-phenanthrolines **1** and **2** as ligands the *exo/ endo* ratio can be shifted towards *exo*[12].

The ligands **1** are 2,9-bisaryl-substituted 1,10-phenanthrolines in which the *ortho*-positions of the two aromatic bridgeheads are connected by polymethylene or polyether chains to form a bimacrocyclic system (see scheme 1) [13]. The geometry of these bimacrocycles resembles a light bulb (representing the nitrogen atoms of the 1,10-phenanthroline) in a lampshade (formed by the phenyl substituents and the side chains) [14]. These concave 1,10-phenanthrolines form strong complexes with transition metal ions [13].

Scheme 1 shows the synthesis of the concave transition metal complexes **1**·M^{2+} by reaction of

* Concave reagents 24. T. Marquardt, U. Lüning (1997). Chem. Commun., 1681.
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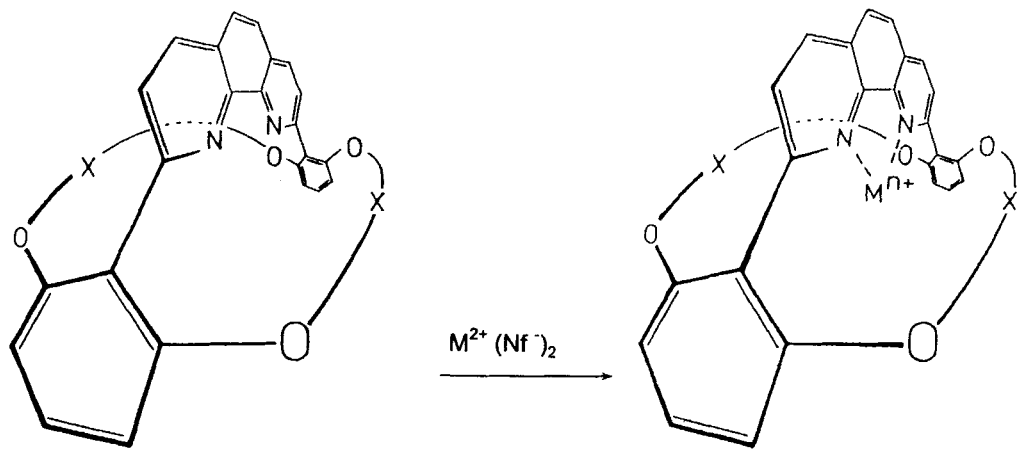
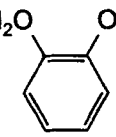


1a-e, 2

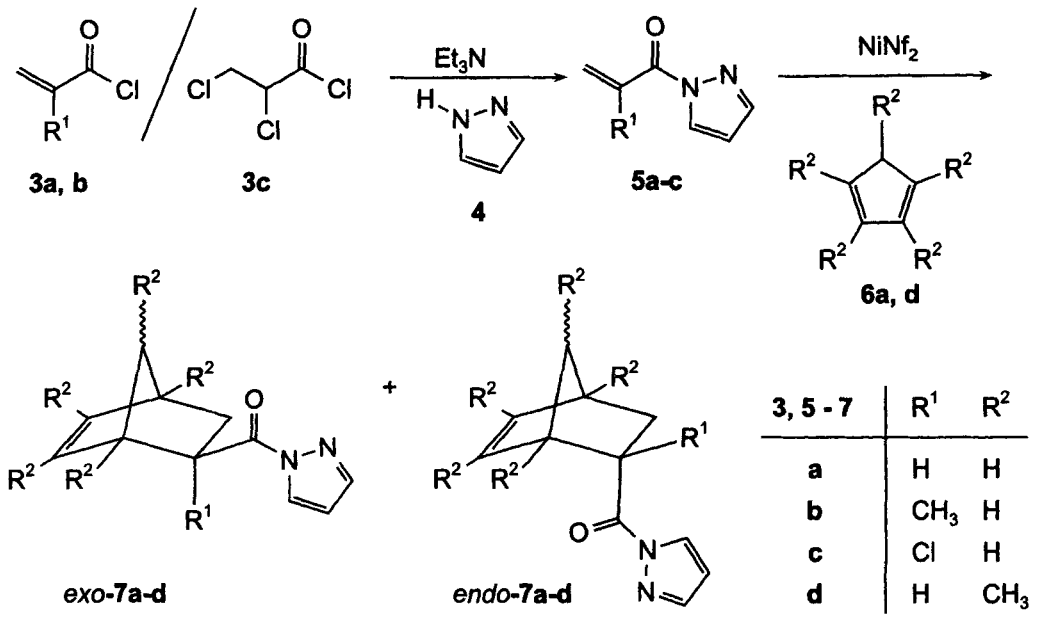
	-X-
1a	$-(CH_2)_8-$
1b	$-(CH_2)_{10}-$
1c	$-CH_2(CH_2OCH_2)_2CH_2-$
1d	$-CH_2(CH_2OCH_2)_3CH_2-$
1e	$-CH_2CH_2O$  OCH_2CH_2-
2	$-CH_3$ H_3C-

SCHEME 1

the ligands **1a-e** (and **2**) [13, 14a] with the metal salt MNf_2 [15] and gives an impression of the three-dimensional structure of the products.

Acryloyl pyrazoles **5** were chosen as dienophiles in the Diels-Alder reactions because they comply with several requirements by acting as bisdentate-ligands coordinating to the transition-metal ions via the carbonyl-oxygen and the nitrogen atom of the pyrazole. In the resulting complexes the coordinative interaction is strong enough to fix the alkene at the metal ion and to decrease the electronic density of the conjugated double bond.

The acryloyl pyrazoles **5** were synthesized by reaction of the commercially available acrylic acid chlorides **3a** and **3b** with pyrazole (**4**) in benzene in the presence of triethylamine as base [16]. α-Chloroacryloyl pyrazole (**5c**) was synthesized under analogous conditions by reaction of 2,3-dichloropropionyl chloride (**3c**) with pyra-



zole (**4**) in the presence of two equivalents of triethylamine. The formation of the amide bond and the elimination of HCl occured in one step. Polymerisation reactions during distillation explain isolated yields of 40–82%. **5a-c** were analysed by NMR and MS and the purity was checked by GC. The Diels-Alder reaction to give **7** (fully characterized) is another structural proof.

For isolation and characterization of the norbornenes **7**, an acryloyl pyrazole **5** was mixed with 0.1 equivalents of $NiNf_2$ [15] in dry dichloromethane/acetone (6:1) [17] at room temperature. After drying [18] and stirring for 1 h, the cyclopentadiene **6** was added at 30–32°C. After 20 h and filtration through silica gel (eluent: CH_2Cl_2), the corresponding *N*-pyrazolyl-norborn-5-ene-2-carboxamides **7a-d** could be isolated as colorless oils in yields (Σ*exo*/*endo*-norbornene) between 56% and 88%.

The effect of the ligands on the diastereoselectivity was investigated by adding (concave) 1,10-phenanthrolines **1a-e** and **2** as ligands. Screening with the **5b/6a** system showed, that Ni^{2+} and Co^{2+} are the most effective metal ions for catalysis of this cycloaddition [19]. The reactions were carried out as described above. Reaction time and temperature were varied for some systems (see Tab. I). All norbornenes **7** were found as *exo*/*endo*-mixtures. Tables I and II list the diastereoselectivity for various ligands, four diene/dienophile combinations and two metal salts at 30 and –23°C.

For all diene/dienophile/metal ion combinations the use of 2,9-bis-substituted 1,10-phenanthroline ligands leads to an increase of the *exo*/*endo*-ratios. In Figure 1, the influence of different ligands **1** and **2** on the diastereoselectivity of four cycloadditions is shown on a logarithmic scale. In comparison to the catalyses in the absence of 1,10-phenanthroline ligands, the introduction of the open-chain-ligand **2** leads to an increased formation of *exo*-**7**. Bridging of the four methoxy groups of **2** to form the bimacrocyclic 1,10-phenanthrolines **1** has two different effects on the stereoselectivity: with a "matching" ring size (e.g.: **1d**), an increase of the exo-selectivity can be observed while other ring sizes lead to a smaller *exo*/*endo* ratio than obtained with **2**.

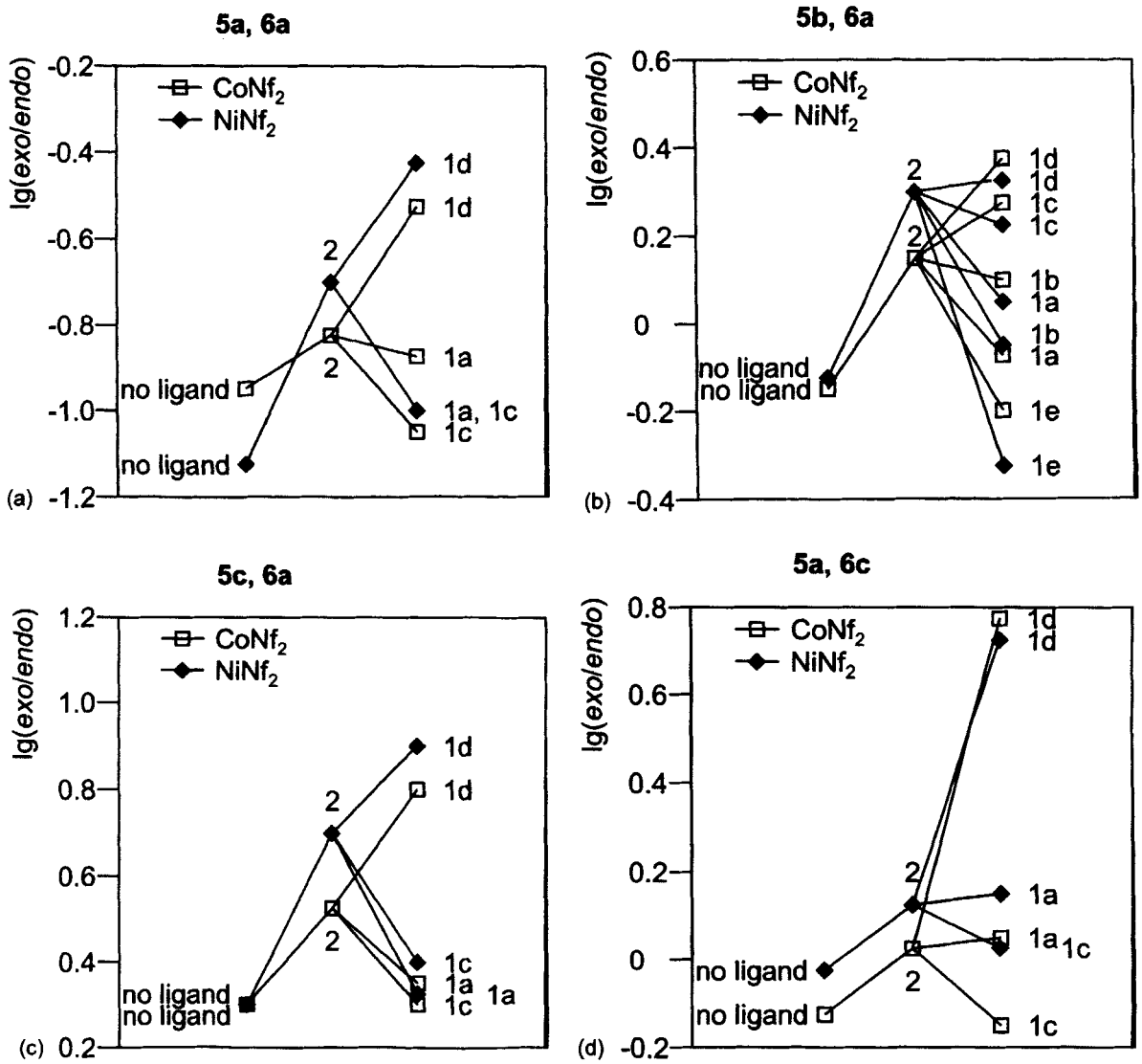


FIGURE 1 Influence of the ligands **1** and **2** on the *exo*/*endo*-selectivity (logarithmic scale in order to be parallel to ΔG) of the transition metal catalyzed reaction of acryloyl pyrazoles **5** with dienes **6** to form **7** at 30–32°C

A possible explanation for the enhanced *exo*-selectivity using **1d**-complexes as catalysts is given in Figure 2. As shown in cases **A** and **B**, the attack of the cyclopentadiene with the 2,3-carbon atoms forward (**B**, leading to *endo*-**7**) is sterically more hindered by the bimacrocycle than the attack with the 5-position forward (**A**, leading to *exo*-**7**). But when a smaller bimacrocycle like **1c** is used there will be a stronger interaction between the vinyl group and the bimacrocycle, and the transition states **C** and **D** may also become important. In these cases, the attack of the cyclopentadiene with the 5-position forward (**C**, leading to the *exo*-isomer) is sterically more hindered than with 2,3-position forward because of the interaction of the hydrogen atoms at the sp^3-hybridized C-5 with the pyrazole-ring. This may explain why **1d** gives a

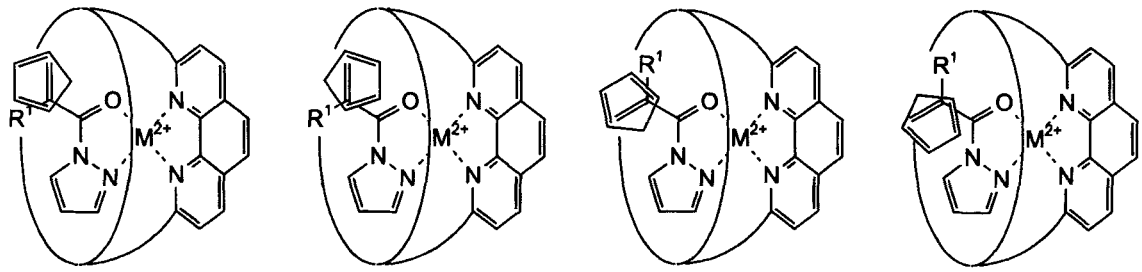


FIGURE 2 Suggested (schematic) geometries for transition states of [4 + 2]-cycloadditions using concave 1,10-phenanthroline metal ion complexes as catalysts. A(→ *exo*) B(→ *endo*) C(→ *exo*) D(→ *endo*)

larger *exo*/*endo*-ratio than **1c**. The small influence of **1a** on the *exo*/*endo*-selectivity may be explained by its smaller association constants for transition metal ions [13].

Variation of the temperature had no significant influence on the diastereoselectivity, but in the **5b**/**6a**system no reaction occured at low temperature.

The reaction rates of selected systems have been investigated semiquantitatively [20]. For the reactions catalyzed by ligand-free $NiNf_2$ or $CoNf_2$ a large increase of the reaction rate has been found (up to 10^3 for the reaction of **5a** with **6a**). Besides that, there is a change of the rate law from 2nd order in the uncatalyzed reaction to 1st order. Apparently the reaction rate is determined by formation of a transition metal acryloyl pyrazole complex in a pre-equilibrium that leads to a rate law of 1st order. With 1,10-phenanthroline ligands **1**, rate enhancements by a factor of 40 and rate orders between 1 and 2 have been found.

The catalysis of [4 + 2]-cycloadditions by the weak Lewis acids Co^{2+} and Ni^{2+} with concave 1,10-phenanthrolines as ligands offers new pathways for diastereoselective syntheses by tailoring the "lamp shade" around the catalytically active transition metal ion. Further investigations are in progress to increase the *exo*/*endo*-ratios and to verify the proposed transition state geometries. Using copper as the catalytic transition metal, also diastereoselective cyclopropanations can be carried out [21].

EXPERIMENTAL

Syntheses of Substituted Acryloyl Pyrazoles 5a – c. General Procedure [16]

Pyrazole (4) and triethylamine were dissolved in 100 ml of dry benzene and the mixture was cooled down to 10°C. A solution of an acrylic acid chloride **3** in 20 ml of dry benzene was added during 1 h. After stirring for 1 h the mixture was filtered and the solvent was evaporated. The crude residue was purified by distillation. **Remark**: The acid chlorides **3a** – **c** and the acryloyl pyrazoles **5a** – **c** tend to decompose. Storage at –30°C is recommended!

Acryloyl pyrazole (5a)

According to the general procedure, 8.17 g (90.3 mmol) of acryloyl chloride (**3a**) was added to a mixture of 5.00 g (73.4 mmol) of pyrazole (**4**) and 9.12 g (90.3 mmol) of triethylamine. Workup yielded 7.35 g (82%) of a colorless liquid, b.p. 68°C (16 Torr). – IR (film): $\tilde{\nu}$ = 3131 cm^{-1}(C=CH), 1797, 1716 (C=O), 1622 (C=C). – ^1H NMR (60 MHz, $CDCl_3$): δ = 5.94 (dd, *J*=10 Hz, *J*=2 Hz,

1 H, HC=C), 6.39 (m_c, 1 H, H-pyr), 6.58 (dd, J=18 Hz, J=2 Hz, 1 H, HC=C), 7.50 (dd, J=18 Hz, J=10 Hz, 1 H, HC=C), 7.61 (m_c, 1 H, H-pyr), 8.21 (d, J=3 Hz, 1 H, H-pyr). – MS (CI, isobutane): m/z (%): 123 (100, M^++1), 69 (36, pyr H^+). – GC [22] (SE 30/25 m): $t_{ret.}$ = 2.5 min, purity: 100%. – Additional conformation of structure by reaction to norbornene **7a**.

α-Methylacryloyl pyrazole (5b)

According to the general procedure, 9.44 g (90.3 mmol) of α-methylacryloyl chloride (**3b**) was added to a mixture of 5.00 g (73.4 mmol) of pyrazole (**4**) and 9.12 g (90.3 mmol) of triethylamine. Workup yielded 6.65 g (66%) of a colorless liquid, b. p. 82°C (16 Torr). – IR (film): $\tilde{\nu}$ = 3131 cm^{-1} (C=CH), 2982 (CH_3), 1783, 1704 (C=O), 1630 (C=C). – ^1H NMR (60 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 5.80 (s, 1 H, HC=C), 6.08 (s, 1 H, HC=C), 6.39 (m_c, 1 H, H-pyr), 7.66 (m_c, 1 H, H-pyr), 8.21 (d, J=3 Hz, 1 H, H-pyr). – MS (70 eV): m/z (%): 136 (100, M^+), 69 (35, pyr H^+). – GC [22] (SE 30/25 m): $t_{ret.}$=3.7 min, purity: 100%. – Additional conformation of structure by reaction to norbornene **7b**.

α-Chloroacryloyl pyrazole (5c)

According to the general procedure, 2.87 g (17.8 mmol) of 2,3-dichloropropionic acid chloride (**3c**) was added to a mixture of 1.24 g (17.8 mmol) of pyrazole (**4**) and 3.65 g (36.1 mmol) of triethylamine. Workup yielded 1.12 g (40%) of a colorless liquid, b. p. 80°C (0.2 Torr). – IR (film): $\tilde{\nu}$ = 3132 cm^{-1} (C=CH), 1713 (C=O), 1607 (C=C), 917, 769 (C–Cl). – ^1H NMR (200 MHz, $CDCl_3$): δ = 6.32 (d, J=2 Hz, 1 H, HC=C), 6.50 (dd, J=2 Hz, J=1 Hz, 1H, H-pyr), 6.70 (d, J=2 Hz, 1 H, HC=C), 7.72 (br. s, 1 H, H-pyr), 8.25 (d, J=1Hz, 1 H, H-pyr). – MS (CI, isobutane): m/z (%): 159, 157 (M^++1, 7, 31), 139 (M^+-18, 28), 121 (M^+-Cl, 3), impurity at 175 (M^++18, 100). – GC [22] (SE 30/ 25 m): $t_{ret.}$ = 7.52 min, purity: 90%. Additional conformation of structure by reaction to norbornene **7c**.

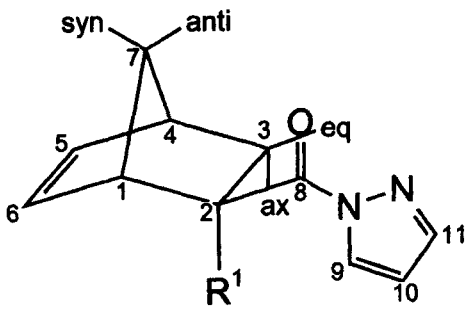
Syntheses of N-pyrazolyl-norborn-5-ene-2-carboxamides 7a-d. General procedure

In a small vial (height: 5 cm, diameter: 2 cm, closed by a polyethylene-snap-cap taped by parafilm), 10 to 13 mg of the (substituted) acryloyl pyrazole **5** and 6.4 mg of $NiNf_2$ were dissolved in 3.0 mL of dry dichloromethane and 0.5 mL of dry acetone. The mixture was dried with six beads of activated molecular sieve (4 Å, Ø: 3 mm, Fa. Janssen). After stirring for 60 min at room temperature, the corresponding diene (cyclopentadiene was cracked by distillation) was added by a microliter-syringe. The mixture was stirred for 20 h at 30–32°C and then mixed with 5 mL of dichloromethane. Extraction with 5 mL of saturated EDTA-solution and evaporation of the solvent led to the crude product which was purified by filtration through silica gel (short column: Ø=5 μm, length=5 cm, eluent dichloromethane).

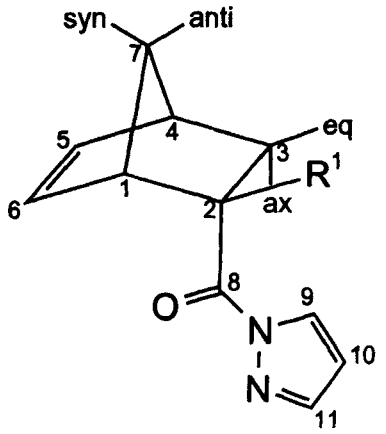
Atoms of the norbornenes are numbered as shown below:

N-pyrazolyl-norborn-5-ene-2-carboxamide (7a)

According to the general procedure, 5.8 mg (88 μmol) of cyclopentadiene (**6a**) was added to a mixture of 10.8 mg (88 μmol) of acryloyl pyrazole (**5a**) and 6.4 mg (8.8 μmol) of $NiNf_2$. Workup yielded 11.2 mg (67%) of **7a** as a little volatile colorless oil. – IR(film) : $\tilde{\nu}$ = 3144 cm^{-1}(C=CH), 2974, 2942, 2869 (CH_2), 1734 (C=O), 1382 (N–N). – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.2–1.7 (m, 3 H, H_{3ax}, H_{7syn}, H_{7anti}), 2.04 (m_c, 1 H, H_{3eq}), 3.01 (m_c, 1 H, H_4), 3.15 (m_c, 0.8 H, H_{1exo}), 3.45 (m_c, 0.2 H, H_{1endo}), 3.50 (ddd, J=6.5 Hz, J=4.5 Hz, J=3.5 Hz, 0.8 H, H_{2exo}), 4.11 (ddd, J=6.5 Hz, J=4.5, J=3.5 Hz, 0.2 H, H_{2endo}), 5.88 (dd, J=6 Hz, J=3.5 Hz, 0.2 H, H_{5endo}), 6.23 (dd, J=2 Hz, J=0.5 Hz, 1.6 H, H_{5exo}, H_{6exo}), 6.29 (ddd, J=6 Hz,



exo-norbornene



endo-norbornene

J=3 Hz, *J*=0.5 Hz, 0.2 H, H_{6endo}), 6.43 (dd, *J*=3 Hz, *J*=2 Hz, 1 H, H_{10}), 7.73 (dd, *J*=2 Hz, *J*=1 Hz, 1 H, H_{11}), 8.20 (dd, *J*=3 Hz, *J*=1 Hz, 0.2 H, H_{9endo}), 8.28 (dd, *J*=3 Hz, *J*=1 Hz, 0.8 H, H_{9exo}). – ^{13}C NMR (75 MHz, $CDCl_3$): δ =29.68 (t, CH), 31.12 (t, CH), 41.99 (d, CH), 42.16 (d, CH), 42.77 (d, CH), 43.05 (d, CH), 46.95 (d, CH), 47.64 (t, CH), 50.29 (t, CH), 53.57 (t, CH), 108.98 (d, C=C), 109.24 (d, C=C), 128.34 (d, C=C), 128.44 (d, C=C), 131.49 (d, C=C), 135.83 (d, C=C), 138.08 (d, C=C), 138.41 (d, C=C), 143.62 (d, C=C), 143.71 (d, C=C), 173.09 (s, C=O), 174.80 (s, C=O). – MS (CI, isobutane): m/z (%): 189 (M^++1, 100), 121 (M^+-pyrazole, 5). - GC [22] (SE 30/25 m): *exo*-**7a**: $t_{ret.}$=13.4 min (6.5%), *endo*-**7a**: $t_{ret.}$=13.47 (90.9%). – $C_{11}H_{12}N_2O$ (188.23), calcd.: C 70.19 H 6.43 N 14.88, found: C 70.76 H 6.72 N 14.26.

N-pyrazolyl-2-methylnorborn-5-ene-2-carboxamide (7b)

According to the general procedure, 4.9 mg (74.2 μmol) of cyclopentadiene (**6a**) was added to a mixture of 10.0 mg (74.2 μmol) of α-methylacryloyl pyrazole (**5b**) and 6.4 mg (8.8 μmol) of $NiNf_2$. Workup yielded 8.3 mg (56%) of **7b** as a little volatile colorless oil. – IR (film): $\tilde{\nu}$ = 3144 cm^{-1}(C=CH), 2969, 2874 (CH_2, CH_3), 1722 (C=O), 1378 (N–N). - ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (dd, *J*=12.7 Hz, *J*=3 Hz, 0.3 H, $H_{3ax,exo}$), 1.35 (m_c, 0.3 H, $H_{7anti,exo}$), 1.45 (s, 0.9 H, CH_{3exo}), 1.50 (ddt, J_d=8.8 Hz, J_d=3 Hz, J_t=2 Hz, 1 H, H_{8endo}), 1.52 (m_c, 0.3 H, $H_{7syn,exo}$), 1.69 (m_c, 0.7 H, $H_{7syn,endo}$), 1.71 (s, $CH_{3,endo}$, dd, *J*=12.4 Hz, *J*=3 Hz, 2.8 H, $H_{3eq,endo}$), 2.27 (ddd, *J*=12.3 Hz, *J*=3 Hz, J=1 Hz, $H_{3ax,endo}$, 3H), 2.59 (dd, *J*=12.7 Hz, *J*=4 Hz, 0.3 H, $H_{3eq,exo}$), 2.84 (m_c, 0.3 H, H_{4exo}), 2.86 (m_c, 0.7 H, H_{4endo}), 3.48 (m_c, 0.7 H, H_{1endo}), 3.54 (m_c, 0.3 H, H_{1exo}), 5.91 (dd, *J*=6 Hz, *J*=3 Hz, 0.7 H, H_{6endo}), 6.11 (ddt, J_d=5.7 Hz, J_d=3 Hz, J_t=1 Hz, 1 H, H_{5endo}), 6.15 (dd, *J*=5.6 Hz, *J*=3 Hz, 0.3 H, H_{6exo}), 6.31 (ddt, J_d=6 Hz, J_d=3 Hz, J_t=1 Hz, 1 H, H_{5exo}), 6.35 (dd, *J*=3 Hz, *J*=2 Hz, 0.7 H, H_{10endo}), 6.37 (dd, *J*=3 Hz, *J*=2 Hz, 0.3 H, H_{10exo}), 7.70 (*t*, *J*=1 Hz, H_{11endo}, dt, J_d=2 Hz, J_t=1 Hz, H_{11exo}, 1 H), 8.18 (dd, *J*=3 Hz, *J*=1 Hz, 0.7 H, H_{9endo}), 8.28 (dd, *J*=3 Hz, *J*=1 Hz, 0.3 H, H_{9exo}). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.85 (q, CH_{3exo}), 26.45 (q, CH_{3endo}), 39.87 (t, C_{3exo}), 39.92 (t, C_{3endo}), 42.28 (d, C_{4endo}), 42.90 (d, C_{4exo}), 46.62 (t, C_{7endo}), 49.41 (t, C_{7exo}), 49.90 (d, C_{1exo}), 51.33 (s, C_{2endo}), 51.58 (d, C_{1endo}), 52.63 (s, C_{2exo}), 108.02(d, C_{10exo}), 108.07 (d, C_{10endo}), 129.61 (d, C_{9endo}), 129.81 (d, C_{9exo}), 133.65 (d, C_{6exo}), 135.48 (d, C_{6endo}), 137.84 (d, C_{5endo}),

139.18 (d, C_{5exo}), 143.04 (d, C_{11exo}), 143.15 (d, C_{11endo}), 175.42 (s, C_{8endo}), 176.76 (s, C_{8exo}). – GC (SE 30/25 m): acryloyl pyrazole: $t_{ret.}$=3.66 min, *endo*-**7b**: $t_{ret.}$=12.49 min (44%), *exo*-**7b**: $t_{ret.}$=12.81 min (31.5%). – GC/MS (OV-1/50 m, CI, isobutane): *endo*-**7b**: $t_{ret.}$=19.9 min, m/z (%): 203 (M^++1, 100), 135 (M^+-pyrazole, 87); *exo*-**7b**: $t_{ret.}$=20.4 min, m/z (%): 203 (M^++1, 72), 135 (M^+-pyrazole, 100). – $C_{12}H_{14}N_2O$ (202.26), calcd.: C 71.26 H 6.98 N 13.85, found: C 70.57 H 6.93 N 14.08.

N-pyrazolyl-2-chloronorborn-5-ene-2-carboxamide (7c)

According to the general procedure, 5.5 mg (83 μmol) of cyclopentadiene (**6a**) was added to a mixture of 13.0 mg (83 μmol) of α-chloroacryloyl pyrazole (**5c**) and 6.4 mg (8.8 μmol) of $NiNf_2$. Workup yielded 15.8 mg (81%) of **7c** as a little volatile colorless oil. – IR (film): $\tilde{\nu}$ = 3140 cm^{-1}(C=CH), 2977 (CH_2), 1726 (C=O), 1341 (N–N), 818 (C–Cl). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (m_c, 0.8 H, $H_{7anti,exo}$), 1.71 (m_c, 0.8 H, $H_{7syn,exo}$), 1.78 (m_c, 0.2 H, $H_{7syn,endo}$), 2.00 (dd, *J*=14 Hz, *J*=4 Hz, 0.8 H, $H_{3ax,exo}$), 2.15 (m_c, 0.2 H, $H_{7anti,endo}$), 2.50 (dd, *J*=14 Hz, *J*=4 Hz, 0.2 H, $H_{3ax,endo}$), 2.66 (dd, *J*=14 Hz, *J*=4 Hz, 0.2 H, $H_{3eq,endo}$), 2.90 (dd, *J*=14 Hz, *J*=4 Hz, 0.8 H, $H_{3eq,exo}$), 2.95 (m_c, 1 H, $H_{4endo/4exo}$), 3.85 (m_c, 0.2 H, H_{1endo}), 3.93 (m_c, 0.8 H, H_{1exo}), 5.95 (dd, *J*=6 Hz, *J*=3 Hz, 0.2 H, H_{6endo}), 6.27 (dd, *J*=6 Hz, *J*=3 Hz, 1 H, $H_{5endo/5exo}$), 6.42 (dd, *J*=3 Hz, *J*=1.5 Hz, 1 H, $H_{10exo/10endo}$), 6.50 (dd, *J*=6 Hz, *J*=3Hz, 0.8 H, H_{6exo}), 7.79 (dd, *J*=1.5 Hz, *J*=1 Hz, 1 H, $H_{11exo/11endo}$), 8.22 (dd, *J*=3 Hz, *J*=1 Hz, 0.2 H, H_{9endo}), 8.28 (dd, *J*=3 Hz *J*= 1 Hz, 0.8 H, H_{9exo}). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.70, 42.10, 42.45, 43.92, 44.04, 47.61, 48.80, 51.98, 54.84, 71.15, 109.04 (C_{10exo}), 109.10 (C_{10endo}), 130.30 (C_{9exo}), 130.54 (C_{9endo}), 133.04 (C_{5endo}), 133.78 (C_{5exo}), 139.58 (C_{6exo}), 141.13 (C_{6endo}), 143.87 (C_{11exo}), 143.97 (C_{11endo}), 167.29 (C_{8endo}), 168.65 (C_{8exo}). – MS (CI, isobutane): m/z (%): 225, 223 (M^++ 1, 33, 100), 159, 157 pyrazole, 14, 34). – GC [22] (SE 30/25 m, T-program: 80_5-10°C/ min-150_{20}): *endo*-**7c**: $t_{ret.}$=16.57 min (35.4%), *exo*-**7c**: $t_{ret.}$=17.34 min (64.6%) – $C_{11}H_{12}ClN_2O$ (222. 68), calcd.: C 59.33 H 4.98 N 12.58, found: C 59.32 H 5.29 N 11.48.

N-pyrazolyl-1,4,5,6,7-pentamethylnorborn-5-ene-2-carboxamide (7d)

According to the general procedure, 12.0 mg (88.4 μmol) of 1,2,3,4,5-pentamethylcyclopentadiene (**6d**) was added to a mixture of 10.8 mg (88.4 μmol) of acryloyl pyrazole (**5a**) and 6.4 mg (8.8 μmol) of $NiNf_2$. Workup yielded 20.0 mg (88%) of **7d** as a little volatile colorless oil. – IR (film): $\tilde{\nu}$ = 3144 cm^{-1}(C=CH), 2955, 2927, 2870 (CH_3, CH_2), 1726 (C=O), 1382 (N–N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.51 (d, *J*=6.5 Hz, 1.8 H, $CH_{3-7syn,exo}$), 0.53 (d, *J*=6.5 Hz, 1.2 H, $CH_{3-7syn,endo}$), 0.86 (s, 1.8 H, CH_{3-4exo}), 0.99 (s, 1.2 H, $CH_{3-4endo}$), 1.02 (s, 1.2 H, $CH_{3-4endo}$), 1.05 (s, 1.8 H, CH_{3-1exo}), 1.18 (m_c, 0.4 H, $H_{3ax,endo}$), 1.35–1.55 (m, 6.4 H, CH_{3-6}, CH_{3-5}, $H_{3ax,exo}$, $H_{3eq,endo}$), 1.76 (m_c, 1 H, $H_{3eq,exo}$, $H_{7anti,endo}$), 1.95 (q, *J*=6.5 Hz, 0.6 H, $H_{7anti,exo}$), 3.66 (dd, *J*=9 Hz, *J*=5 Hz, 0.6 H, H_{2exo}), 4.02 (dd, *J*=9 Hz, *J*=5 Hz, 0.4 H, H_{2endo}), 6.35, 6.36 (dd, *J*=3 Hz, *J*=1 Hz; dd, *J*=3 Hz, *J*=1 Hz, 1 H, $H_{10endo/10exo}$), 7.51, 7.52 (dd, *J*=3 Hz, *J*=2 Hz; dd, *J*=3 Hz, *J*=1 Hz, 1 H, $H_{11endo/11exo}$), 8.12 (dd, *J*=3 Hz, *J*=1 Hz, 0.4 H, H_{9endo}), 8.21 (dd, *J*=3 Hz, *J*=1 Hz, 0.6 H, H_{9exo}). – ^{13}C NMR (75 MHz, $CDCl_3$): δ=7.94 (q, CH_3), 9.61 (q, CH_3), 9.81 (q, CH_3) 10.01 (q, CH_3), 11.60 (q, CH_3), 12.28 (q, CH_3), 14.51 (q, CH_3), 14.84 (c, CH_3), 14.84 (q, CH_3), 15.01 (q, CH_3), 15.16 (q, CH_3), 40.42 (t, CH_2), 41.33 (t, CH_2), 46.73 (d, CH), 49.94 (d, CH), 53.10 (d, CH), 53.31 (d, CH), 55.33 (d, CH), 60.14 (d, CH), 60.55 (d, CH), 62.18 (d, CH), 62.42 (d, CH), 109.02 (d, C=C), 109.28 (d, C=C), 128.01 (d, C=C), 128.05 (d, C=C), 131.39 (d, C=C), 134.57 (d, C=C), 135.87 (d, C=C), 137.03 (d, C=C), 143.12 (d, C=C), 143.33 (d, C=C), 173.77 (C_{8endo}), 174.83 (C_{8exo}). – GC [22] (SE 30/25 m): *endo*-**7d**: $t_{ret.}$=18.06 min (24%), *exo*-**7d**: $t_{ret.}$=19.48 (73%), *exo*-**7d** with the methylgroup *anti* to the double bond: $t_{ret.}$=19.03 (2.3%). – GC/MS (OV-1/50 m,

CI, isobutane): *endo*-**7d**: t_{ret}=39.2 min: m/z (%): 259 (M^++1, 100), 191 (M^+ – pyrazole, 53), 137 ($C_5H_2Me_5$, 61); *exo*-**7d**: $t_{ret.}$=41.9 min, m/z (%): 259 (M^++1, 100), 191 (M^+-pyrazole, 94), 137 ($C_5H_2Me_5$, 20), 123 (propionyl pyrazole, 20); *exo*-**7d** with the methylgroup *anti* to the double bond: $t_{ret.}$=40.4, m/z (%): 259 (M^++1, 100), 191 (M^+-pyrazole, 100), 163 (M^+-CO-pyrazole, 38), 137 (C_5HMe_5, 4). – $C_{16}H_{22}N_2O$ (258.16), calcd.: C 74.43 H 8.52 N 10.85, found: C 74.32 H 8.47 N 10.78.

TABLE I Transition metal catalyzed reaction of acryloyl pyrazoles **5** with dienes **6**. Effect of ligands **1** and **2** on the diastereo-selectivity[a] in the formation of **7** at 30–32°C and at –23°C (in parentheses)

alkene, diene	*ligand*	*$CoNf_2$*		*$NiNf_2$*	
		7[exo/endo] 30–32°C (-23°C)	*yield [%]*	*7[exo/endo] 30–32°C (-23°C)*	*yield [%]*
5a, 6a[b]	-	10 : 90 (7 : 93)	> 97 (98)	7 : 93 (4 : 96)	> 97 (97)
	2	13 : 87	> 97	17 : 83 (6 : 94)	> 97 (93)
	1a	12 : 88 (7 : 93)	> 97 (98)	9 : 91	> 97
	1c	8 : 92 (4 : 96)	> 97 (98)	9 : 91	> 97
	1d	23 : 77	> 97	27 : 73 (28 : 72)	> 97 (84)
5b, 6a[c]	-	39 : 61 (31 : 69)	53 (32)	43 : 57 (34 : 66)	68 (39)
	2	58 : 42	44	67 : 33 (64 : 36)	88 (26)
	1a	46 : 54	26	53 : 47[d]	38[d]
	1b	55 : 45	43	47 : 53	82
	1c	65 : 35[d]	98[(d)]	63 : 37	95
	1d	70 : 30 (66 : 34)	87 (11)	68 : 32	96
	1e	38 : 62	96	32 : 68	93
5c, 6a[b]	-	66 : 34 (67 : 33)	88 (93)	67 : 33 (67 : 33)	78 (81)
	2	77 : 23 (69 : 31)	97 (63)	83 : 17 (73 : 27)	> 97 (94)
	1a	69 : 31 (72 : 28)	>97 (96)	68 : 32 (66 : 34)	> 97 (97)
	1c	67 : 33 (72 : 28)	97 (86)	72 : 28 (77 : 23)	> 97 (97)
	1d	86 : 14 (88 : 12)	>97 (97)	89 : 11 (91 : 9)	> 97 (97)
5a, 6d[c]	-	43 : 57 (44 : 56)	95 (91)	49 : 51 (53 : 47)	93 (72)
	2	52 : 48	92	57 : 43 (60 : 40)	88 (85)
	1a	53 : 47 (49 : 51)	88 (85)	58 : 42	92
	1c	41 : 59 (39 : 61)	80 (85)	52 : 48	92
	1d	86 : 14	97	84 : 16 (84 : 16)	95 (89)

a. The *exo/endo*-ratios were determined by gaschromatography with an estimated error of +3%.
b. Reaction time: 20 h (65 h).
c. Reaction time: 65 h (65 h).
d. No reaction at –23°C.

TABLE II Reactions of Table I carried out without metal salt as catalyst at 30–32°C and at –23°C (in parentheses)

alkene, diene	*7 [exo/endo]*		*yield [%]*	
	30–32°C	*(- 23°C)*	*30–32°C*	*(-23°C)*
5a, 6a[a]	9 : 91	(0 : 100)	95	(19)
5b, 6a[b]	c	(0 : 100)	c	(4)
5c, 6a[a]	68 : 32	c	59	c
5a, 6d[b]	18 : 82	(19 : 81)	>97	(68)

a. Reaction time: 20 h (65 h).
b. Reaction time: 65 h (65 h).
c. No reaction.

Kinetic measurements

For time dependent measurements, samples of the reaction mixture were worked up quickly and cooled down to –78°C to stop the background reaction. The samples were investigated by gaschromatography by measuring the decrease of the starting acryloyl pyrazole **5**.

Determination of *exo/endo*-selectivities: GC-conditions

HRGC 5300 Mega-Series, Fa. Carlo Erba, stationary phase: SE 30/25 m, Fa. Macherey & Nagel, Ø=0.32 mm, 0.25 µm film. Split: 1:20. FID: 250°C. N_2-flow: 2 ml/min. The results listed are the mean values of at least two runs. *Remark*: the *exo/endo*-ratios listed in Table I differ from the values determined for isolated material by NMR due to diastereomeric enrichment during purification.

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[18] Molecular sieve, 4 Å particle size: ø ca 4 mm, Fa. Janssen, Belgium. Application of molecular sieve is useful to prevent side reactions like hydrolysis or water addition.

[19] In analogous experiments also $MnNf_2$, $FeNf_2$ and $CuNf_2$ were used as metal salt component. In these runs neither good yields (max. turnover of the starting materials: 70%) nor satisfactory selectivities favoring one isomer were found.

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